Information for Authors

AIM AND SCOPE

*Journal of Advances in Environmental Health Research (JAEHR)*is a quarterly peer-reviewed scientific journal published by Kurdistan University of Medical Sciences. The manuscripts on the topic of environmental science and engineering will be published in this journal. This contains all aspects of solid waste management, air pollution, water and wastewater, environmental monitoring and modeling, innovative technologies and studies related to the environmental science.

Instruction to Authors

MANUSCRIPTS

Manuscripts containing original material are accepted for consideration if neither the article nor any part of its essential substance, tables, or figures has been or will be published or submitted elsewhere before appearing in the *Journal of Advances in Environmental Health Research*. This restriction does not apply to abstracts or press reports published in connection with scientific meetings. Copies of any closely related manuscripts must be submitted along with the manuscript that is to be considered by the *Journal of Advances in Environmental Health Research*. Authors of all types of articles should follow the general instructions given below.

HUMAN AND ANIMAL RIGHTS

The research involves human beings or animals must adhere to the principles of the Declaration of Helsinki (http://www.wma.net/e/ethicsunit/helsinki.htm).

Types of Articles

- *Original article* which reports the results of an original scientific research should be less than 4000 words.
- *Review article* which represents the researches and works on a particular topic.
- *Brief communication* is a short research article and should be limited to 1500 words. This article contains all sections of an original article.
- *Case report* is a detailed report of an individual patient that may represent a previously non-described condition and contains new information about different aspects of a disease. It should be less than 2000 words.
- *Letter to the Editor* must be less than 400 words in all cases.
- *Book Review* must be less than 1000 words on any book topics related to the scope of *Journal of Advances in Environmental Health Research*.

SUBMISSION

- Only online submission is acceptable. Please submit online at: http://www.jaehr.muk.ac.ir
- This manuscripts should be divided into the following sections: (1) Title page, (2) Abstract and Keywords, (3) Introduction, (4) Materials and Methods, (5) Results and Discussion, (6) Acknowledgements, (7) Author contribution, (8) References, (9) Figure legends, (10) Tables and (11) Figures (figures should be submitted in separate files if the file size exceeds 2 Mb).
- Please supply a word count in title page.
- Use normal page margins (2.5 cm), and double-space throughout the manuscript.
- Use Times New Roman (12) font throughout the manuscript.
- Prepare your manuscript text using a Word processing package (save in .doc or .rtf format). Submissions of text in the form of PDF files are not permitted.

COVER LETTER

A covering letter signed by all authors should identify the corresponding author (include the address, telephone number, fax number, and e-mail address). Please make clear that the final manuscript has been seen and approved by all authors, and that the authors accept full responsibility for the design and conduct of the study, had access to the data, and controlled the decision to publish.

Authors are also asked to provide the names and contact information for three potential reviewers in their cover letter. However, the journal is not obliged to use the suggested reviewers. Final selection of reviewers will be determined by the editors.

AUTHORSHIP

As stated in the Uniform Requirements for Manuscripts Submitted to Biomedical Journals (http://www.icmje.org/icmje-recommendations.pdf), credit for authorship requires substantial contributions to: 1. Substantial contributions to the conception or design of the work; or the acquisition, analysis, or interpretation of data for the work; AND 2. Drafting the work or revising it critically for important intellectual content; AND 3. Final approval of the version to be published; AND 4. Agreement to be accountable for all aspects of the work in ensuring that questions related to the accuracy or integrity of any part of the work are appropriately investigated and resolved. Each author must sign authorship form attesting that he or she fulfills the authorship criteria. There should be a statement in manuscript explaining contribution of each author to the work. Acknowledgments will be limited to one page of *Journal of Advances in Environmental Health Research*, and those acknowledged will be listed only once.

Any change in authorship after submission must be approved in writing by all authors.

ASSURANCES
In appropriate places in the manuscript please provide the following items:
- If applicable, a statement that the research protocol was approved by the relevant institutional review boards or ethics committees and that all human participants gave written informed consent
- The source of funding for the study
- The identity of those who analyzed the data
- Financial disclosure, or a statement that none is necessary

TITLE PAGE
With the manuscript, provide a page giving the title of the paper; titles should be concise and descriptive (not declarative). Title page should include an abbreviated running title of 40 characters, the names of the authors, including the complete first names, the name of the department and institution in which the work was done, the institutional affiliation of each author. The name, post address, telephone number, fax number, and e-mail address of the corresponding author should be separately addressed. Any grant support that requires acknowledgment should be mentioned on this page. Word count of abstract and main text as well as number of tables and figures and references should be mentioned on title page. If the work was derived from a project or dissertation, its code should also be stated.

Affiliation model: Department, Institute, City, Country.
Example: Department of Environmental Health Engineering, School of Health, Kurdistan University of Medical Sciences, Sanandaj, Iran.

ABSTRACT
Provide on a separate page an abstract of not more than 250 words. This abstract should consist of ONE paragraph (Non-structured Abstract). It should briefly describe the problem being addressed in the study, how the study was performed, the salient results, and what the authors conclude from the results respectively. Three to seven keywords may be included. Keywords are preferred to be in accordance with MeSH (http://www.ncbi.nlm.nih.gov/mesh) terms.

CONFLICT OF INTEREST
Authors of research articles should disclose at the time of submission any financial arrangement they may have with a company whose product is pertinent to the submitted manuscript or with a company making a competing product. Such information will be held in confidence while the paper is under review and will not influence the editorial decision, but if the article is accepted for publication, a disclosure will appear with the article.
Because the essence of reviews and editorials is selection and interpretation of the literature, the *Journal of Advances in Environmental Health Research* expects that authors of such articles will not have any significant financial interest in a company (or its competitor) that makes a product discussed in the article.

REVIEW AND ACTION

Submitted papers will be examined for the evidence of plagiarism using some automated plagiarism detection service. Manuscripts are examined by members of the editorial staff, and two thirds are sent to external reviewers. Communications about manuscripts will be sent after the review and editorial decision-making process is complete within **3-6 weeks** after receiving the manuscript. After acceptance, editorial system makes a final language and scientific edition. No substantial change is permitted by authors after acceptance. It is the responsibility of corresponding author to answer probable questions and approve final version.

COPYRIGHT
Journal of Advances in Environmental Health Research is the owner of all copyright to any original work published by the

JOURNAL STYLE

Tables

Double-space tables and provide a title for each.

Figures

Figures should be no larger than 125 (height) x 180 (width) mm (5 x 7 inches) and should be submitted in a separate file from that of the manuscript. The name of images or figures files should be the same as the order that was used in manuscript (fig1, fig2, etc.). Only JPEG, tif, gif and eps image formats are acceptable with CMYK model for colored image at a resolution of at least 300 dpi. Graphs must have the minimum quality: clear text, proportionate, not 3 dimensional and without disharmonic language. Electron photomicrographs should have internal scale markers.

If photographs of patients are used, either the subjects should not be identifiable or the photographs should be accompanied by written permission to use them. Permission forms are available from the Editorial Office.

Scientific illustrations will be created or recreated in-house. If an outside illustrator creates the figure, the *Journal of Advances in Environmental Health Research* reserves the right to modify or redraw it to meet our specifications for publication. The author must explicitly acquire all rights to the illustration from the artist in order for us to publish the illustration. Legends for figures should be an editable text as caption and should not appear on the figures.

References

The Vancouver style of referencing should be used. References must be double-spaced and numbered as **superscripts** consecutively as they are cited. References first cited in a table or figure legend should be numbered so that they will be in sequence with references cited in the text at the point where the table or figure is first mentioned. List all authors when there are six or fewer; when there are seven or more, list the first six, then "et al." The following are sample references:

1. Maleki A, Shahmoradi B, Daraei H, Kalantar E. Assessment of ultrasound irradiation on inactivation of gram negative and positive bacteria isolated from hospital in aqueous solution. J Adv Environ Health Res 2013; 1(1): 9-14.

2. Buckwalter JA, Marsh JL, Brown T, Amendola A, Martin JA. Articular cartilage injury. In: Robert L, Robert L, Joseph V, editors. Principles of Tissue Engineering. 3rd ed. Burlington, MA: Academic Press; 2007. p. 897-907.

3. Kuczmarski RJ, Ogden CL, Grammer-Strawn LM, Flegal KM, Guo SS, Wei R, et al. CDC growth charts: United States. Advance data from vital and health statistics. No. 314. Hyattsville, Md: National Center for Health Statistics, 2000. (DHHS publication no. (PHS) 2000-1250 0-0431)

4. World Health organization. Strategic directions for strengthening nursing and midwifery services [online]. Available from: URL:http://www.wpro.who.int/themesfocuses/theme3/focus2/nursingmidwifery.pdf2002

Units of Measurement

Authors should express all measurements in conventional units, with Système International (SI) units given in parentheses throughout the text. Figures and tables should use conventional units, with conversion factors given in legends or footnotes. In accordance with the Uniform Requirements, however, manuscripts containing only SI units will not be returned for that reason.

Abbreviations

Except for units of measurement, abbreviations are discouraged. Consult Scientific Style and Format: The CBE Manual for Authors, Editors, and Publishers (Sixth edition. New York: Cambridge University Press, 1994) for lists of standard abbreviations. Except for units of measurement, the first time an abbreviation appears, it should be preceded by the words for which it stands.

Chemical Structure

Structures should be produced with a chemical drawing program, preferably ChemDraw 4.5 or higher, and submitted in TIFF format to allow use of electronic files in production. Structures should also be submitted in native file formats, e.g., RDX.

For any more detail about the writing style for your manuscripts refer to:
http://www.jaehr.muk.ac.ir

Authorship Form

Title of the manuscript:

....

....

We, the undersigned, certify that we take responsibility for the conduct of this study and for the analysis and interpretation of the data. We wrote this manuscript and are responsible for the decisions about it. Each of us meets the definition of an author as stated by the International Committee of Medical Journal Editors (see http://www.icmje.org/icmje-recommendations.pdf). We have seen and approved the final manuscript. Neither the article nor any essential part of it, including tables and figures, will be published or submitted elsewhere before appearing in the *Journal of Advances in Environmental Health Research* [All authors must sign this form or an equivalent letter.]

Name of Author	Contribution	Signature

<mark>Please scan this form and upload it as a supplementary file in "Step 4" of submitting articles.</mark>

Table of Contents

Original Article(s)

Developing a questionnaire on strategies for increasing housewives' participation in source separation of municipal solid waste based on the theory of planned behavior

Soran Erami[1], Tahereh Pashaei[2], Behzad Shahmoradi[3]

1 Department of Environmental Health Engineering, School of Health, Kurdistan University of Medical Sciences, Sanandaj, Iran
2 Department of Public Health, School of Health, Kurdistan University of Medical Sciences, Sanandaj, Iran
3 Environmental Health Research Center, Kurdistan University of Medical Sciences, Sanandaj, Iran

Abstract

Original Article

Creating awareness and recognizing behavioral factors associated with recycling is essential for waste management. To identify factors influencing recycling behavior, a theory of planned behavior (TPB)-based questionnaire was designed. The aim of this study was to assess the validity and reliability of the questionnaire. This psychometric study was conducted through a multistage random sampling on 283 homemakers of Mahabad Town, Iran, in 2014. The method recommended by Ajzen and Francis was used for designing the questionnaire. Its validity was evaluated using quantitative and qualitative face validity, ration and content validity index, and qualitative judgment of an expert panel of 8 members and its structural validity using exploratory factor analysis. In addition, its reliability was assessed using internal consistency (Cronbach's alpha coefficient) and retest (intraclass correlation) methods. Of the 53 initial questions, after calculating the content validity ratio (CVR) with values higher than 0.80 and content validity index (CVI) with values higher than 0.79, we modified 3 questions and deleted 8 questions; therefore, 45 questions were approved. Using exploratory factor analysis with a varimax rotation, 9 factors with a value of higher than 1 were selected, which were able to predict 91.81% of the total variation. The reliability of the tool was confirmed through calculating Cronbach's alpha (0.87). Results of retest indicated the consistency of the questionnaire. This research found that the Persian version of the Theory of Planned Behavior Questionnaire (TPB questionnaire) has suitable validity and reliability and can be used in research and administrative activities on increasing the participation of homemakers in municipal solid waste source separation.

KEYWORDS: Factor Analysis, Questionnaire, Recycling, Waste Management

Citation: Erami S, Pashaei T, Shahmoradi B. **Developing a questionnaire on strategies for increasing housewives' participation in source separation of municipal solid waste based on the theory of planned behavior.** J Adv Environ Health Res 2015; 3(1): 1-7.

Introduction

Technological development and rapid population growth have caused an increase in consumption and household waste production level. It, in turn, may lead to crises such as water and soil pollution, greenhouse gas emission, and negative impacts on the quality of human life.[1] These problems are more common and visible in developing countries, where garbage collection does not occur at all.[2] If one wants to reduce such pollution, it would be essential to apply waste management procedures along with economic and engineering principles to eliminate waste disposal.[3]

According to the Waste Management Act,

Corresponding Author:
Behzad Shahmoradi
Email: bshahmorady@gmail.com

enacted in 2004, urban authorities should apply procedures with the aim of achieving functional elements in waste management to prevent unsafe disposal of waste and to encourage private sector and citizen participation.[4] Cost-effective techniques for waste minimization include increasing awareness, providing educational packages for the public, and encouraging citizens to cooperate in the design of household waste recycling processes.[5] Recycling is a process whereby materials used previously are collected, processed, rebuilt, and reused. Recycling requires two methods of separation; separation of material from waste, and source separation.[6]

Material separation of waste has some consequences, but source separation is more efficient and cheaper compared with no action in this regard. Today, source separation recycling is performed as one of the most efficient and economical processing methods in most countries. This approach reduces the cost of transportation. If household waste separation and recycling management be performed correctly, a part of the national capital is returned.[7] Around 40,000 tons of solid waste is generated in Iran daily, only 10% of which is recycled and the remaining is buried using unsanitary methods, while more than half of this amount is recyclable.[8] In contrast, in developed countries, 80% of household waste is recycled and returned to the consumption cycle. In Australia and the UK, around 60% of household waste is recycled.[9]

Waste recycling and reusing is not an easy task and requires scientific, technical, and cultural infrastructures. Perhaps, the most important part of this task is the cultural factor.[10] Citizens must be educated to generate less waste, and categorize waste at their house in order to simplify the recycling programs.[11]

There is a need to test and conduct theory-based studies to understand the mechanisms responsible for recycling behaviors. Several behavior change theories have been applied to explain the factors influencing recycling behavior, including Schwartz's Norm Activation Model[12], the theory of reasoned action, and the theory of reasoned planned behavior.[13] The theory of planned behavior (TPB) provides a theoretical framework for the systematic examination of factors that affect behavioral change.[14] According to the TPB, a persons' behavior is based on his/her readiness to perform a given behavior (i.e. intention).[15] TPB considers intention as immediate antecedent of behavior, and intention is based on attitudes toward behavior, subjective norms, and perceived behavioral control.[16] Attitude toward a behavior is a persons' positive or negative evaluation of that behavior. It is assumed to have two components; behavioral belief, and evaluation of consequences of the behavior, which leads to acquisitive attitude toward behavior. Subjective norms are perceived social pressure to perform or not to perform the behavior in question. This perception or opinion has been labeled as the individual's normative belief, which is often multiplied by the motivation to comply with that norm. Perceived behavioral control is the extent to which one believes he/she can successfully enact a behavior (i.e., to what extent the performance of a behavior is under his/her control). Behavioral intention is indicative of the extent of intention and will of the individual to perform the target behavior. Behavior always proceeds behavioral intention and is attached to it.[17]

In TPB, the most important determinant factor of an individual's behavior is his behavioral intention.[18] Therefore, in order to increase the prediction of source separation behavior, it was attempted to add other factors that can contribute along with subscales of this theory[17,18]. No standard questionnaire based on Ajzen's theory existed to conduct a TPB-based study. Hence, it is essential to conduct a study in order to design a new questionnaire suited to the characteristics of the target population, and a trial to ensure the psychometric properties of the

TPB scale.[13,19]

Despite numerous TPB questionnaires in English, no study has yet been conducted to validate the questionnaires for citizens' participation in the source separation of solid waste in Iran. Hence, this study was aimed at developing and evaluating the psychometric properties of the TPB-based questionnaire in relation to public participation in source separation of household solid wastes in Mahabad Town, Iran.

Materials and Methods

This was a psychometric study performed in 2014. The target population comprised of homemakers in Mahabad, Iran. As family planners, homemakers have to be aware of environmental problems and ways to deal with them. They can play a crucial role in changing consumption patterns and reducing pollution. After consideration of literature review and the recommendations of experts, the recommended procedures of Aijen[13] and Francis[12] were used for primary designing of the questionnaire. Therefore, in the first stage, 8 questions related to factors effective on participating in source separation were distributed among 30 housewives who referred to 8 health centers in different parts of the town. This stage was performed in order to identify salient beliefs, benefits, factors, perceived barriers, and effective reference groups in participation. In the next stage, the answers to each question were classified according to different concepts (attitude, subjective norm, perceived behavioral control, and self-identity, action planning, perceived barriers, perceived benefits, facilitating factors, and behavioral intention). The most indicated responses to each question were selected. Then, the questionnaire was designed through holding several meetings with an expert panel and obtaining their views regarding the relevance of expressions in terms of clarity (use of simple and understandable words) and use of common language (avoiding the use of technical words). The questionnaire

was based on a 5-point Likert scale. The pilot questionnaire was prepared to determine its reliability and validity. The qualitative and quantitative methods were used to determine the validity of the questionnaire.

In the qualitative method, the pilot questionnaire was distributed among 8 panel members via e-mail, which is approximately 2 times more than the minimum number proposed by Lawsche.[20] They were asked to review and provide feedback on the questionnaire based on the application of appropriate simple words, observations, writing, grammar, and the placement of items in the right place. In the qualitative approach, in order to ensure that the most important and most accurate content (essential items) are selected, content validity ratio (CVR) was used. CVR values of higher than 0.75, in accordance with Lawsche's Table, were accepted in the present study. Moreover, in order to ensure that tool items are designed to measure the content, the content validity index (CVI) was used. Therefore, the panel members were asked to express their ideas on each item in terms of simplicity, clarity, and relevance through four-episode range for each item, and finally, those items with a CVI of higher than 0.79 were accepted.

In the third stage, in order to determine the validity of the tool, both qualitative and quantitative methods were used. İn the qualitative method, an interview was carried out with 10 housewives in order to obtain feedback on difficulty in understanding the phrases and words, the possibility of ambiguity, and incomplete interpretations of the meanings of words. Then, to specify the quantitative validity, the impact of each item was used. To do this, the questionnaire was given to 10 housewives. After completion of the questionnaire, using the impact of items formula (score = frequency × importance), the impact of each item was calculated and the impact scores of higher than 1.5 were accepted.

Since the research tool was designed for the

first time, in order to identify patterns of correlations between the items in each domain, exploratory factor analysis was used.[21] In this analysis, the ratio of variables to subjects should be at least equivalent to 1 to 5. Therefore, with respect to the number of items, the minimum sample required for this study was estimated to be 265 subjects. In order to increase the accuracy, 300 subjects were enrolled in the study. However, 17 questionnaires were eliminated due to incompleteness, and exploratory factor analysis was conducted using the data of 283 questionnaires. To determine the reliability of the instrument, with an emphasis on internal consistency, Cronbach's alpha was used. The reliability coefficient ranges from 0 to +1. Therefore, the revised questionnaire was distributed among 30 women referred to the 8 urban health centers. By collecting the data, Cronbach's alpha value was calculated, and values greater than 0.7 were accepted. In order to check the repeatability of the questionnaire, intraclass correlation coefficient (ICC) was used. For this purpose, the modified questionnaire was distributed in two steps at a time interval of 14 days for each of the 30 women referred to those health centers. Each homemaker answered the questionnaires anonymously and indicated their awareness on the study purposes by signed a consent letter. The data was collected and analyzed using SPSS software (version 16, SPSS Inc., Chicago, IL, USA).

Results and Discussion

The mean ± standard deviation of age of homemakers who participated in this study was 37.94 ± 10.52. In addition, 53.03% of subjects had a diploma, and 48.4% of them had incomes in the range of 1-1.5 million Tomans (Table 1). In qualitative evaluation of content validity, cases, such as using simple and appropriate words, following writing rules, and aligning the items in the right place, were considered. As a result, several items of the tool were considered for revision and necessary changes. To obtain CVR,

based on the number of experts according to Lawsche's Table[20], estimating numerical mean of the judgments of panel members was estimated., Questions with a CVR of higher than 0.75 and mean value higher than 1.5 were accepted. Ultimately, based on these results, 5 questions were eliminated.

For CVI, those items with a CVI of higher than 0.79 were accepted; hence, 3 questions were eliminated. Therefore, 45 out of 53 questions, which had suitable content validity, were entered into the next stages of validity.

Table 1. Demographic characteristic variables of the study participants

Variable	Frequency (%)
Age (year)	
20–29	69 (24.38)
30-39	123 (43.46)
40–49	50 (17.66)
> 50	41 (14.50)
Qualification	
Secondary school	48 (16.97)
Diploma/certificate	150 (53.03)
University degree	85 (30.00)
Income (million Rials)	
5-10	87 (30.75)
10.1-15	137 (48.40)
> 15	59 (20.85)
Having the knowledge to separate household waste at home	
Yes	170 (60.00)
No	113 (40.00)
Having the space to separate household waste at home	
Yes	27 (80.00)
No	56 (20.00)
Having the time to separate household waste at home	
Yes	225 (90.00)
No	28 (10.00)

In the qualitative evaluation of face validity, 4 items needed to be corrected based on comments received from participants. The necessary changes were carried out for clarification. In the quantitative evaluation stage, as the efficiency level of all the items was above

1.5, all items were identified to be appropriate. In exploratory factor analysis, the value of Kaiser-Meyer-Olkin (KMO) Measure of Sampling Adequacy index was determined to be 0.875, which is much higher than 0.6. This is indicative of sufficient sampling for factor analysis. Bartlett's test of sphericity was significant (as the degree was 0 and P < 0.005). This indicated that the data were suitable for factor interactions. The calculated share extractive values for all items were shown to be between 0.748 and 0.923, indicating suitability of all items. The analysis of exploratory factor with a varimax rotation indicated 9 valuable factors greater than 1, which provided evidences of the multidimensionality of the questionnaire. According to the content of the questions, these 9 factors were namely attitude (5 questions), subjective norm (3 questions), perceived behavioral control (4 questions), self-identity (6 questions), action planning (4 questions), facilitating factors (5 questions), perceived benefits (5 questions), perceived barriers (9 questions), and behavioral intention (4 questions) (Table 2). These factors accounted for 91.81% of the total variance (Table 3).

The reliability of the questionnaire was tested through internal consistency and stability. To assess internal consistency, Cronbach's alpha was used, and the value of Cronbach's alpha for the scale was equal to 0.87 for each subscale (Table 4). The alpha values calculated for each subscale and domain of this study were greater than 0.7. Hence, the reliability of the instrument was well assessed and approved. To estimate the stability of repeatability, test-retest method and ICC were used, and the test-retest for the entire questionnaire was 0.89 (Table 4). In order to prepare a household waste recycling behavior questionnaire, several studies have been conducted based on TBP.[22,23] In our study, there were insignificant differences among some indices compared with previous studies, which might be due to the cultural differences and participants. Cronbach's alpha for the total scale was 0.87 and for subscales it ranged from 0.74 to 0.95. These results were very close to the results obtained in a study by Karim Ghani et al. in Malaysia.[17] The review by Davis and Morgan in 2008 indicated that Cronbach's alpha for TPB-based study ranged from 0.56 to 0.87.[22] In a study conducted in the United States, the internal consistency of the instrument equaled 0.82.[23]

Table 2. Weight of factor extracted from the exploratory factor analysis with varimax rotation

Perceived barriers	Self-identity	Attitude	Perceived benefits	Facilitating factors	Intention	Perceived behavior control	Action planning	Subjective norms
0.63	0.58	0.83	0.78	0.64	0.66	0.64	0.66	0.55
0.71	0.63	0.75	0.44	0.52	0.47	0.43	0.41	0.56
0.53	0.43	0.63	0.52	0.41	0.56	0.58	0.52	0.67
0.66	0.54	0.47	0.58	0.74	0.74	0.71	0.69	
0.71	0.63	0.68	0.64	0.58				
0.64	0.68							
0.64	0.68							
0.74								
0.77								

Table 3. Total variance of exploratory factor analysis

Attitude	Self-identity	Perceived barriers	Perceived benefits	Facilitating factors	Intention	Perceived behavioral control	Action planning	Subjective norms
17.46	15.7	13.54	12.64	11.4	9.29	6.25	3.13	2.40

http://jaehr.muk.ac.ir

Table 4. The reliability results of the questionnaire subscales in theory of planned behavior (TPB) based study

Questionnaire dimensions	Number of Questions	Cronbach's alpha	Stability
Attitude	5	0.74	0.78
Subjective norm	3	0.88	0.85
Perceived behavioral control	4	0.79	0.84
Self-identity	6	0.87	0.91
Action planning	4	0.92	0.89
Facilitating factors	5	0.91	0.92
Perceived benefits	5	0.95	0.93
Perceived barriers	9	0.92	0.94
Intention	4	0.85	0.92

Test-retest results revealed that the prepared questionnaire has remarkable and full stability and this indicates that the questionnaire can provide reliable results in various circumstances of time and place. In addition, to determine the correlation pattern among the items in each domain, the exploratory factor analysis was used. However, it was not used in similar studies.[17,22,23] The results of exploratory factor analysis shows a nine-factor structure. In General, these factors show a 91.8% variance, indicating that most variables stated are related to the attitude factor. This is consistent with the study by Pakpour et al.[18] Structures of this study showed a 88.2% variance, among them attitude had the highest variance.

In the present study, the average score of the subscales for this instrument was 18.45, which was higher than the average scores (13.45 and 12.45) reported in literature.[22] This might be due to the differences in the study populations. In this study, the mean attitude subscale score was 20.52, which was higher than the average score (16.48) reported by Davis and Morgan.[22] The mean facilitator subscale score in this study was 15.85, which was similar to the score (15.45) reported by Karim Ghani et al.[17] This indicates that the presence of incentives and situational factors have a similar effective role in the source separation of wastes.

Finally, this study proved that the designed questionnaire has acceptable reliability and validity and is a useful instrument for researches and similar activities. One of the limitations of this study was that only 1 group of homemakers was investigated. Therefore, it is recommended that similar studies be conducted in the future in other parts of the country with different customs.

Conclusion

In most studies, designing and measuring the validity and reliability of the tool and data collection are time consuming and costly. Access to a reliable and valid tool, the psychometric properties of which have been approved, will increase the process speed and reduce the costs. In this study, the questionnaire had acceptable level of reliability and validity and contributed greatly to the identification of factors influencing recycling behavior.

Conflict of Interests

Authors have no conflict of interests.

Acknowledgements

References

1. Tchobanoglous G, Theisen H, Vigil SA. Integrated solid waste management: engineering principles and management issues. New York, NY: McGraw-Hill; 1993.

http://jaehr.muk.ac.ir

2. Kanat G. Municipal solid-waste management in Istanbul. Waste Manag 2010; 30(8-9): 1737-45.
3. Beede DN. Essay on the economics of the generation and management of waste [PhD Thesis]. New York, NY: University of Colombia; 1996.
4. Abduli MA, Tavakolli H, Azari A. Alternatives for solid waste management in Isfahan, Iran: a case study. Waste Manag Res 2013; 31(5): 532-7.
5. Abduli MA, Azimi E. Municipal Waste Reduction Potential and Related Strategies in Tehran. International Journal of Environmental Research 2010; 36(4): 901-12.
6. Alavi Moghadam MR, Mokhtarani N, Mokhtarani B. Municipal solid waste management in Rasht City, Iran. Waste Manag 2009; 29(1): 485-9.
7. Omrani G A. Solid waste management, collection, transportation, sanitary and composting. Tehran, Iran: Scientific Publication Center of Islamic Azad University; 1994. [In Persian].
8. Salvato JA, Nemerow NL, Agardy FJ. Environmental Engineering. New Jersey, NJ: John Wiley & Sons; 2003.
9. Gamba RJ, Oskamp S. Factors Influencing Community Residents' Participation in Commingled Curbside Recycling Programs. Environment and Behavior 1994; 26(5): 587-612.
10. Ayatollahi SAR., Mohammad Poor Asl A, Rajaeefard AR. Predicting Three Stages of Smoking Acquisition in the Male Students of Shiraz High Schools. Med J Tabriz Univ Med Sci 2005; 26(4): 10-5. [In Persian].
11. Bartelings H, Sterner T. Household Waste Management in a Swedish Municipality: Determinants of Waste Disposal, Recycling and Composting. Environmental and Resource Economics 1999; 13(4): 473-91.
12. Francis JJ, Eccles MP, Johnston M, Walker A, Grimshaw J, Foy R, et al. Constructing Questionnaires Based on the Theory of Planned Behaviour: A Manual for Health Services Researchers04. Callaghan, Australia: Centre for Health Services Research, University of Newcastle; 2004.
13. Ajzen I. The Theory of Planned Behavior. Organ Behav Hum Decis Process 1991; 50(2): 179-211.
14. Shamsi Meymandi M, Ziaeddini H, Sharifi Yazdi A. Opinion of high school students of Kerman towards affecting factors on narcotics tendency. J Qazvin Univ Med Sci 2008; 12(3): 80-8. [In Persian].
15. Tavousi M. The effectiveness of a modified theory of reasoned action on substance abuse prevention among Adolescents in Tehran [Thesis]. Tehran, Iran: Tarbiat Modares University; 2009. [In Persian].
16. Barati M, Allahverdipour H, Moinei B, Farhadinasab A, Mahjub H. Evaluation of Theory of Planned Behavior-Based Education in Prevention of MDMA (ecstasy) use among University Students . Med J Tabriz Univ Med Sci 2011; 33(3): 23-9. [In Persian].
17. Karim Ghani WA, Rusli IF, Biak DR, Idris A. An application of the theory of planned behaviour to study the influencing factors of participation in source separation of food waste. Waste Manag 2013; 33(5): 1276-81.
18. Pakpour AH, Zeidi IM, Emamjomeh MM, Asefzadeh S, Pearson H. Household waste behaviours among a community sample in Iran: an application of the theory of planned behaviour. Waste Manag 2014; 34(6): 980-6.
19. Ajzen I. Constructing a TpB Questionnaire: Conceptual and Methodological Considerations [Online]. [cited 2002]; Available from: URL: http://www.uni-bielefeld.de/ikg/zick/ajzen%20construction%20a%20tpb%20questionnaire.pdf
20. Lawsche CH. A quantitative approach to content validity. Personnel Psychology 1975; 28(4): 563-75.
21. Dixon JK. Factor Analysis. In: Munro BH, editor. Statistical Methods for Health Care Research: With Online Articles. 4th ed. Philadelphia: Lippincott Williams & Wilkins; 2001.
22. Davis G, Morgan A. Using the Theory of Planned Behaviour to determine recycling and waste minimisation behaviours: A case study of Bristol City, UK. The Australian Community Psychologist 2008; 20(1): 105-17.
23. Largo-Wight E, Bian H, Lange L. An Empirical Test of an Expanded Version of the Theory of Planned Behavior in Predicting Recycling Behavior on Campus. American Journal of Health Education 2012; 43(2): 66-73.

http://jaehr.muk.ac.ir

Photocatalytic degradation of methylene blue dye over immobilized ZnO nanoparticles: Optimization of calcination conditions

Reza Darvishi Cheshmeh Soltani[1], Abbas Rezaee[2], Reza Rezaee[3], Mahdi Safari[3], Hassan Hashemi[4]

1 Department of Environmental Health, School of Health, Arak University of Medical Sciences, Arak, Iran
2 Department of Environmental Health, School of Medical Sciences, Tarbiat Modares University, Tehran, Iran
3 Environmental Health Research Center, Kurdistan University of Medical Sciences, Sanandaj, Iran
4 Research Center for Health Sciences, Shiraz University of Medical Sciences, Shiraz, Iran

Original Article

Abstract

In the present study, calcination conditions during the synthesis of zinc oxide nanoparticles were optimized using response surface methodology (RSM) based on central composite design (CCD). After that, the effect of the type of UV irradiation on the photocatalysis of methylene blue (MB) dye was studied based on the kinetic model obtained at optimum conditions. Analysis of variance (ANOVA) exhibited a reasonable high correlation coefficient between the predicted and experimental values (R^2 = 0.95). For a decolorization efficiency of 90%, the optimum calcination temperature and calcination time were identified to be 459 °C and 3.65 h, respectively. According to the reaction rate constant (k), the time required for the removal of MB using UVC lamps (0.027 1/min) was shorter than that of UVA lamps (0.0098 1/min), indicating higher exciting potential of the UVC irradiation for the generation of hydroxyl radicals through photocatalysis.

KEYWORDS: Nanoparticles, Methylene Blue, Zinc oxide, Hydroxyl Radical, Kinetics

Introduction

In recent decades, advanced oxidation processes (AOPs) have been proposed as efficient techniques for the degradation of organic pollutants such as dyes.[1,2] The most widely investigated AOPs for the treatment of wastewater containing dye are photocatalytic processes.[2] Among the various photocatalysts employed in photocatalytic processes, TiO_2 and ZnO are known to be efficient photocatalysts for the degradation of various environmental contaminants.[3-5] Compared to TiO_2, ZnO nanoparticles have a large area-to-volume ratio, high UV absorption capacity and long life-span. When ZnO nanoparticles are irradiated with UV light, highly reactive hydroxyl radicals (OH) are produced, which promote the degradation of target pollutants.[6,7] To mitigate the toxicity of ZnO nanoparticles for aqueous ecosystems and to make their use more economical, in the present study, ZnO nanoparticles were immobilized onto glass plates.[8] One of the most important parameters influencing the structure and activity of the photocatalyst is calcination conditions.[9,10] Therefore, a photocatalytic process consisting of low-pressure UV lamps and

Corresponding Author:
Mahdi Safari
Email: safari.m.eng@gmail.com

immobilized ZnO nanoparticles was used to characterize the photocatalytic activity of ZnO nanoparticles toward the degradation of methylene blue (MB) dye under different calcination conditions. To better evaluate the effect of calcination conditions, response surface methodology based on central composite design was used due to its advantages compared to the "one-factor-at-a-time" statistical approach.[11-14] In the following, the effect of the type of UV irradiation on photocatalytic decolorization of MB was evaluated at optimum calcination conditions.

Materials and Methods

The ZnO nanoparticles were prepared via co-precipitation method. First, 3.6 g ammonium nitrate was dissolved in 40 mL deionized water. Then, 0.9 mL aqueous ammonia was added to the abovementioned solution. Subsequently, 10 mL zinc nitrate was added dropwise to a stirred solution for 3 h at room temperature. After that, nitric acid was added to adjust the pH of the solution to 6.0. After aging for 24 h, 40 ml hydrogen peroxide (10 wt%) was added the stirred solution for 1 h. The precipitate was filtered and washed with deionized water, then, was dried in an oven at 80 °C. The resulted powder was immobilized on the glass plates via the heat attachment method.[15] To functionalize the surfaces of the glass plates (3 × 20 cm in size) with hydroxyl groups, concentrated industrial grade NaOH (50%) was used.[16] The functionalization with hydroxyl groups would be beneficial to achieve a stronger attachment of the ZnO nanoparticles to the plates. A 5% suspension of amorphous ZnO powder was prepared. After sonication in an ultrasonic bath (Starsonic 18-35, Liarre, Italy) at a frequency of 30 kHz for 90 min, the sonicated suspension was coated on the surface of the glass plates. Next, it was dried in an oven at 90 °C for 1 h. Finally, ZnO nanoparticle-coated glass plates were calcined in an electric furnace at different exposure times and temperatures based on the experimental design obtained using central composite design (CCD).

The photocatalytic process was carried out in a 600 ml rectangular reactor. Then, 5 low-pressure mercury vapor lamps (6 W) (Philips, Holland) were placed in the reactor top of the 3 glass plates containing immobilized ZnO nanoparticles. Recirculation of the solution was carried out via a peristaltic pump (Heidolph 5001, Germany). All the experiments were carried out with the solutions containing 5 mg/l MB at neutral pH.

Residual MB in the solution was measured with a UV-Vis spectrophotometer (Unico 2100) at 663 nm. Furthermore, the X-ray diffraction (XRD) patterns of the samples were obtained using a diffractometer (XRD, X'Pert MPD, Philips, Netherlands).

To evaluate the effect of calcination conditions on decolorization efficiency, two main variables regarding calcination conditions were selected; the calcination temperature and time. The number of required experimental runs was calculated via equation (Eq). 1:[12,13]

$$N = 2^k + 2k + x_o \quad (1)$$

where N is the number of required experimental runs (fact), k is the number of variables, and x_o (axial) is the number of central points. Thus, according to Eq. 1, the total number of required experimental runs is 13 (k = 2, x_o = 5). Design-Expert software (Stat-Ease, Inc., Minneapolis, MN, USA) was used for the analyses of the obtained data. The variables X_i were coded as x_i for statistical analysis according to Eq. 2:[14]

$$x_i = \frac{X_i - X_0}{\delta X} \quad (2)$$

where X_o and δX are the values of X_i at the center point and step change, respectively. The experimental ranges of the variables concerning MB removal are summarized in table 1.

Due to low melting point of the glass plates and the high energy required, the immobilized ZnO nanoparticles could not be calcined at above 500 °C. The catalyst was prepared

according to the calcination conditions described in the experimental runs, then, the photocatalytic MB removal (%) was measured at constant MB concentration of 5 mg/l, reaction time of 120 min, and neutral pH. The process can be described by means of a second-order model as represented in Eq. 3:

$$Y = b_0 + \sum_{i=1}^{n} b_i x_i + \left(\sum_{i=1}^{n} b_{ii} x_i\right)^2 + \sum_{i=1}^{n-1} \sum_{j=i+1}^{n} b_{ij} x_i x_j \quad (3)$$

where Y is the dependent variable [decolorization efficiency (%)], b_o is a coefficient constant, b_i are linear coefficients, b_{ij} are interaction coefficients, and b_{ii} are quadratic coefficients. Moreover, x_i and x_j are the coded values for the experimental variables.[12-14]

Results and Discussion

CCD model results

Using the CCD model, an empirical mutual relationship was established between the response [decolorization efficiency (%)] and independent variables based on the coded variables according to Eq. 4:

$$Y = 86.74 + 5.92x_1 - 0.68\, x_2 - 2.37\, x_1 x_2 - 4.12 x_1^2 - 1.83 x_2^2 \quad (4)$$

where Y is the decolorization efficiency (%). The CCD matrix, experimental results, and predicted values for the photocatalytic decolorization are summarized in table 2. The statistical significance of the quadratic model was assessed through analysis of variance (ANOVA). The ANOVA results are presented in table 3. Table 3 demonstrates that the regression model has a high coefficient of determination ($R^2 = 0.95$), indicating that 95% of the variations of decolorization can be explained by the independent parameters. In fact, the model fails to explain only 5% of the variation. The low P-values obtained in the ANOVA indicate the significance of the results.[11]

Table 1. Ranges of the experimental parameters

Parameters	Ranges and levels				
	-2	-1	0	+1	+2
Calcination temperature (°C)	250	287.00	375.0	463.00	500
Calcination time (h)	3	3.44	4.5	5.56	6

Table 2. Experimental and predicted results of applied central composite design (CCD)

Run	Calcination temperature (°C)	Calcination time (h)	Decolorization efficiency (%)		
			Experimental	Predicted	Residual
1	375	4.50	85.12	86.74	-1.62
2	375	4.50	86.60	86.74	-0.14
3	463	3.44	91.56	89.77	1.79
4	375	4.50	88.21	86.74	1.47
5	463	5.56	86.23	83.68	2.55
6	375	6.00	80.35	82.13	-1.78
7	287	5.56	77.24	76.56	0.68
8	500	4.50	84.32	86.88	-2.56
9	375	4.50	86.56	86.74	-0.18
10	375	3.00	83.36	84.05	-0.69
11	250	4.50	70.23	70.13	0.10
12	287	3.44	73.10	73.19	-0.09
13	375	4.50	87.23	86.74	0.49

Table 3. Analysis of variance (ANOVA) for the photocatalytic methylene blue (MB) removal

Source of variations	Sum of squares	Degree of freedom	Mean square	F-value	P (Probe > F)
Regression	436.43	5	87.29	23.96	0.0003
Residuals	25.51	7	5.10		
Total	461.93	12			

R^2: 0.95; adjusted R^2: 0.91; adequate precision: 15.14; C.V: 2.30%
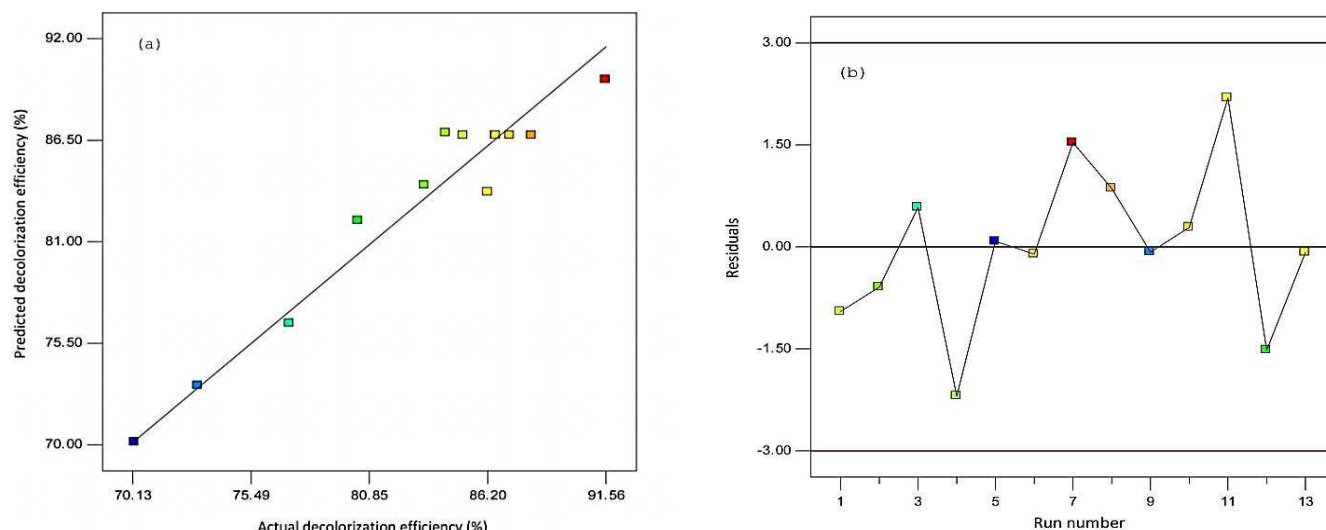
Figure 1. (a) Predicted versus actual decolorization efficiency and (b) residual versus run number for the photocatalytic methylene blue (MB) removal

It is important to note that "Adequate precision" measures the difference between the signal and noise (signal-to-noise ratio), and a ratio of greater than 4 is favorable.[13] As shown in table 3, the obtained ratio of 15.14 indicated an adequate signal. In addition, the low value of the coefficient of variation (CV = 2.30%) exhibited the relatively high reliability of the model for describing the removal of MB dye via the photocatalytic process.

In order to evaluate the adequacy of the model, experimental and predicted data were compared [Figure 1 (a)]. Figure 1 (a) demonstrates a good agreement between the predicted decolorization efficiency (%) and the experimental values (R^2 = 0.95). Residuals (Table 2) indicate how well the model satisfies the assumptions of ANOVA.[11,13] The plot of residuals versus run number is depicted in figure 1 (b). Figure 1 (b) shows no apparent dispersal of residuals for each experimental run, indicating suitability of the model for satisfying the assumptions of ANOVA.

Interactive effects of the independent parameters

Response surface and corresponding contour plot were applied for interaction of any two parameters. The effects of calcination temperature and calcination time on photocatalytic MB removal are shown in figure 2. These plots visualize how high and low values of calcination temperature affect MB removal during the photocatalytic process. At low calcination temperature, the synthesized nanoparticles have a wide range of particle size, while with increasing calcination temperature, the average particle size of aggregated particles increases as a result of increasing primary size of the nanoparticles during heat aggregation.[10] In agreement with our study, another investigation has demonstrated that increasing calcination temperature results in the increasing of average crystallite size.[17] Moreover, Yu and Wang[9], and

Yu et al.[18] showed that calcination temperature has a great effect on the structure and photocatalytic activity of TiO₂ nanotube arrays and TiO₂ film prepared by liquid phase deposition.

Figure 2. a) Response surface plot of photocatalytic methylene blue (MB) removal (%) as the function of calcination temperature and calcination time

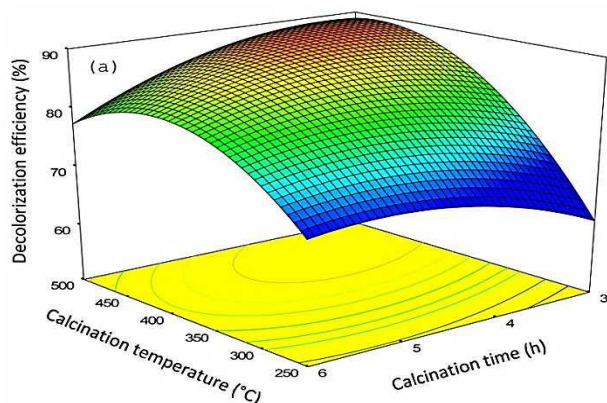As can be seen in figure 2, at low calcination temperature, decolorization efficiency (%) increased with increasing calcination time from the lowest value of 3 h to the moderate values. Then, it became constant as the calcination time increased from the moderate values to the highest value of 6 h. At high calcination temperature, increasing calcination time led to an evident drop in decolorization efficiency (%). A desirable value for each independent variable and response can be selected by using numerical optimization. Using this approach, the maximum decolorization efficiency (%) by the photocatalytic process was 90% at a calcination temperature of 459 ᵒC and a calcination time of 3.65 h. In accordance with our study, Lai et al., in their study, showed that photocatalytic activity depends on calcination temperature.[19] According to their finding, the calcination temperature of 450 °C had the highest photocatalytic activity for degradation of methyl orange.[19] In a comparative photocatalytic study carried out using TiO₂ film, it was exhibited that

the photocatalytic activity of TiO₂ film calcined at 700 °C was 2.5 times higher than that of the thin film calcined at 500 °C.[18]

Characteristics of synthesized ZnO nanoparticles

To determine the actual crystallite size of ZnO nanoparticles, XRD analysis was performed and the result is depicted in figure 3. Figure 3 displays the excellent crystal structure of synthesized ZnO nanoparticles. The crystallite size of ZnO nanoparticles was determined using the Debye–Scherrer's equation.[7] Accordingly, the average crystallite size of the ZnO nanoparticles was about 47.4 nm.
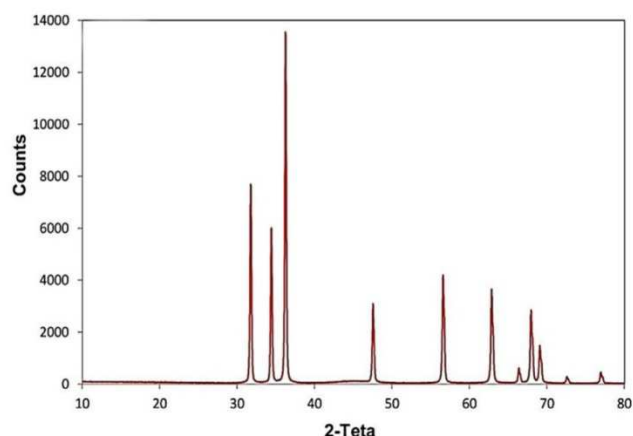
Figure 3. X-ray diffraction (XRD) spectrum of as-synthesized ZnO nanoparticles in optimal calcination conditions (Calcination temperature = 459 ᵒC, calcination time = 3.65 h)

Kinetics for photocatalytic MB removal

The rate of a reaction is of principal concern. The rate at which a reaction occurs is usually determined by the concentration of the reactant as the reaction proceeds. To evaluate the reaction rate of photocatalytic MB removal using different types of UV lights, an integrated form of pseudo-first-order kinetic model was used (Figure 4).

The obtained correlation coefficients for both UVA and UVC ($R^2 > 0.99$) indicated that the amount of MB removal is directly proportional to the concentration of MB in the solution. Nishio et al., in their study, showed that

photocatalytic azo dye removal with ZnO powder followed pseudo-first-order kinetic model.[20] This finding is in agreement with our findings. As is evident from figure 4, the reaction rate constant (*k*) of MB removal for the UVC and UVA lamps was found to be 0.027 1/min and 0.0098 1/min, respectively, implying that the time required for MB removal by UVC lamps is shorter than that of UVA light. As reason, the application of UVC lamps produces more photons to excite more electron-hole pairs for photocatalytic decomposition of MB. Moreover, the application of UVC lamps results in decreasing the electron-hole recombination rate, which is one of the most important reasons for decreasing photocatalytic activity of a photocatalyst.[21]
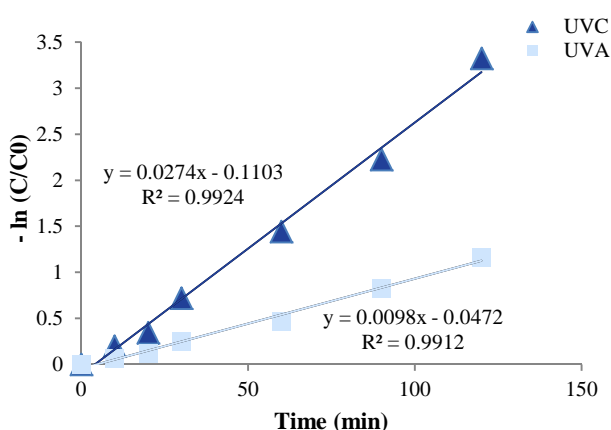
Figure 4. Effect of the type of UV light on decolorization efficiency (%) [Methylene blue (MB) concentration = 5 mg/l, reaction time = 120 min, and pH = neutral]

Conclusion

In the present study, the effect of the calcination conditions on the photocatalytic activity of synthesized nitrogen-doped ZnO nanoparticles has been studied in the context of response surface methodology (RSM). ANOVA analysis indicated a satisfactory fit between the regression model and the experimental results. According to the model, the highest rate of dye removal was attained at a calcination temperature of 459 °C and a calcination time of 3.65 h. Further experiments in optimum calcination conditions revealed an evident increment in decolorization efficiency (%) using UVC lamps instead of UVA lamps.

References

1. Darvishi Cheshmeh Soltani R, Rezaee A, Safari M, Khatae AR, Karimi B. Photocatalytic degradation of formaldehyde in aqueous solution using ZnO nanoparticles immobilized on glass plates. Desalination and Water Treatment 2015; 53(6): 1613-20.
2. Darvishi Cheshmeh Soltani R, Rezaee A, Khataee A. Combination of Carbon Black-ZnO/UV Process with an Electrochemical Process Equipped with a Carbon Black-PTFE-Coated Gas-Diffusion Cathode for Removal of a Textile Dye. Ind Eng Chem Res 2013; 52(39): 14133-42.
3. Darvishi Cheshmeh Soltani R, Rezaee A, Khataee AR, Safari M. Photocatalytic process by immobilized carbon black/ZnO nanocomposite for dye removal from aqueous medium: Optimization by response surface methodology. J Ind Eng Chem 2014; 20(4): 1861-8.
4. Khataee A, Darvishi Cheshmeh Soltani R, Hanifehpour Y, Safarpour M, Gholipour Ranjbar H, Joo SW. Synthesis and Characterization of Dysprosium-Doped ZnO Nanoparticles for Photocatalysis of a Textile Dye under Visible Light Irradiation. Ind Eng Chem Res 2014; 53(5): 1924-32.
5. Khataee AR, Fathinia M, Aber S, Zarei M. Optimization of photocatalytic treatment of dye solution on supported TiO2 nanoparticles by central composite design: intermediates identification. J Hazard Mater 2010; 181(1-3): 886-97.
6. Akyol A, Bayramoglu M. Photocatalytic degradation of Remazol Red F3B using ZnO catalyst. J Hazard Mater 2005; 124(1-3): 241-6.
7. Rezaee A, Masoumbeigi H, Darvishi Cheshmeh Soltani R, Khataee AR, Hashemiyian SJ. Photocatalytic decolorization of methylene blue using immobilized ZnO nanoparticles prepared by solution combustion method. Desalination and Water Treatment 2012; 44(1-3): 174-9.
8. Peralta-Videa JR, Zhao L, Lopez-Moreno ML, de la Rosa G, Hong J, Gardea-Torresdey JL. Nanomaterials and the environment: a review for the biennium 2008-2010. J Hazard Mater 2011; 186(1): 1-15.

9. Yu J, Wang B. Effect of calcination temperature on morphology and photoelectrochemical properties of anodized titanium dioxide nanotube arrays. Applied Catalysis B: Environmental 2010; 94(3-4): 295-302.
10. Zhou M, Yu J, Liu S, Zhai P, Jiang L. Effects of calcination temperatures on photocatalytic activity of SnO2/TiO2 composite films prepared by an EPD method. J Hazard Mater 2008; 154(1-3): 1141-8.
11. Khataee AR, Zarei M, Moradkhannejhad L. Application of response surface methodology for optimization of azo dye removal by oxalate catalyzed photoelectro-Fenton process using carbon nanotube-PTFE cathode. Desalination 2010; 258(1−3): 112-9.
12. Rezaee A, Darvishi Cheshmeh Soltani R, Khataee AR, Godini H. Optimization of combined photocatalytic involving immobilized ZnO nanoparticles and electrochemical processes for ammoniacal nitrogen removal from aqueous solutions. Journal of Materials and Environmental Science 2012; 3(5): 955-66.
13. Darvishi Cheshmeh Soltani R, Rezaee A, Godini H, Khataee AR, Hasanbeiki A. Photoelectrochemical treatment of ammonium using seawater as a natural supporting electrolyte. Chemistry and Ecology 2013; 29(1): 72-85.
14. Darvishi Cheshmeh Soltani R, Rezaee A, Khataee AR, Godini H. Optimisation of the operational parameters during a biological nitrification process using response surface methodology. The Canadian Journal of Chemical Engineering 2012; 92(1): 13-22.
15. Behnajady MA, Modirshahla N, Mirzamohammady M, Vahid B, Behnajady B. Increasing photoactivity of titanium dioxide immobilized on glass plate with optimization of heat attachment method parameters. J Hazard Mater 2008; 160(2-3): 508-13.
16. Fathinia M, Khataee AR, Zarei M, Aber S. Comparative photocatalytic degradation of two dyes on immobilized TiO2 nanoparticles: Effect of dye molecular structure and response surface approach. Journal of Molecular Catalysis A: Chemical 2010; 333(1−2): 73-84.
17. Yu J, Qi L, Cheng B, Zhao X. Effect of calcination temperatures on microstructures and photocatalytic activity of tungsten trioxide hollow microspheres. Journal of Hazardous Materials 2008; 160(2−3): 621-8.
18. Yu JG, Yu HG, Cheng B, Zhao XJ, Yu JC, Ho WK. The Effect of Calcination Temperature on the Surface Microstructure and Photocatalytic Activity of TiO2 Thin Films Prepared by Liquid Phase Deposition. J Phys Chem 2003; 107(50): 13871-9.
19. Lai YK, Huang JY, Zhang HF, Subramaniam VP, Tang YX, Gong DG, et al. Nitrogen-doped TiO2 nanotube array films with enhanced photocatalytic activity under various light sources. Journal of Hazardous Materials 2010; 184(1−3): 855-63.
20. Nishio J, Tokumura M, Znad HT, Kawase Y. Photocatalytic decolorization of azo-dye with zinc oxide powder in an external UV light irradiation slurry photoreactor. J Hazard Mater 2006; 138(1): 106-15.
21. Anandan S, Vinu A, Mori T, Gokulakrishnan N, Srinivasu P, Murugesan V, et al. Photocatalytic degradation of 2,4,6-trichlorophenol using lanthanum doped ZnO in aqueous suspension. Catalysis Communications 2007; 8(9): 1377-82.

Accumulation and distribution of persistent organochlorine pesticides and their contamination of surface water and sediments of the Sabarmati River, India

Tanveer Alam S. Hashmi[1], Shobhana K. Menon[1]

1 Department of Forensic Science, School of Sciences, Gujarat University, Gujarat, India

Abstract

Original Article

Pesticides are chemical substances used to control pests in an effort to increase crop production and quality, and food storage. The levels of pesticides in different environmental compartments, such as water, soil, agricultural foods, and products of animal origin, have become a relevant issue. In this study, the levels of pesticide residues in Sabarmati River of Gujarat, India, have been investigated using surface water and sediment samples as a case study to find the extent of contamination and accumulation in the River. Thus, 3 organochlorine pesticides (OCPs), namely dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexane (HCH), and endosulfan, and their isomers were analyzed in the River through gas chromatography (GC) (Shimadzu, 2010) using an electron capture detector (ECD). The present research is very vital and holds a great significance for a developing nation like India. There is a lack of such studies in India and a similar study has not been carried out on the Sabarmati River since 1998. In some cases detected concentrations were higher than the standard set by the Indian Bureau of Standards as well as theEuropean Union. ∑OCP residues detected in surface water and sediments samples of the Sabarmati River ranged between below detection limit (BDL) and 392.71 µg/l and BDL-1393.81 ng/g.

KEYWORDS: Organochlorine Pesticides Residue, Analytical Determination, Gas Chromatography

Citation: Hashmi TAS, Menon SK. **Accumulation and distribution of persistent organochlorine pesticides and their contamination of surface water and sediments of the Sabarmati River, India.** J Adv Environ Health Res 2015; 3(1): 15-26.

Introduction

Dichlorodiphenyltrichloroethane (DDT), hexachlorocyclohexane (HCH) and endosulfan are very dangerous chemical substances and have been banned, but some farmers still use these substances to control pests. Some factories also produce organochlorine pesticides (OCPs). OCPs are very toxic and they may affect the biota and human consumers.[1] An epidemiological study has shown OCPs to be a potential risk factor for liver, breast, prostate, and testicular cancer, and lower sperm count in humans.[2] In 1993, DDT residues in excess of 100 mg/kg were reported in dried fish taken from rice fields in Bangladesh.[3] The present research is vital and holds a great significance for a developing nation like India. There is a lack of such studies in India and a similar study has not been carried out on the Sabarmati River, India, since 1998. Rivers in India are an important source of water supply and unfortunately are exposed to pesticide pollution. Therefore, it is very important to monitor water quality in terms of the presence of pesticides prior to its distribution in the society. In Ahmedabad, near the Sabarmati river, approximately 7 pesticide producing industries are situated. Many pesticide manufacturers and industries illegally dump their wastes directly into the river. A

Corresponding Author:
Tanveer Alam S. Hashmi
Email: shobhanamenon07@gmail.com

potential pathway for adverse effects of pesticides is via hydrologic systems, which supply water to natural ecosystems. Water is one of the primary ways through which pesticides are transported from an applied area to other locations in the environment. According to the guidelines of the World Health Organization (WHO), a concentration level of up to 2000 ng/l of HCH and DDT in drinking water is considered safe for humans and other living bodies.[4] There was a report of poisoning due to pesticides in India in Madhya Pradesh in 1967-68 where 12 people were affected and over 12 people died due to high levels of HCH.[5] A case study in Uttar Pradesh (India) in 1978 reported poisoning and death due to HCH in 250 and 4 individuals, respectively.[5]

The main objective of this study was to present a general overview of the existence of different pesticides in various locations of the respective river. This study was undertaken due to the necessity of monitoring pesticide residues in the river system, after the ban on the use of these pesticides, in order to assess any health/ecological risks. The study shows that the amount of OCPs found in agricultural areas is higher than that found in industrial and residential areas. Pesticides applied on soil eventually find their way to the aquatic system, thus, contaminating it. OCPs can persist in soil and water for several years, and subsequently, become accumulated in aquatic biota.[6].

Materials and Methods

All solvents (HPLC grade) were purchased from SD Fine-Chem Limited (SDFCL). Dichloromethane (DCM), acetone, hexane, sodium chloride (AR grade), and sodium sulphate (AR grade) were procured from SDFCL. Analytical standards of 4, 4′ DDT, endosulfan, and HCH were purchased from Sigma-Aldrich Laborchemikalien GmbH. The standard solutions (1.0 μg/ml) of organochlorine pesticides alone or in combination were prepared in hexane. Millipore Milli-Q purified water was used throughout the experiment.

The study area and sampling locations were identified based on the possible potential for water contaminations by pesticides. Sample collection was performed in two different phases. In phase I, samples were collected during May 2011, May 2012, and May 2013 to check the levels of pesticide residue in succeeding years and weather the concentration of pesticide gradually increased or decreased. In phase II, sampling was performed during January 2013, May 2013, and September 2013 to check the variation in levels of pesticides due to season in the Sabarmati River, Ahmedabad, Gujarat, India (Figure 1).

The Sabarmati River is located in Western India. It is one of the largest rivers of north Gujarat and originates from Dhebar Lake in Aravalli Range of the Udaipur District of Rajasthan and meets the Gulf of Cambay of the Arabian Sea. The millions of liters of 'treated' effluent water of 3,365 units of Vatva, Odhav, and Naroda pumped into the river by the Gujarat Industrial development corporation (GIDC) Mega pipeline at the Vasana-Narol Bridge near Ahmedabad. These effluents are 15 times more polluted than the accepted norms. The sampling locations were selected closer to the places where intensive agricultural and industrial activities are carried out. Surface water and sediment samples were collected from 8 sampling locations of the Sabarmati River because many industries are situated in nearby areas.

The river water (144 samples) and sediment (144 samples) samples were collected and analyzed once in each season (summer, monsoon, and winter) during the study period. The river water samples (2 l) collected from midstream of the river (40 cm below the surface) in high purity glass bottles were transported to the laboratory, refrigerated at 4 °C, and analyzed for residues of OCPs. The sediment samples collected in the polyethylene bags, approximately 500 g, were transported to the laboratory and pebbles, shells, and vegetable matter were removed, and the samples were air-dried at room temperature. The air-dried samples were then grounded with pestle and

mortar and sieved to 200-250 British Standard Sieve (BSS) mesh size. The samples were collected approximately between 0–50 Km ranges of the Sabarmati River.

For the extraction of OCPs, 10 g sediment samples were obtained from each location.[7] Then, 7 ml of 0.2 M NH_4Cl solution was added to the 10 g dried sediment samples. A mixture of 100 ml hexane:acetone (1:1) was used as a solvent to extract pesticides through overnight shaking for 12 hours on reciprocal or wrist action shaker at 180 rpm. The extract was carefully decanted through activated Florisil column (2-3 cm), and the sediments were washed twice with 25 ml hexane:acetone (1:1). The eluate was washed with 200 ml water, and then, aqueous layer was extracted again with 50 ml hexane. Finally, the hexane layer was washed with 100 ml water, and then, evaporated until dry with a vacuum rotary evaporator. The concentrated extract was then passed through a chromatographic column [30 cm x 10 mm internal diameter (i.d.)] containing 2 g Florisil (lower) and 1 g sodium sulphate (upper) which is pre-wetted with hexane: acetone (1:1). OCPs were eluted with 25 ml hexane: acetone (1:1). Solvent evaporation was performed using a rotary evaporator and final volume of solvent was adjusted to 5 ml, which is used for gas chromatographic analysis. All sediments were analyzed for HCH, DDT, and endosulfan.

NaCl (10 g) was dissolved in 1000 ml of water sample and kept in a separating funnel with a stopcock on a vertical stand. Then, 60 ml of DCM (dichloromethane) was added to the separating funnel and the separating funnel was shaken for 2-3 minutes. Next, the produced gas was released by opening the stopcock and the separating funnel was replaced on the stand in its original position. The organic layer was then separated and passed through a bed of anhydrous sodium sulphate and the extract was collected in a round bottom flask (RB). The whole process was repeated by adding 30 ml DCM twice and passing the whole extract through a bed of sodium sulphate. Evaporation, near to dryness, was performed using a rotary evaporator. The residue was extracted with acetone: hexane mixture (1:9) and heated until it evaporated almost to dryness. Subsequently, a mixture of acetone: hexane (1:9) was added until the residue reached 1 ml, and then, it was used for GC analysis.[8]

1. Indira bridge (Agriculture area)
2. Indira bridge 2.0 km away (Agriculture area)
3. Subhash bridge (Non Industrial area)
4. Gandhi bridge (Non Industrial area)
5. Nehru bridge (Non Industrial area)
6. Ellis bridge (Industrial area)
7. Sardar bridge (Industrial area)
8. Ambedkar bridge (Industrial area)

Map of the Sabarmati river Ahmedabad, Gujarat (India) showing sampling locations
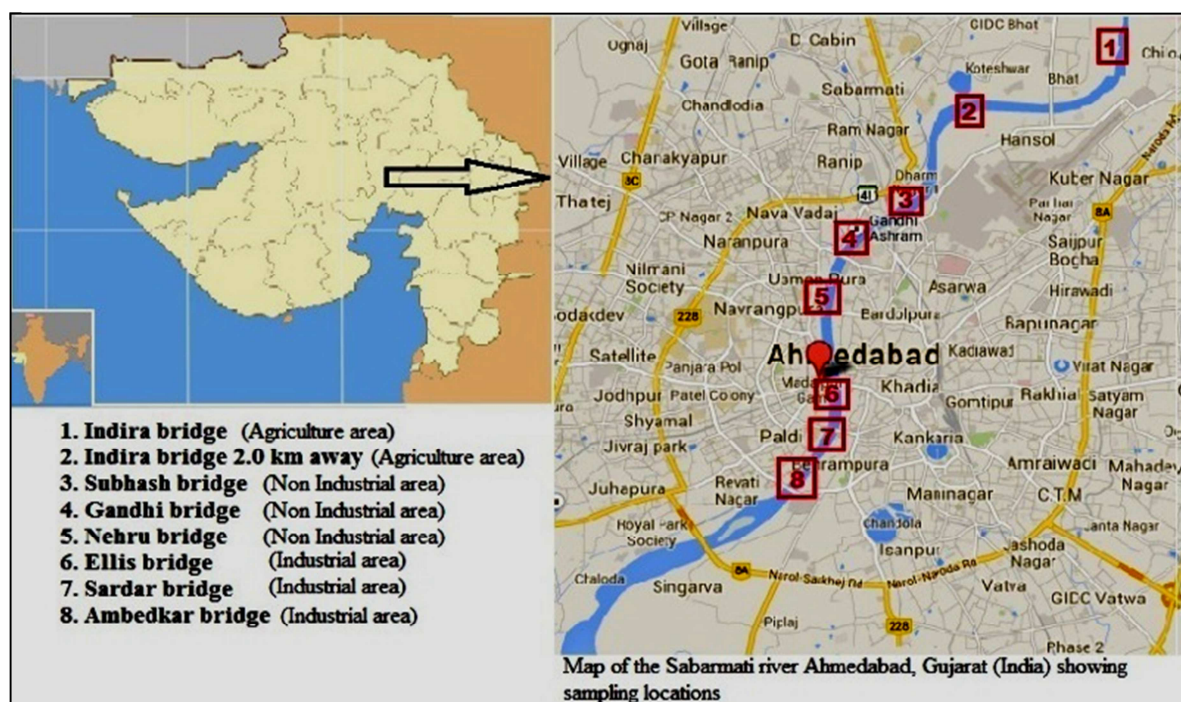
Figure 1. Map of the Sabarmati River Ahmedabad, Gujarat

Stock standard solutions (1000 µg/ml) were prepared individually by dissolving the appropriate quantity of pesticide in hexane. Working standard solutions (10-100 ppm), as per requirement, were prepared from pesticide stock solution in hexane. The obtained solutions were stored in a refrigerator at 2-8 ˚C. The pesticide residues were analyzed using a gas chromatograph (GC 2010, SHIMADZU) equipped with an auto sampler and supported by an electron capture detector (ECD) and GC solution software. This detector allows the detection of contaminants at trace level concentration in the lower ppb range in the presence of a multitude of compounds extracted from the matrix to which this detector does not respond. A 30 m x 0.25 mm i.d. x 0.25 µm fused silica capillary column was used for the chromatographic separation of pesticides. Nitrogen was used as the carrier gas and make up gas and the injection technique was in the split mode. Injector temperature was set at 270 ˚C and a volume of 1 µl of each sample was injected. The column flow was set at 0.7 ml/minute and detector temperature was set at 300 ˚C. The limit of detection (LOD) and limit of quantification (LOQ) for OCPs were 0.001 µg/l and 0.002 µg/l, respectively (Table 1).

Table 1. Pesticide residue limits (Bureau of Indian Standards)

Pesticides	Limit (µg/l)	Rt (minute)
α-HCH	0.01	7.60
ß-HCH	0.04	8.40
γ-HCH	2.00	8.65
δ-HCH	0.04	9.47
o,p-DDT	1.00	22.61
p,p-DDT	1.00	24.91
α-endosulfan	0.40	18.12
ß-endosulfan	0.40	21.76

HCH: Hexachlorocyclohexane; DDT: Dichlorodiphenyltrichloroethane

Results and Discussion

The present study has been undertaken to find the extent of pesticide contamination and accumulation in the Sabarmati River. Moreover, attempts have been made to check the presence of banned pesticides like DDT, HCH, and ndosulphan. All processes were performed in triplicate. The basic statistics of ∑OCPs at different sites in sediment and water samples of the Sabarmati River during the study period is summarized in table 2.

Hexachlorocyclohexane (HCH)

The solubility of lindane (γ-HCH) in water is 10 mg/l. The WHO classifies lindane as a "moderately hazardous" pesticide. The United States Environmental Protection Agency (USEPA) (2005) has reported that lindane does not contaminate drinking water in excess of the agency's level of concern. However, exposure to large amounts of linden can negatively affect the nervous system, producing a range of symptoms from headache and dizziness to convulsions, and very rarely death.[9] In water and sediment samples of the Sabarmati River collected from the Indira bridge, residual concentration of ∑HCH ranged from below the detection limit (BDL) to 8.59 µg/l and BDL to 1494.62 ng/g, respectively. In water samples collected from 2 km away from the Indira Bridge, ∑HCH residue concentration ranged from BDL to 194.93 µg/l. Nevertheless, the detected concentration of ∑HCH in sediment samples was BDL-1372.2 ng/g. Similarly, in water samples taken from the Ellis Bridge, ∑HCH residue concentration ranged from BDL to 169.44 µg/l, where as in sediment samples, it ranged from BDL to 4.22 ng/g. In water samples collected from the Nehru Bridge, ∑HCH residue concentration was in the range of BDL-232.59 µg/l. In the sediment samples, α-HCH and δ-HCH concentrations were in the range of BDL-5.65 ng/g and BDL-14.21 ng/g, respectively. In water samples taken from the Gandhi Bridge, residues of ∑HCH concentration was in the range of BDL-107.45 µg/l, and in sediment samples, isomers of HCH were not detected. Similarly, in water and sediment samples taken from the Subhash Bridge, residual concentration of ∑HCH ranged between BDL and 46.36 µg/l, and BDL and 15.45 ng/g, respectively. In water and sediment samples collected from the Sardar Bridge, ∑HCH residue concentration ranged from BDL to 11.07 µg/l, and BDL to 34.76 ng/g, respectively. In water samples taken from the Ambedkar Bridge, residual concentration of α-HCH was in the range

of BDL-5.09 µg/l, while others were not detected. In sediment samples, α-HCH and δ-HCH concentrations were in the range of BDL-3.84 ng/g and BDL-12.25 ng/g, respectively.

Table 2. Basic statistics of organochlorine pesticides (OCP) residues in water and sediment samples of the Sabarmati River

Pesticides	Water (µg/l)			Sediment (ng/g)		
	Range	Mean ± SD	Median	Range	Mean ± SD	Median
Indira Bridge						
α-HCH	BDL-0.95	0.87 ± 0.09	0.89	BDL-64.52	52.97 ± 11.51	52.90
ß-HCH	BDL-2.34	2.34 ± 0.16	2.34	BDL-524.62	512.98 ± 12.01	513.72
γ-HCH	BDL-1.60	1.41 ± 0.16	1.34	BDL-845.58	836.52 ± 10.30	838.68
δ-HCH	BDL-3.70	3.27 ± 0.30	9.82	BDL-59.90	58.54 ± 1.25	58.30
o,p-DDT	BDL-0.07	0.03 ± 0.03	0.03	BDL-0.51	0.46 ± 0.05	0.49
p, p-DDT	BDL-0.05	0.02 ± 0.02	0.02	BDL-0.02	0.01 ± 0.01	0
α-Endosulfan	BDL-0.07	0.02 ± 0.03	0.01	BDL-0	0 ± 0	0
ß-Endosulfan	BDL-0.08	0.03 ± 0.03	0.04	BDL-0	0 ± 0	0
Indira Bridge 2 km away						
α-HCH	BDL-0.08	0.03 ± 0.04	0.02	BDL-155.32	148.36 ± 7.60	149.52
ß-HCH	BDL-0.06	0.02 ± 0.03	0.01	BDL-41.52	38.37 ± 3.24	38.58
γ-HCH	BDL-4.58	4.53 ± 0.03	4.52	BDL-1120.84	1088.02 ± 33.09	1088.59
δ-HCH	BDL-190.21	189 ± 0.85	189.62	BDL-54.52	45.91 ± 8.06	44.69
o,p-DDT	BDL-65.52	65.03 ± 0.42	64.89	BDL-21.53	14.95 ± 6.18	14.08
p,p-DDT	BDL-80.51	79.55 ± 1.12	79.84	BDL-0.02	0.00 ± 0.01	0
α-Endosulfan	BDL-14.52	14.14 ± 0.54	14.39	BDL-0.04	0.01 ± 0.02	0
ß-Endosulfan	BDL-37.23	36.61 ± 0.83	36.95	BDL-0.02	0.01 ± 0.01	0.01
Ellis Bridge						
α-HCH	BDL-0.43	0.41 ± 0.02	0.42	BDL-4.21	3.58 ± 0.68	3.69
ß-HCH	BDL-7.04	7.01 ± 0.03	7.02	BDL-0	0 ± 0	0
γ-HCH	BDL-160.55	155.96 ± 4.22	155.12	BDL-0	0 ± 0	0
δ-HCH	BDL-1.42	1.24 ± 0.22	1.32	BDL-0.01	0.0 ± 0.00	0.01
o,p-DDT	BDL-0.04	0.02 ± 0.02	0.02	BDL-3.02	2.78 ± 0.24	2.79
p,p-DDT	BDL-0.02	0.01 ± 0.01	0.01	BDL-0.02	0.01 ± 0.01	0.01
α-Endosulfan	BDL-0.06	0.02 ± 0.03	0.02	BDL-0.65	0.45 ± 0.20	0.46
ß-Endosulfan	BDL-0.04	0.02 ± 0.02	0.02	BDL-5.25	3.83 ± 1.27	3.47
Nehru Bridge						
α-HCH	BDL-0.02	0.01 ± 0.0	0.01	BDL-5.65	4.72 ± 1.05	4.49
ß-HCH	BDL-5.19	5.05 ± 0.20	5.15	BDL-0	0 ± 0	0
γ-HCH	BDL-225.85	224.52 ± 1.89	225.38	BDL-0	0 ± 0	0
δ-HCH	BDL-1.53	1.33 ± 0.32	1.51	BDL-14.21	13.30 ± 0.84	13.15
o,p-DDT	BDL-0.08	0.03 ± 0.04	0.02	BDL-14.25	12.60 ± 1.70	12.71
p,p-DDT	BDL-0.03	0.01 ± 0.02	0.01	BDL-12.94	11.69 ± 1.08	11.18
α-Endosulfan	BDL-0.08	0.07 ± 0.01	0.07	BDL-7.98	6.83 ± 1.04	6.58
ß-Endosulfan	BDL-0.03	0.01 ± 0.04	0.01	BDL-10.25	9.64 ± 0.64	9.69
Gandhi Bridge						
α-HCH	BDL-0.39	0.37 ± 0.04	0.39	BDL-0	0 ± 0	0
ß-HCH	BDL–3.03	2.88 ± 0.25	3.02	BDL-0	0 ± 0	0
γ-HCH	BDL-103.99	102.22 ± 1.88	102.42	BDL-0	0 ± 0	0
δ-HCH	BDL-0.04	0.02 ± 0.02	0.02	BDL-0	0 ± 0	0
o,p-DDT	BDL-0.05	0.01 ± 0.03	0.01	BDL-0	0 ± 0	0

Table 2. Basic statistics of organochlorine pesticides (OCP) residues in water and sediment samples of the Sabarmati River (Continue)

Pesticides	Water (µg/l)			Sediment (ng/g)		
	Range	Mean ± SD	Median	Range	Mean ± SD	Median
p,p-DDT	BDL-0.03	0.01 ± 0.01	0.02	BDL-0	0 ± 0	0
α-Endosulfan	BDL-0.04	0.01 ± 0.02	0.01	BDL-0	0 ± 0	0
ß-Endosulfan	BDL-0.04	0.02 ± 0.02	0.02	BDL-0	0 ± 0	0
Subhash Bridge						
α-HCH	BDL-0.04	0.02 ± 0.02	0.02	BDL-0	0 ± 0	0
ß-HCH	BDL-0.82	0.74 ± 0.10	0.79	BDL-0	0 ± 0	0
γ-HCH	BDL-44.72	44.37 ± 0.59	44.71	BDL-0	0 ± 0	0
δ-HCH	BDL-0.78	0.77 ± 0.01	0.77	BDL-15.45	11.50 ± 3.62	10.74
o,p-DDT	BDL-0.06	0.03 ± 0.03	0.04	BDL-0	0 ± 0	0
p,p-DDT	BDL-0.08	0.03 ± 0.04	0.02	BDL-0	0 ± 0	0
α-Endosulfan	BDL-0.02	0.01 ± 0.01	0.01	BDL-4.54	3.44 ± 1.09	3.41
ß-Endosulfan	BDL-0.06	0.02 ± 0.03	0.02	BDL-0	0 ± 0	0
Sardar Bridge						
α-HCH	BDL- 0.15	0.13 ± 0.01	0.14	BDL-15.94	14.68 ± 1.11	14.25
ß-HCH	BDL-6.35	6.22 ± 0.20	6.32	BDL-3.87	2.68 ± 1.05	2.33
γ-HCH	BDL-4.07	3.92 ± 0.21	4.02	BDL-0	0 ± 0	0
δ-HCH	BDL-0.5	0.37 ± 0.15	0.40	BDL-14.95	12.56 ± 2.31	12.41
o,p-DDT	BDL-0.04	0.02 ± 0.02	0.02	BDL-9.87	8.72 ± 1.00	8.31
p,p-DDT	BDL-0.05	0.02 ± 0.02	0.03	BDL-11.54	10.43 ± 1.22	10.6
α-Endosulfan	BDL-0.06	0.02 ± 0.03	0.01	BDL-1.85	1.51 ± 0.42	1.65
ß-Endosulfan	BDL-0.04	0.02 ± 0.02	0.02	BDL-10.22	9.41 ± 0.78	9.35
Ambedkar Bridge						
α-HCH	BDL-5.09	5.03 ± 0.04	5.02	BDL- 3.84	2.58 ± 1.17	2.39
ß-HCH	BDL-0.09	0.05 ± 0.04	0.06	BDL-0	0 ± 0	0
γ-HCH	BDL-0.07	0.04 ± 0.03	0.05	BDL-0	0 ± 0	0
δ-HCH	BDL-0.06	0.02 ± 0.03	0.01	BDL-12.25	12.16 ± 0.08	12.17
o,p-DDT	BDL-0.02	0.01 ± 0.01	0.01	BDL-14.1	13.34 ± 0.71	13.25
p,p-DDT	BDL-0.06	0.03 ± 0.03	0.04	BDL-20.61	19.63 ± 0.48	19.67
α-Endosulfan	BDL-0.06	0.02 ± 0.03	0.02	BDL-2.98	2.79 ± 0.27	2.90
ß-Endosulfan	BDL-0.08	0.04 ± 0.04	0.04	BDL-14.6	14.09 ± 0.84	14.54

BDL: Below the detection limit; HCH: Hexachlorocyclohexane; DDT: Dichlorodiphenyltrichloroethane; SD: Standard deviation

The comparison of the residues of OCPs between different sampling sites showed that the location 2 km away from the Indira Bridge had the maximum concentration of these persistent compounds (1393.22 ng/g in sediment). However, this concentration was 392.71 µg/l in water sample. The high concentration of OCPs in this area is due to the fact that this is an agricultural area and two pesticide industries are situated near this location. Nevertheless, the concentration of OCPs at the Ambedkar Bridge (water sample) was lower (5.53 µg/l in water). However, sediment samples taken from the Gandhi Bridge had no detectable amount of OCPs (Figure 2).

As shown in table 3, the concentration of ∑HCH increased during the study period. As compared to residual concentration of ∑HCH in 2011, it has gradually increased in succeeding years. This is evidence of the use of HCH until today. This study has been performed mostly for Indian rivers like Gomti River (Uttar Pradesh), Kaveri River (Tamil nadu), Ganga River (Uttar Pradesh), Hugli River (Kolkata), Kuano River (Uttar Pradesh), and Yamuna River (Haryana-

Delhi). The level of ∑HCH ranged from 5.08 to 232.127 µg/l in water and BDL to 1494.62 ng/g in the sediments of the Sabarmati River. Gomti River showed lower concentration of ∑HCH (0.00163-0.368 µg/l) in water and (BDL-155.17 ng/g) sediments.[10] Ganga River also showed lower levels of ∑HCH in water (BDL-99.517 µg/l).[11]
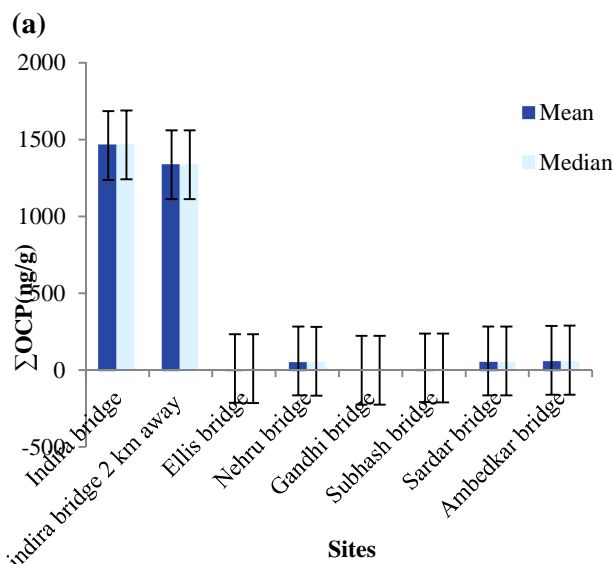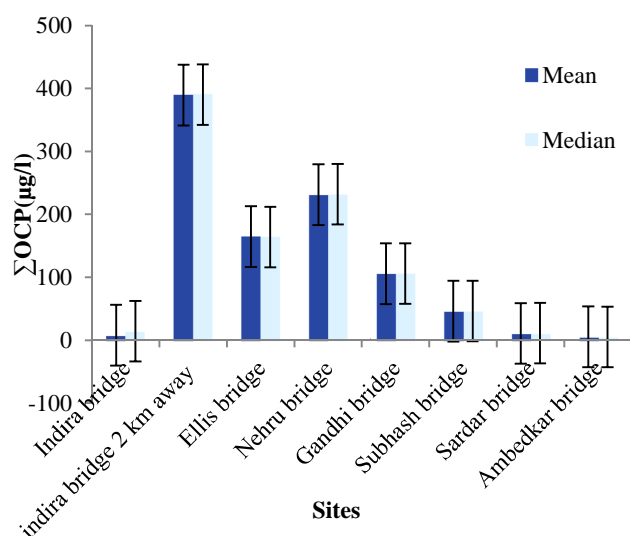

(a)

(b)

Figure 2. ∑ organochlorine pesticides (OCPs) (OCPs) residues in the (a) water and (b) sediments of the Sabarmati River

The concentration of ∑HCH in the Kaveri River ranged from 4.35 to 158.4 ng/g,[12] which is lower than the concentration found in our study. In surface water, levels of lindane (γ-HCH) were found to be in the range of 0.01-0.43 µg/l, which is less than that in the Hugli River, Kolkata.[13] The total concentration of HCH in the Kuano River ranged from 0.0008 to 0.020 µg /l[14], and in the Yamuna River from 0.01276 to 0.5934µg/l.[15] In the water samples of the Sabarmati River, the concentration of ∑HCH residues are relatively higher than that found in the Pearl River estuary (0.039–0.282 µg/l).[16] In the rivers of Taiwan and Mar Menor Lagoon, these values are lower than that of the Minjiang River estuary.[17] In this study, it can be said that HCH has the predominant residue concentration in the Sabarmati River. In rivers in the Southern part of Okinawa, in Japan, the highest concentration of HCH detected in water samples was 0.049 µg/l,[18] which is lower than our results. In sediments, the concentration level of HCH detected range from 0.44 to 17.9 ng/g in the West Central coast of India in the rabian Sea.[19] HCH is a widespread contaminant that has entered the environment through its manufacturing, use as a pesticide, and its formation as a by-product during production of a variety of chlorinated compounds.

Dichlorodiphenyltrichloroethane (DDT)

In water and sediment samples collected from the Indira Bridge, residual concentration of ∑DDT ranged from BDL to 0.12 µg/l and BDL to 0.52 ng/g, respectively. In water and sediment samples collected from 2 km away from the Indira Bridge, the ranges of residual concentration of op-DDT and pp-DDT were BDL-65.52 µg/l and BDL-80.51 ng/g, and BDL-21.53 µg/l and BDl-0.02 ng/g, respectively. In sediment samples taken from the Ellis Bridge, residual concentration of ∑DDT was 3.04 ng/g. In sediment samples collected from the Nehru Bridge, residual concentration of op-DDT and pp-DDT ranged from BDL to 14.25, and BDL to 12.94 ng/g, respectively. In sediment samples collected from the Sardar Bridge, residual concentration of ∑DDT was 19.15 ng/g.

In sediment samples collected from the

Ambedkar Bridge, residual concentration of op-DDT and pp-DDT ranged between BDL and 14.1, and BDL and 20.61 ng/g, respectively. In the remaining samples received from the Subhash and Gandhi Bridges, no residual concentrations of DDT isomers were detected. As shown in table 3, concentration of ∑DDT decreased during the study period. As compared to residual concentration of ∑DDT in 2010, it has gradually decreased in succeeding years. This may be due to the ban on the use of DDT. In this study, the range of residue levels of op-DDT and pp-DDT were BDL-65.52 and BDL-80.51 µg/l in water samples, and BDL-21.53 and BDL-0.02 ng/g in sediment samples from the Sabarmati River. This range was BDL-0.0688, BDL-0.01376 µg/l in water samples and BDL-345.66, BDL-206.12 ng/g in sediment samples of the Gomti River.[10] In surface water, levels of DDT were found to be 0.03-0.65 µg/l in

the Hugli River, Kolkata,[13] which is lower than that found in the Sabarmati River. In the Kuano River of Uttar Pradesh, total DDT concentration ranged from 0.0002 to 0.003 µg/l,[14] which is lower than that in the Sabarmati River.

The level of ∑DDT concentration in the Sabarmati River water (BDL-144.54 µg/l) is higher than that found in the Ganga River (0.14-66.51 µg/l),[11] Yamuna River (0.07-0.72 µg/l),[15] Minjiang River estuary (0.04-0.23 µg/l),[17] and water supply of El-Haram (2.30-61.00 µg/l).[20] The level of ∑DDT concentrations in the sediments (BDL-108.48 ng/g) of the Sabarmati River are higher than those reported in the sediments of the Minjiang River estuary (1.6-13.1 ng/g dry weight). However, in the case of Haihe and Dagu Drainage rivers, ∑DDT concentration ranged between 0.32 and 80.18 ng/g, and 3.60 and 83.49 ng/g dry weight, respectively.[21]

Table 3. Concentrations of organochlorine pesticides (OCP) in sediments (ng/g) of the Sabarmati River, Ahmedabad, India

Location	OCPs	2011	2012	2013
		Mean ± SD	Mean ± SD	Mean ± SD
Site-1	∑HCH	7.69 ± 18.93	548.60 ± 13.81	1461.01 ± 35.07
	∑DDT	nd	nd	0.47 ± 0.06
	∑endosulfan	nd	nd	nd
Site-2	∑HCH	42.00 ± 18.93	498.21 ± 17.01	1320.66 ± 51.99
	∑DDT	87.40 ± 34.98	17.51 ± 7.14	14.95 ± 6.19
	∑endosulfan	21.21 ± 8.16	9.12 ± 3.14	0.02 ± 0.03
Site-3	∑HCH	nd	nd	3.58 ± 0.68
	∑DDT	6.00 ± 34.98	3.53 ± 0.01	2.79 ± 0.25
	∑endosulfan	3.93 ± 8.16	1.93 ± 0.02	4.20 ± 81.47
Site-4	∑HCH	13.02 ± 18.93	15.69 ± 3.93	18.02 ± 1.89
	∑DDT	49.3 ± 34.98	20.09 ± 2.08	24.29 ± 2.78
	∑endosulfan	16.27 ± 8.16	15.50 ± 0.09	16.47 ± 1.68
Site-5	∑HCH	nd	nd	nd
	∑DDT	nd	nd	nd
	∑endosulfan	nd	nd	nd
Site-6	∑HCH	6.15 ± 18.93	8.19 ± 3.02	11.50 ± 3.62
	∑DDT	nd	nd	nd
	∑endosulfan	nd	nd	3.44 ± 1.09
Site-7	∑HCH	25.16 ± 18.93	30.15 ± 17.02	29.92 ± 4.47
	∑DDT	33.90 ± 34.98	25.56 ± 12.03	19.15 ± 2.22
	∑endosulfan	10.40 ± 8.16	9.14 ± 2.02	10.92 ± 1.20
Site-8	∑HCH	10.28 ± 18.93	8.15 ± 0.04	14.74 ± 1.25
	∑DDT	60.50 ± 34.98	51.52 ± 11.09	32.97 ± 1.19
	∑Endosulfan	17.50 ± 8.16	nd	16.88 ± 1.11

HCH: Hexachlorocyclohexane; DDT: Dichlorodiphenyltrichloroethane; SD: Standard deviation; nd = not detected; OSP: Organochlorine pesticides

In the rivers in Taiwan the level ranged between 0.21 and 8.81 ng/g in dry weight.[22] In the Ogba River (Nigeria), op-DDT and pp-DDT levels ranged between 0.67 and 0.71 and 0.73 and 0.75 µg/l, respectively.[23] The range of concentration of DDT in sediments detected were 7.01-179.10 ng/g in the West Central cost of India in the Arabian Sea.[18] In sediments of the Sabarmati River, the residue levels of op-DDT and pp-DDT were higher than those in the sediments of the Qiantang River (op-DDT: 0.28-9.61 ng/g, pp-DDT: 0.46-22.78 ng/g).[24] The range of ∑DDT concentration was BDL-146.71 µg/l in water and BDL-108.48 ng/g in sediment samples of the Sabarmati River. DDT has been banned for agricultural use in 1989, but it is still used in public health sectors for malaria control.[25]

Endosulfan

The concentration level of ∑endosulfan in water and sediment samples obtained from 2 km away from the Indira Bridge ranged from BDL to 51.75 µg/l and BDL to 0.06 ng/g, respectively. In water and sediment samples collected from the Ellis Bridge, residual concentration of ∑endosulfan ranged from BDL to 0.10 µg/l and BDL to 5.90 ng/g, respectively. The concentration level of ∑endosulfan residues in the water sample obtained from the Nehru Bridge ranged from BDL to 0.11µg/l, whereas it ranged from BDL to 18.23 ng/g in the sediment sample. ∑endosulfan residues in sediment samples obtained from the Subhash Bridge ranged from BDL to 4.54 ng/g. In the Sardar Bridge, the concentration level of ∑endosulfan residues in sediment samples ranged from BDL to 12.07 ng/g. The concentration level of ∑endosulfan in sediment samples taken from the Ambedkar Bridge ranged from BDL to 17.58 ng/g. In the Gomti River of India, ∑endosulfan ranged from BDL to 0.094 µg/l in water samples, and BDL-1.00 ng/g in sediment samples; this is lower than the concentration of endosulfan (BDL-51.75 µg/l) in the Sabarmati River. In Hindon River Uttar Pradesh, India, endosulfan concentration range from 9.2 to 23.5 µg/l.[26] In this study levels of α-endosulfan (BDL-14.52µg/l) and ß-endosulfan (BDL-37.23µg/l) metabolites are higher than the concentration range of α-endosulfan in water (BDL-0.739 µg/l) and in sediment samples (35.5-50.47 ng/g). Nevertheless, the range of β-endosulfan level was BDL-0.157 µg/l in water and 34.40-303.09 ng/g in sediment samples of the Ganga River.[27] The levels of α-endosulfan (0.00146-0.0961 µg/l) and ß-endosulfan (0.00549-0.135 µg/l) found in the water of Pearl River estuary was relatively low (Table 4).[28]

Table 4. Comparison of organochlorine pesticides (OCP) concentrations in sediment samples from various locations in the world

Location	∑DDTs	∑HCH	References
Sabarmati River, India	nd-34.71[f]	nd-1494.62[***]	Present study
Gomti River, India	1.63-368.70[**]	nd-155.17[***]	Malik et al.[10]
Kaveri River, India	0.69-4.85[**]	4.35-158.4[*]	Rajendran and Subramanian[12]
Haihe, China	0.32-80.18[**]	1.88-18.76[***]	Yang et al.[21]
Qiantang River, China	1.14-100.20[**]	8.22-152.1[***]	Zhou et al.[24]
Manzala Lake, Egypt	0.20–5.17[£]	nd-3.42[***]	Barakat et al.[29]
Peacock River, China	0.10-1.54[**]	0.13-6.58[***]	Chen et al.[30]
Scheldt River, Belgium	6.6-27.60[ʃ]	nd[*]	Covaci et al.[31]
Ebro River, Spain	0.85-9.03[§]	0.001-0.026[€]	Fernandez et al.[32]
Chaohu Lake, China	0.30-31.00[£]	0.2-1.8[***]	Liu et al.[33]
Mekong River, Vietnam	nd-110.00[ʃ]	nd-1.3[*]	Minh et al.[34]

nd = not detected; [*] Sum of α-,β-, and γ-HCH; [**] Sum of p,p'-DDE,p,p'-DDD,o,p'-DDT, and p,p'-DDT'; [***] Sum of α-,β-,γ-, and δ-HCH; [£] Sum of o,p'-DDE,p,p'-DDE,o,p'-DDD,p,p'-DDD,o,p'-DDT, and p,p'-DDT; [€] Sum of α- and γ-HCH; [§] Sum of dichlorobenzophenone,p,p'-DDE,p,p'-DDD, and p,p'-DDT; [ʃ] Sum of p,p'-DDE,p,p'-DDD, and p,p'-DDT; [f] Sum of o,p'-DDT and p,p'-DDT; HCH: Hexachlorocyclohexane; DDT: Dichlorodiphenyltrichloroethane

Samples were collected in January 2013, May 2013, and September 2013. As observed in figure 3, 404883 µg/1 ∑OCPs was found in water sample during the summer which is very high compared to the other seasons. During winter, the concentration of ∑OCPs was lower compared to other seasons. During the monsoon season, heavy water flow causes erosion of river sediments and their resuspension into the river water column, and thus, the pollutants sorbed on the sediment particles may be diluted by runoff.
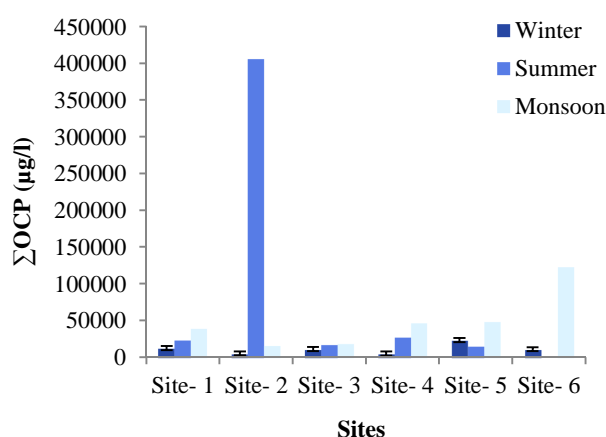

Figure 3. Seasonal variations of ∑ organochlorine pesticides (OCPs) residues in the Sabarmati River

The river flow, during the winter, becomes normalized and the river system starts to stabilize with the settling of eroded sediments. However, during summer, the river system is under stabilized conditions except in the case of some man-made disturbances or other activities like bathing, swimming, and boating. Thus, the biota and aquatic flora and fauna also fluctuate with the changing concentration of organochlorine pesticides. The same results were reported by Kouzayha et al. for Lebanon's water resources.[35] They reported that variation in pesticide concentration follows seasonal patterns, this may be due to the timing of agricultural activities and pesticide applications in addition to the runoff condition.[35]

Conclusion

The present study provides information on the current contamination status of the Sabarmati River located in the Ahmadabad city of Gujarat, India. During the study period, all samples from the Sabarmati River showed the presence of pesticide residue, specifically HCH, which is present in high concentrations. This suggests that the water of this river is not safe for drinking purpose and is harmful for aquatic life. DDT and endosulfan pesticides were also present in all the above samples. Organochlorine pesticides are one of the major environmental pollutants. Moreover, many pesticide manufacturers and industries dump their wastes directly into this river illegally. It also enters into natural waters through percolation and runoff and from urban city sewage sites. Even though the use of these OCPs are restricted and banned in India according to Section 5 of the Insecticide Act, 1968, they are still detected in water of the studied river, which shows that they are still in use for agriculture or industrial purposes. Hence, these levels indicate that the Sabarmati River receives intermittent inputs of organochlorine pesticides, which are the main cause of the pesticide pollution of this river. Assessment of the river water and sediment contamination in this study reflects that sediment and water are contaminated with OCPs. This may have toxic effects on biota and also humans who are consuming the water of this river.

Conflict of Interests

Authors have no conflict of interests.

References

1. Malik A, Singh KP, Mohan D, Patel DK. Distribution of polycyclic aromatic hydrocarbons in Gomti river system, India. Bull Environ Contam Toxicol 2004; 72(6): 1211-8.
2. Davis DL, Bradlow HL. Can environmental estrogens

cause breast cancer? Sci Am 1995; 273(4): 167-72.

3. Welbourn P. Environmental Toxicology. Cambridge, UK: Cambridge University Press; 2002.

4. Mishra K, Sharma RC. Contamination of aquatic system by chlorinated pesticides and their spatial distribution over North-East India. Toxicology and Environmental Health Sciences 2011; 3(3): 144-55.

5. Gupta PK. Pesticide exposure--Indian scene. Toxicology 2004; 198(1-3): 83-90.

6. Kaur M, Sharma JK, Gill JP, Aulakh RS, Bedi JS, Joia BS. Determination of organochlorine pesticide residues in freshwater fish species in Punjab, India. Bull Environ Contam Toxicol 2008; 80(2): 154-7.

7. AOAC: Official methods of analysis. Arlington, VA: Association of Official Analytical Chemists, Inc.; 1976.

8. Horwitz W. Official methods of analysis of the AOAC. Arlington VA: Association of Official Analytical Chemists; 2000.

9. U.S. Department of Health And Human Services. Toxicological profile for alpha-, beta-, gamma-, and delta-hexachlorocyclohexane. Atlanta, GA: Public Health Service Agency for Toxic Substances and Disease Registry; 2005.

10. Malik A, Ojha P, Singh KP. Levels and distribution of persistent organochlorine pesticide residues in water and sediments of Gomti River (India)-a tributary of the Ganges River. Environmental Monitoring and Assessment 2009; 148(1-4): 421-35.

11. Nayak AK, Raha P, Das AK, Raha R. Organochlorine pesticide residues in middle stream of the Ganga River, India. Bull Environ Contam Toxicol 1995; 54(1): 68-75.

12. Rajendran RB, Subramanian AN. Chlorinated pesticide residues in surface sediments from the River Kaveri, south India. J Environ Sci Health B 1999; 34(2): 269-88.

13. Ghose NC, Saha D, Gupta A. Synthetic Detergents (Surfactants) and Organochlorine Pesticide Signatures in Surface Water and Groundwater of Greater Kolkata, India. J Water Resource and Protection 2009; 4(1): 290-8.

14. Singh S, Mishra RN. Occurrence of organochlorine pesticides residue in Kuano river of eastern Uttar Pradesh. J Environ Biol 2009; 30(3): 467-8.

15. Kaushik CP, Sharma HR, Jain S, Dawra J, Kaushik A. Pesticide residues in river Yamuna and its canals in Haryana and Delhi, India. Environ Monit Assess 2008; 144(1-3): 329-40.

16. Zhang Z, Hong H, Zhou JL, Yu G, Chen W, Wang X. Transport and fate of organochlorine pesticides in the River Wuchuan, southeast China. J Environ Monit 2002; 4(3): 435-41.

17. Zhang ZL, Hong HS, Zhou JL, Huang J, Yu G. Fate and assessment of persistent organic pollutants in water

and sediment from Minjiang River Estuary, Southeast China. Chemosphere 2003; 52(9): 1423-30.

18. Imo ST, Hirosawa E, Sheikh MA, Tamaki F, Oomori T. Persistent Organochlorine Pesticides in River Waters of Southern Part of Okinawa Island, Japan. Asian Journal of Water, Environment and Pollution 2007; 4(2): 37-42.

19. Sarkar A, Sen GR. Chlorinated pesticide residues in sediments from the Arabian Sea along the central west coast of India. Bull Environ Contam Toxicol 1987; 39(6): 1049-54.

20. El-Kabbany S, Rashed MM, Zayed MA. Monitoring of the pesticide levels in some water supplies and agricultural land, in El-Haram, Giza (A.R.E.). J Hazard Mater 2000; 72(1): 11-21.

21. Yang RQ, Lv AH, Shi JB, Jiang GB. The levels and distribution of organochlorine pesticides (OCPs) in sediments from the Haihe River, China. Chemosphere 2005; 61(3): 347-54.

22. Doong RA, Sun YC, Liao PL, Peng CK, Wu SC. Distribution and fate of organochlorine pesticide residues in sediments from the selected rivers in Taiwan. Chemosphere 2002; 48(2): 237-46.

23. Ize-Iyamu OK, sia IO, Egwakhide PA. Concentrations of residues from organochlorine pesticide in water and fish from some rivers in Edo State Nigeria. International Journal of Physical Sciences 2007; 2(9): 237-41.

24. Zhou R, Zhu L, Yang K, Chen Y. Distribution of organochlorine pesticides in surface water and sediments from Qiantang River, East China. J Hazard Mater 2006; 137(1): 68-75.

25. Holoubek I, Roots O. Regionally Based Assessment of Persistent Toxic Substances: Global report 2003. Nairobi, Kenya: UNEP Chemicals; 2003.

26. Ali I, Singh P, Rawat Ms, Badoni A. Analysis of organochlorine pesticides in the hindon river water, India. Journal of Environmental Protection Science 2008; 2: 47-53.

27. Singh L, Choudhary SK, Singh PK. Pesticide concentration in water and sediment of River Ganga at selected sites in middle Ganga plain. International Journal of Environmental Sciences 2012; 3(1): 260.

28. Zhang Z, Dai M, Hong H, Zhou JL, Yu G. Dissolved insecticides and polychlorinated biphenyls in the Pearl River Estuary and South China Sea. J Environ Monit 2002; 4(6): 922-8.

29. Barakat AO, Mostafa A, Wade TL, Sweet ST, El Sayed NB. Assessment of persistent organochlorine pollutants in sediments from Lake Manzala, Egypt. Mar Pollut Bull 2012; 64(8): 1713-20.

30. Chen W, Jing M, Bu J, Ellis BJ, Qi S, Song Q, et al. Organochlorine pesticides in the surface water and sediments from the Peacock River Drainage Basin in

Xinjiang, China: a study of an arid zone in Central Asia. Environ Monit Assess 2011; 177(1-4): 1-21.

31. Covaci A, Gheorghe A, Voorspoels S, Maervoet J, Steen RE, Blust R, et al. Polybrominated diphenyl ethers, polychlorinated biphenyls and organochlorine pesticides in sediment cores from the Western Scheldt river (Belgium): analytical aspects and depth profiles. Environ Int 2005; 31(3): 367-75.

32. Fernandez MA, Alonso C, Gonzalez MJ, Hernandez LM. Occurrence of organochlorine insecticides, PCBs and PCB congeners in waters and sediments of the Ebro River (Spain). Chemosphere 1999; 38(1): 33-43.

33. Liu WX, He W, Qin N, Kong XZ, He QS, Ouyang HL, et al. The residues, distribution, and partition of organochlorine pesticides in the water, suspended solids, and sediments from a large Chinese lake (Lake Chaohu) during the high water level period. Environ Sci Pollut Res Int 2013; 20(4): 2033-45.

34. Minh NH, Minh TB, Kajiwara N, Kunisue T, Iwata H, Viet PH, et al. Pollution sources and occurrences of selected persistent organic pollutants (POPs) in sediments of the Mekong River delta, South Vietnam. Chemosphere 2007; 67(9): 1794-801.

35. Kouzayha A, Al Ashi A, Al Akoum R, Al Iskandarani M, Budzinski H, Jaber F. Occurrence of pesticide residues in Lebanon's water resources. Bull Environ Contam Toxicol 2013; 91(5): 503-9.

Increasing of leachate quality using an integrated aerobic membrane bioreactor

Hassan Hashemi[1], Mahdi Safari[2], Asghar Ebrahimi[3], Abbas Khodabakhshi[4]

1 Research Center for Health Sciences, Shiraz University of Medical Sciences, Shiraz, Iran
2 Environmental Health Research Center, Kurdistan University of Medical Sciences, Sanandaj, Iran
3 Department of Environmental Health Engineering, School of Health, Yazd University of Medical Sciences, Yazd, Iran
4 Department of Environmental Health Engineering, School of Health, Shahrekord University of Medical Sciences, Shahrekord, Iran

Original Article

Abstract

The aim of this study was the increasing of leachate quality using integrated membrane bioreactor (MBR). The reactor was fed with treated leachate with overall 70-1360 mg/l chemical oxygen demand (COD). The analysis of COD, biochemical oxygen demand (BOD_5), total suspended solids (TSS), and total dissolved solids (TDS) were performed in feed and filtrate, whenever the system reached steady state twice a week for 6 months. In all loading rate, BOD_5 concentration was less than the standard limit. The removal efficiency of COD in all experiments was up to 80%. Up to 99% of solids, which may mainly include colloidal solids, were removed with micropore membrane. There was no significant difference between TDS concentration in feed and filtrate. It was concluded that MBR is a versatile technology with high throughput and can treat compost leachate below standard limit if used after appropriate processes.
KEYWORDS: Leachate, Bioreactor, Waste Disposal, Membrane

Citation: Hashemi H, Safari M, Ebrahimi A, Khodabakhshi A,. **Increasing of leachate quality using an integrated aerobic membrane bioreactor.** J Adv Environ Health Res 2015; 3(1): 27-32.

Introduction

With appropriate handling, composting is a sustainable, environmentally friendly, and feasible method for recycling and reducing organic waste volume in developing countries.[1] Approximately 60% of the municipal solid waste (MSW) produced in Isfahan, Iran, is converted to compost and about 50 m³/day leachate is created from high moisture content in delivered organic waste.[2] Hence, the treatment of leachate is one of the key factors in solid waste management which should be performed with regard to its composition.[3] Because of the complexity of composting leachate pollutants, conventional treatments (biological or physicochemical) are no longer sufficient in order to reach the level of purification needed to fully reduce the negative impact of leachates on the environment.[4] Today, a combination of several processes is used for the treatment of these heavy polluted liquids.[5] Membrane separation coupling technology and sequencing batch bioreactors, most commonly called membrane sequencing bioreactor (MSBR), can replace the biomass settling and effluent withdrawing of the original SBR process.[6] Presently, many researchers have shown interest in leachate treatment.[7] Annual marketing growth rates of 10.5% indicate the widespread application (more than 5000 under operation) of

Corresponding Author:
Mahdi Safari
Email: safari.m.eng@gmail.com

this technology throughout the world.[8] Over 50 and 15 membrane bioreactor (MBR) plants for leachate treatment have been installed in Europe and China in the last 5 years, respectively.[9] Integrated bioreactors can attain carbon credit derived from the clean development mechanism (CDM) under the Kyoto protocol 1997, changing the paradigm of wastewater management from 'treatment and disposal' to 'useful utilization' as well as 'beneficial endeavor'.[10] MBR effluent has significantly high quality with minor fluctuation.[5] Sludge treatment cost, in MBR, is minimized when aeration cost is maximized. Economically optimum hydraulic retention time (HRT) and target mixed liquor suspended solids (MLSS) were found to be 16 hour and 11,000 mg/l, respectively.[8] Although it must be stressed that high investment costs, fouling, and high energy consumption (between 0.45 and 0.65 kWh/m^{3} for the highest optimum operation) have been identified as the main limitations to faster commercialization and full scale operations of MBRs.[10] The addition of inorganic coagulants or powdered activated carbon (PAC) to the bioreactor can reduce fouling significantly.[6] Recently, semipermeable membrane, named osmotic membrane bioreactor (OsMBR), was suggested as a low fouling alternative to microporous membrane.[4] In comparison with side stream (sMBR) configuration, submerged or immersed (iMBR) is the most widely used due to lower associated costs of operation.[7] According to literature, separate application of MBR for raw leachate treatment leads to high fouling and increasing of costs. Hence, we decided to upgrade leachate quality using integrated aerobic MBR.

Materials and Methods

The experimental unit consisted of a cylindrical 2 l SBR equipped with an immersed membrane of 0.2 μm nominal pore size and 1 m²/ea effective filtering surface area (ZeeWeed ZW10). The filtrate was extracted from the top header of the

module under slight vacuum with maximum operating transmembrane pressure (TMP) of -0.6-0 Kgf/cm². Details of the MBR and membrane structure used in this study are illustrated in figure 1.
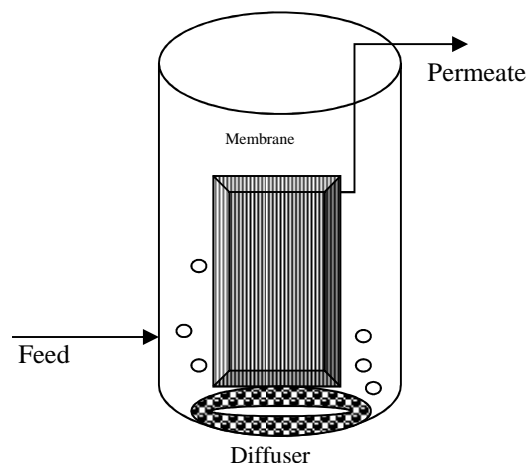

Figure 1. Details of membrane module used in this study

The bioreactor was acclimated by the addition of a sufficient quantity of activated sludge and diluted leachate. Biologically pretreated leachate was fed into the reactor which is continuously aerated using air compressor and diffusers to keep the dissolved oxygen (DO) concentration above 2 mg/l to supply oxygen for the biomass and to scour the membrane.

The process operation was divided into 5 phases; feeding (15 minutes), aeration (12-22 hours), settling (1 hour), filtration (30 minutes), and membrane relaxation (15 minutes). Dependence on the influent fluctuations, F/M ratio, was varied from 0.04 to 0.38 g chemical oxygen demand (COD) (e.g. mixed liquor solids)/d.

Relaxation is used to control the fouling of membrane at the end of run time.[8] The analysis of COD, biochemical oxygen demand (BOD$_5$), total suspended solids (TSS), and total dissolved solids (TDS) were performed in feed and filtrate twice a week according to the Standard Method for the Examination of Water and Wastewater .[11] One-sample t-test and paired sample t-test analyses

were used for the statistical comparison of results.

Results and Discussion

Integrated process was fed with varied organic matter concentrations (85-5356 mg/l COD) and reaction time of 23 and 12 hours. Seasonal variations in leachate characteristics led to changes in the feed concentration. The results of biotreatment and filtration of leachate from compost facilities are presented in figures 2 to 5.

Figure 2 shows the feed and filtrate BOD_5 concentrations during bioreactor operation.

Figure 3 shows the variations of total COD during reactor operation time.

Figure 4 shows the typical trend of TSS evolution, during the start-up and steady state of a process. According to the one-sample t-test analysis, filtrate quality increased significantly below the standard (< 30 mg/l) limit ($P < 0.05$).
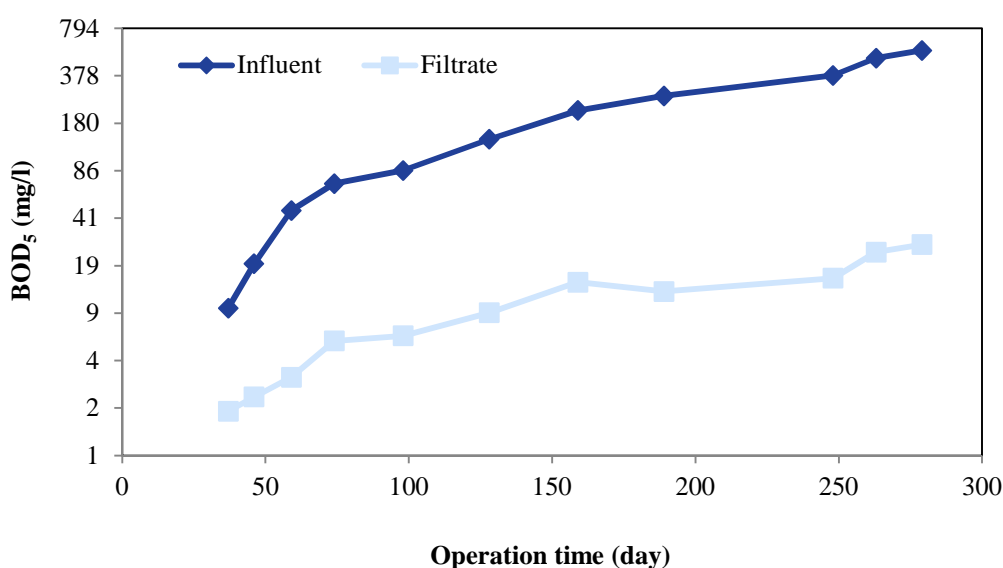

Figure 2. Feed and filtrate biochemical oxygen demand (BOD5) during bioreactor operation
BOD5 concentrations during bioreactor operation; BOD5: Biochemical oxygen demand
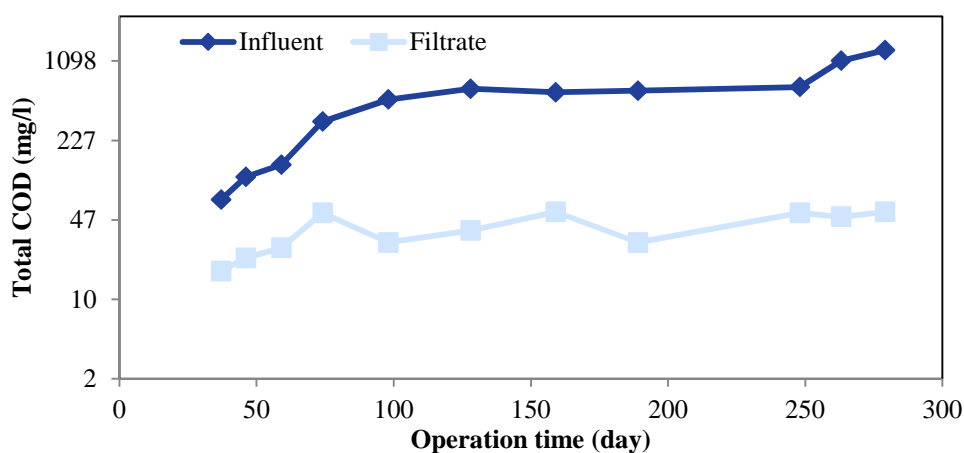

Figure 3. Variations of total chemical oxygen demand (COD) during reactor operation time
COD: Chemical oxygen demand
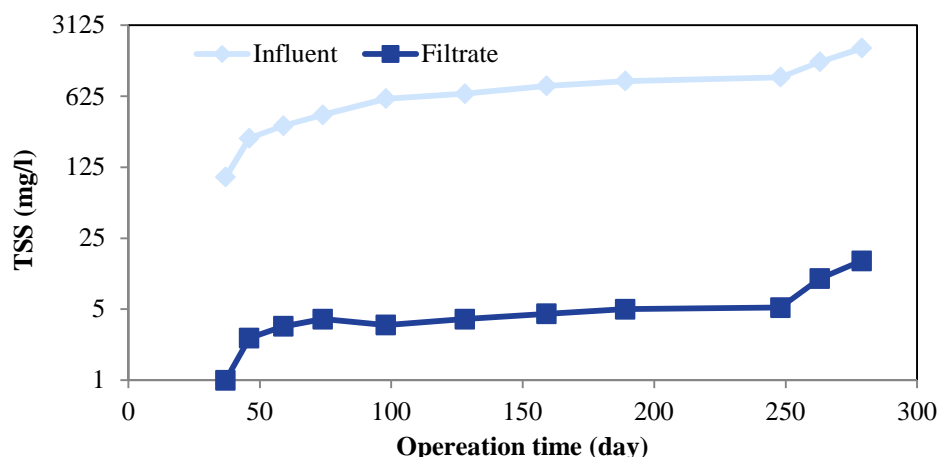
http://jaehr.muk.ac.ir

Figure 4. Changes in concentrations of total suspended solids (TSS) in different run times
TSS: Total suspended solids

Figure 4 shows that up to 99.9% of solids, which may mainly include colloidal solids, was removed with micropore membrane. Using ultrafiltration membrane, 5-10% additional efficiency was achieved.[12] As shown in figure 5, based on paired t-test analysis, there is no significant difference between TDS concentration in feed and filtrate ($P > 0.05$).

It seems that the membrane removed a considerable amount of mineral ions, but low weight molecules of organic acids passed through the membrane easily. In a similar study, TDS concentration in feed and filtrate was 15000 and 16633 mg/l, respectively.[9] Although TDS was not decreased significantly by membrane ($P > 0.05$), the permeate value was less than influent. In the study by Wilkinson, the permeate value was more than feed values.

In this study, after adaptation period, mixed liquor value was 4000 mg/l that increased up to 11000 mg/l within 280 days of operation. The pH values in the bioreactor increased slightly, but decreased in filtrate. The BOD_5 concentration in feed leachate ranged between 100 to 498 mg/l (Figure 2). The removal efficiency was 93%. As shown, in all loading rates, effluent concentration was less than the national standard limit (< 100 mg/l). In a similar study, the concentration of BOD_5 in MBR filtrate was recorded as less than 2 mg/l.[10] At BOD_5 loading rates below 1.71 kg/m³/day, effluent concentration was less than 35 mg/l.[7] The main composition of COD in the membrane permeate is refractory organic matters.[11]

The study by Campagna et al. revealed that an important part of organic matter in landfill leachate can be removed by the primary clarifier and MBR. Furthermore, organic matter of one third percent is particulate or colloidal form and almost half of the organic fraction has a lower molecular weight (MW) than 500 Daltons (Da).[13] The average total COD concentration in the feed was 1332 mg/l. Insel et al. estimated readily and slowly biodegradable COD fractions of raw leachate to be 17% and 52%, respectively.[14]

As shown in figure 3, COD removal efficiency increased up to 70% in all experiments in the bioreactor with time. In spite of high BOD_5 removal in coupled process, overall COD reduction was not as satisfactory as that of BOD_5 degradation. This includes soluble COD portion; considerable soluble chemical oxygen demand (SCOD) values were analyzed (186 mg/l) in filtrate specially in loading more than 3500 mg/l COD. Large variations in feed COD (140-4200 mg/l) and operation conditions did not affect the MSBR effluent quality. This finding is in agreement with that of the study by Chen and

Liu.[3] In the study by Brown et al., The COD of the effluent was successfully reduced by more than 99% from an initial leachate COD of 116 g/l.[15]

Upgrading MBR with activated carbon removed a significant level of recalcitrant and bio-refractory compounds from leachate with reduced fouling. [16] The membrane process coupled with a SBR not only replaces the sedimentation period in the operation of a SBR, but also serves as an advanced treatment unit for suspended solids, which cannot be removed completely through conventional processes.[17]

The membrane used in this study is categorized as high flux anti-fouling microfiltration (MF) and separation via ion size exclusion was its main target based on pore size. In subsequent polishing of landfill leachate treatment, TSS removal was over 99%. In almost all the runs, filtrate TSS was stable. The coupling of membrane and sequencing batch reactor results in the purification of turbid SBR effluent.[18] Usually, the submerged membranes used in MBR are mostly MF or ultrafiltration (UF) membranes which can rarely remove dissolved material. Thus, as shown in figure 5, based on paired t-test analysis, there was no significant difference between TDS concentration in feed and filtrate (P > 0.05).

Conclusion

Complete treatment of leachate due to the omplexity of its composition is today's challenge. MBR is a versatile technology with high throughput and can treat compost leachate. Contrary to previous studies which had used MBR independently, in the application of MSBR process for advanced treatment of pre-anaerobic/aerobic treated compost leachate, a BOD_5 and total COD effluent concentration of below the Iranian standard were obtained. TDS values were higher than the permitted limit. There were no significant differences in MSBR filtrate quality in a varied range of feed concentration. Nevertheless, in high loading, membrane clogging led to filtrate flux loss and increase in the frequency of membrane cleaning and replacement. The acceptable performance of the MBR under different conditions suggests the promising capability of a full-scale, on-site MBR as an efficient and flexible treatment system in handling the fluctuating nature of both the quantity and quality of the leachate. Post-treatment processes, such as nanofiltration (NF), reverse osmosis (RO), or advanced oxidation processes (AOPs), can be used for low residual levels in MBR filtrate to even meet reusable quality.
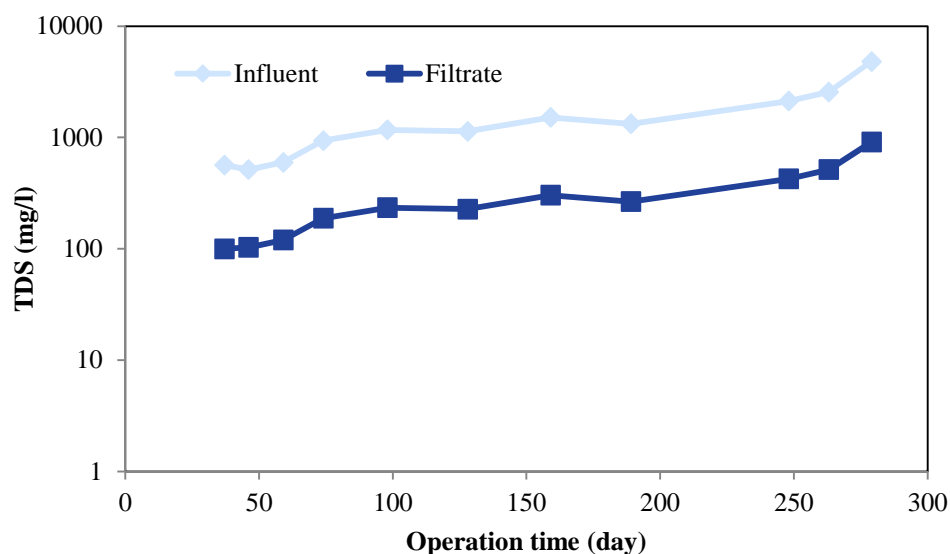

Figure 5. Total dissolved solids (TDS) concentrations during process operation
TDS: Total dissolved solids

Conflict of Interests

Authors have no conflict of interests.

Acknowledgements

References

1. Taiwo AM. Composting as A Sustainable Waste Management Technique in Developing Countries. Journal of Environmental Science and Technology 2011; 4(2): 93-102.
2. Safari E, Jalili Ghazizade M, Shokouh A, Nabi Bidhendi GR. Anaerobic removal of COD from high strength fresh and partially stabilized leachates and application of multi stage kinetic model. International Journal of Environmental Research 2011; 5(2): 255-70.
3. Hashemi H, Ebrahimi A, Khodabakhshi A. Investigation of anaerobic biodegradability of real compost leachate emphasis on biogas harvesting. Int J Environ Sci Technol 2015; 12(9); 2841-6.
4. Castrillon L, Fernandez-Nava Y, Ulmanu M, Anger I, Maranon E. Physico-chemical and biological treatment of MSW landfill leachate. Waste Manag 2010; 30(2): 228-35.
5. Abbas AA, Jingsong G, Ping LZ, Ya PY, Al-Rekabi WS. Review on landfill leachate treatments. Journal of Applied Sciences Research 2009; 5(5): 534-45.
6. Neczaj E, Kacprzak M, Lach J, Okoniewska E. Effect of sonication on combined treatment of landfill leachate and domestic sewage in SBR reactor. Desalination 2007; 204(1-3): 227-33.
7. Hashemi H, Hajizadeh Y, Amin MM, Bina B, Ebrahimi A, Khodabakhshid A, et al. Macropollutants removal from compost leachate using membrane separation process. Desalination and Water Treatment 2015.
8. Kaewsuk J, Thorasampan W, Thanuttamavong M, Seo GT. Kinetic development and evaluation of membrane sequencing batch reactor (MSBR) with mixed cultures

photosynthetic bacteria for dairy wastewater treatment. J Environ Manage 2010; 91(5): 1161-8.
9. Ahmed FN, Lan CQ. Treatment of landfill leachate using membrane bioreactors: A review. Desalination 2012; 287: 41-54.
10. Chan YJ, Chong MF, Law CL, Hassell DG. A review on anaerobic-aerobic treatment of industrial and municipal wastewater. Chemical Engineering Journal 2009; 155(1-2): 1-18.
11. Eaton AD, Franson MA. Standard methods for the examination of water and wastewater. Washington, DC: American Public Health Association; 2005.
12. Laitinen N, Luonsi A, Vilen J. Landfill leachate treatment with sequencing batch reactor and membrane bioreactor. Desalination 2006; 191(1-3): 86-91.
13. Campagna M, alCakmakci M, Busra Yaman F, Ozkaya B. Molecular weight distribution of a full-scale landfill leachate treatment by membrane bioreactor and nanofiltration membrane. Waste Management 2013; 33(4): 866-70.
14. Insel G, Dagdar M, Dogruel S, Dizge N, Ubay CE, Keskinler B. Biodegradation characteristics and size fractionation of landfill leachate for integrated membrane treatment. J Hazard Mater 2013; 260: 825-32.
15. Brown K, Ghoshdastidar AJ, Hanmore J, Frazee J, Tong AZ. Membrane bioreactor technology: A novel approach to the treatment of compost leachate. Waste Management 2013; 33(11): 2188-94.
16. Garces A, De Wilde W, Thoeye C, GueldreG. Operational cost optimization of MBR Schilde. Proceedings of the 4th IWA International Membranes Conference-Membranes for Water and Wastewater Treatment; 2007 May 15-17; Harrogate, UK.
17. Achilli A, Cath TY, Marchand EA, Childress AE. The forward osmosis membrane bioreactor: A low fouling alternative to MBR processes. Desalination 2009; 239(1-3): 10-21.
18. Le-Clech P, Jefferson B, Judd SJ. A comparison of submerged and sidestream tubular membrane bioreactor configurations. Desalination 2005; 173(2): 113-22.

http://jaehr.muk.ac.ir

Spatial distribution and analysis of heavy metal pollution in urban roadside dusts from Sanandaj, Iran

Farshid Ghorbani[1], Jamil Amanollahi[1], Voria Sijanvandi[1], Zahra Kiani[1], Arman Kamangar[1]

1 Department of Environmental Sciences, School of Natural Resources, University of Kurdistan, Iran

Original Article

Abstract

Industrial activities and high traffic density are the most important heavy metal pollution sources in urban areas. Roadside dust created by atmospheric deposition can be one of the best indicators for heavy metal contamination levels. The present study reports the spatial distribution patterns and degree of heavy metal pollution (Cd, Cr, Ni, Pb, Zn, and As) in 50 roadside dust samples from urban areas of Sanandaj, Iran. For this purpose, sampling points were selected on different roads including primary roads, high roads, and main roads. The geographic coordinates of sampling points were recorded by the Global Positioning System (GPS). The geoaccumulation index (I_{geo}) and integrated pollution index (IPI) were used to present the heavy metal contamination levels. The results obtained by the geoaccumulation index suggest that the roadside dust samples were moderately contaminated with Ni and Cr, moderately to heavily contaminated with Pb and Cd, and heavily to extremely contaminated with As and Zn. The assessment of the data shows that 92% of all roadside dust samples had moderate pollution levels with an IPI of higher than 2, indicating that roadside dust in Sanandaj County has moderately been polluted by anthropogenic emissions. In order to compare the heavy metal concentrations in different parts of Sanandaj County, each heavy metal contamination was interpolated in a geographical information system (GIS). Heavy metal distribution maps showed the different hotspots of each pollutant that indicated high traffic density and industrial centers as the important factors affecting their concentrations in Sanandaj County.

KEYWORDS: Heavy Metals, Urban Roadside Dust, Special Distribution, Geographical Information System

Introduction

Today, industrialization of communities and rapid urbanization is a worldwide phenomenon. According to the literature, over half of the world's population now lives in urban areas.[1] Moreover, industrial and economic activities are more concentrated in urban areas, and cities have become the geographic focus of resource consumption and chemical emissions.[2,3] Therefore, urban areas encounter many environmental problems. Environmental pollutants, which accumulate in the form of roadside dust through atmospheric deposition, are often used as indicators of pollution in urban areas.[4,5] Roadside dust is a complex mixture of particles derived from different natural and anthropogenic sources which have been found to contain several pollutants including heavy metals from exhaust and non-exhaust processes.[6] According to numerous studies, roadside dust may act as a temporary storage of metals from a variety of sources and may also act as a source of metals contributing to atmospheric or water source pollutions through resuspension.[7,8] The

Corresponding Author:
Jamil Aamanollahi
Email: j.amanollahi@uok.ac.ir

suspension of a portion of this dust in the ambient atmosphere is caused by transportation and wind. Larger particles with diameters of 500-1000 mm tend to settle on the ground surface while those below 100 mm can become suspended.[9] Heavy metals are among the most important environmental pollutants. Exposure to heavy metal emissions on roadways (including direct ingestion, respiratory uptake, and skin absorption) has been implicated as detrimental to human health and associated with effects of bioaccumulation.[10-13] Due to the higher uptake of heavy metals by children's body system, which is because of the higher sensitivity of their hemoglobin, children are more readily prone to the health hazards of these pollutants, as compared with adults.[2,14] For example, there is substantial evidence that a high Pb level in the environment could affect blood Pb level, intelligence, and behavior of children.[4] Cd, Pb, Zn, Ni, Cr, and As are reasonable indicators of contamination in urban roadside dust because they have anthropogenic sources.[15-18] In roadside dust of urban areas, anthropogenic sources of heavy metals consist of traffic emission (including vehicle exhaust particles, tire and brake lining wear particles, and weathered street asphalt particles), industrial emission (including power plants, metallurgical industries, auto repairs, chemical plants, and etcetera), domestic emission, building and pavement erosion, atmospheric deposition, and etcetera.[11,16,19-21] Wei et al. reported that a direct relationship was observed between spatial distribution pattern of Pb, Zn, and Cr and traffic density in Urumqi, NW, China.[16] On the other hand, Ni showed similar distribution in relation with industrial areas and Cd was mostly accumulated in old towns, near factory sites and industrial parks.[16] Today, due to industrialization and rapid urbanization, air pollution has become a major environmental issue in many developing countries, including Iran. However, no studies have, thus far, reported the level and distribution of heavy metals in urban areas of

Iran. Therefore, the objective of the present study is the determination of spatial distribution patterns and contamination levels of heavy metals in Sanandaj, Iran. For this purpose, 50 samples of roadside dust were collected from different roads and concentrations of Cd, Cr, Ni, Pb, Zn, and As were determined. In addition, 5 deep soil samples (> 50 cm depth) were collected from areas at a distance of more than 100 m from the roads and used as background value. Then, the contamination level of these metals was assessed using the integrated pollution index (IPI) and geoaccumulation index (I_{geo}). Finally, spatial distribution patterns of these metals in Sanandaj were obtained.

Materials and Methods

The study sites, consisting of road surfaces, were selected in Sanandaj, the capital of Kurdistan Province. Sanandaj with approximately 2,906 km² area is the 23rd largest city of Iran and is located in the West of Iran with a population of over 370,000. The urban area of Sanandaj in all directions is surrounded by Zagros Mountains. The city is 1,4501,538 m above sea level with average annual rainfall of 500 mm and a cold semi-arid climate. Environmental pollution in the urban area of Sanandaj may be due to exhaust emissions from natural particulate matter, vehicles, domestic heating, industrial discharging. A major environmental problem in Sanandaj is dust storms created in the deserts of Syria, Iraq, and Saudi Arabia.[22] According to the World Health Organization (WHO), the annual outdoor average of PM_{10} in Sanandaj was 254 µg.m^{-3} in 2011, which ranked it as the third most polluted city in the world.[23] The city has been undergoing rapid urbanization in the past decade with most of the industrial parks and automobile service businesses located around its urban area.

During April 2014, 50 samples of roadside dust were collected from different roads (including primary roads, high roads, and main

roads) within the city of Sanandaj. The samples were collected in order to investigate the spatial distribution and contamination levels of heavy metals in these areas. The sampling points are shown in figure 1. At each sampling point, 3 roadside dust samples were taken (with a minimum distance of 100 m), and then, mixed thoroughly to obtain a representative bulk sample. The central point position of the 3 subsamples was recorded by a Global Positioning System (GPS) instrument. The roadside dust samples were mainly collected by sweeping an area of about 1 m² of road surface of each sampling site. Sample dusts, which were collected and gathered into coded plastic bags using a clean dustpan and a brush, weighed 100–150 g. From areas at a distance of more than 100 m from the roads (Figure 1), 5 deep soil samples (> 50 cm depth) were collected to be used as background values.[18] Finally, the roadside dust and deep soil samples were transferred to the laboratory for analytical characterization. The weather condition was stable during the sampling period and there had been no rainfall during the two weeks prior to sampling.

Analytical grade of nitric acid (90%) and hydrogen peroxide solution (30 wt.% in H_2O) were purchased from Aldrich and used without further purification. Deionized distilled water was used in the preparation of analysis solutions. The roadside dust samples were dried thoroughly and then sieved through a < 0.5 mm sieve. Sieved dust samples were digested with HNO_3 and H_2O_2 using the 3050B methods suggested by the United States Environmental Protection Agency (USEPA).[24] The digested samples were centrifuged, and then deionized water was added to the supernatant to make 25 ml of the analysis solutions. Finally, the concentrations of the heavy metals, including As, Cd, Pb, Ni, Cr, and Zn, in the digestion solution were analyzed using a graphite furnace atomic absorption spectrometer (GFAAS) (Phoenix-986, China).
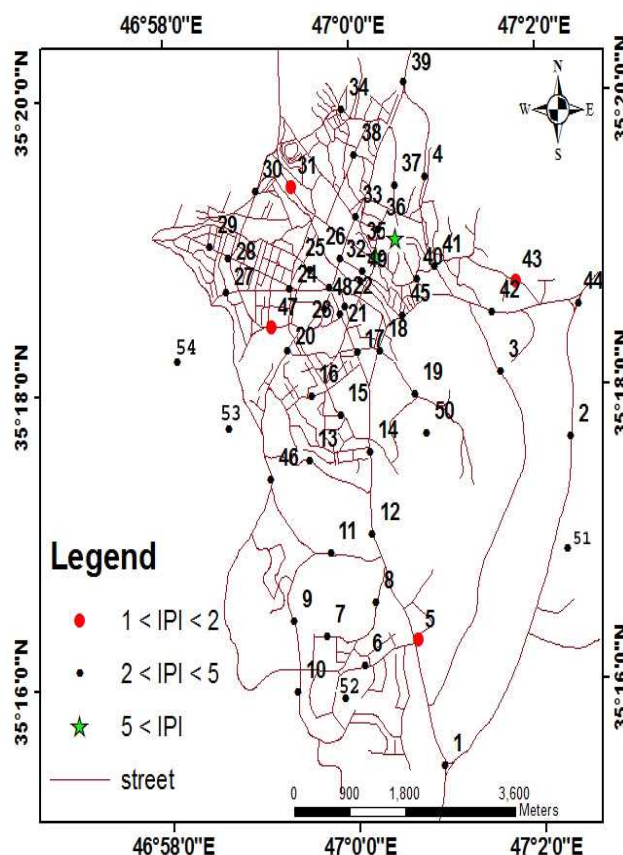

Figure 1. Sampling pointes (1-50 sampling points and 51-55 control points) and spatial distribution of the integrated pollution index (IPI) in the studied area

The contamination levels of heavy metals in urban roadside dust were assessed using the I_{geo} introduced by Muller.[25] The I_{geo} was computed using the following equation:[26]

$$I_{geo} = \log_2 \left(1.5 \times \frac{C_n}{B_n} \right) \qquad (1)$$

where Cn is the measured concentration of the elements in the environment, Bn is the geochemical background value in soil (average value of 5 control points in the present study). The constant 1.5 allows us to analyze natural fluctuations in the content of a given substance in the environment and to detect very small anthropogenic influences.16 The I_{geo} was calculated and categorized for each element according to Muller's classification (Table 1).

Table 1. Classification of the geoaccumulation index (I_{geo})

Class	I_{geo} value	Sample quality
0	$0 \leq I_{geo}$	Practically uncontaminated
1	$I_{geo} \leq 1 < 0$	Uncontaminated to moderately contaminated
2	$I_{geo} \leq 2 < 1$	Moderately contaminated
3	$I_{geo} \leq 3 < 2$	Moderately to heavily contaminated
4	$I_{geo} \leq 4 < 3$	Heavily contaminated
5	$I_{geo} \leq 5 < 4$	Heavily to extremely contaminated
6	$I_{geo} \geq 5$	Extremely contaminated

I_{geo}: Geoaccumulation index

The contamination levels of the heavy metals in dust samples of Sanandaj were further evaluated by calculating the pollution index (PI) and the IPI of the selected metals. The PI of each element was defined as the ratio of the metal concentration in the roadside dust samples (C_n) to the background concentration of the corresponding metal (B_n), calculated by the following formula:

$$PI = C_n / B_n \qquad (2)$$

The IPI is defined as the mean value of the PI of an element[16,27,28]. In this study, The PI and IPI classifications are presented in table 2.

Table 2. Classification of pollution index (PI) and integrated pollution index (IPI)

Class	PI value	IPI value	Pollution level
1	$1 \geq PI$	$1 < IPI \leq 2$	Low
2	$1 < PI \leq 3$	$2 < IPI \leq 5$	Moderate
3	$PI > 3$	$IPI > 5$	High

PI: Pollution index; IPI: Integrated pollution index

SPSS software for Windows (version 16, SPSS Inc., Chicago, IL, USA) was used to analyze the normality of data, using the Kolmogorov-Smirnov test, and to determine the Pearson correlation coefficients between the heavy metal concentrations in the study area. All GPS recorded sample points were geocoded with the universal transverse mercator (UTM) projection (Datum WGS-1984, zone 38). The sample points were added to geographical information system (GIS) environment (Arc GIS version 9.3), using DNR Garmin (version 5.4, Minnesota Department of Natural Resources, USA), and then, placed on a layer of Sanandaj city road (Figure 1). The heavy metals of the samples were interpolated to Sanandaj area using the inverse distance weighted (IDW) algorithm in GIS environment (Figure 2).

Results and Discussion

Statistical analysis and normality test

The descriptive statistical parameters of dust heavy metals are presented in table 3. The results indicated that Cr, Ni, and As had passed the normality test of Kolmogorov–Smirnov (P > 0.05) with an exception of the other variables including Pb, Zn, and Cd. The minimum and maximum concentrations, and the mean values and standard deviations for each heavy metal are also presented in table 3. In addition, the background values of the metals in Sanandaj deep soil (> 50 cm) that is the average value of the 5 control points were also calculated. The results show that the mean concentrations of Cd (112.83 mg.k^{-1}), Cr (1.80 mg.k^{-1}), Ni (2.76 mg.k^{-1}), Pb (9.8 mg.k^{-1}), and particularly Zn (410.99 mg.k^{-1}) as well as As (11.31 mg.k^{-1}) were higher than their background values. These results suggest that the studied elements in Sanandaj roadside dust were influenced by anthropogenic pollution sources. The coefficient variation (C.V.) values of heavy metals in the study ranged from 0.26 to 0.70 indicating moderate variations. The highest C.V. of the 6 heavy metals belonged to Cd (0.70), suggesting that Cd has the greatest variation among the roadside dust samples. Thus, it would have the highest possibility of being influenced by point-anthropogenic sources such as industrial emission. This is in agreement with the previous study.[16] On the other hand, the lowest C.V. belonged to Pb (0.26), suggesting that Pb has a weak variation and its content would have the highest possibility of being influenced by non-point anthropogenic sources such as traffic emissions.
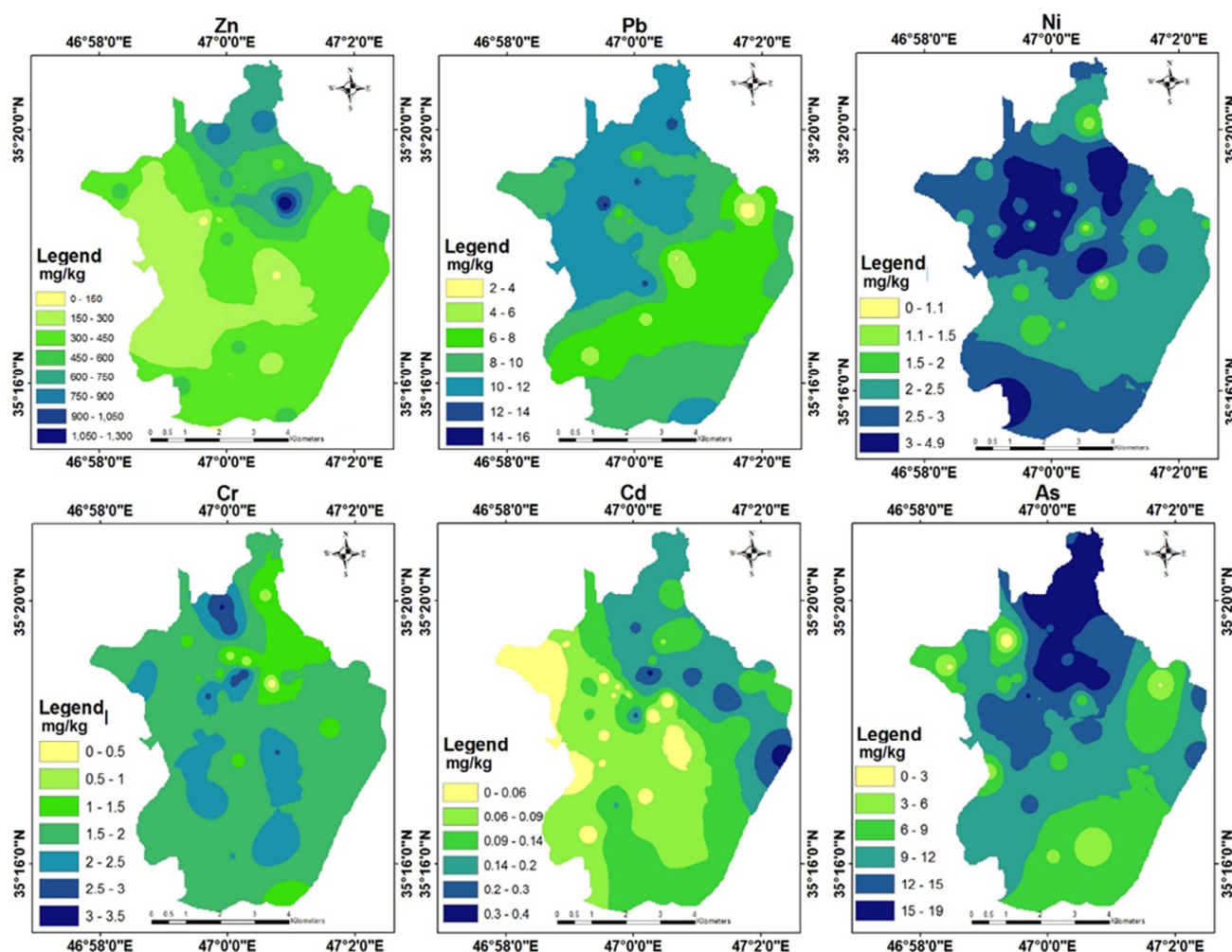
Figure 2. The spatial distribution maps of 6 heavy metal contents

Table 3. Descriptive statistics parameters and tests of normality for roadside dust heavy metals

Heavy metals	Concentration (mg.kg^{-1})			SD*	C.V**	(K-S)† (P > 0.05)	Distribution
	B$_n$††	Min.	Mean	Max.			
Cd	105.00	23.88	112.83	333.78	79.18	0.70	0.003	Abnormal
Cr	1.23	0.23	1.80	3.03	0.59	0.33	0.200	Normal
Zn	100.54	130.58	410.99	1259.68	213.24	0.52	0.007	Abnormal
Ni	1.56	1.06	2.76	4.05	0.89	0.32	0.200	Normal
Pb	4.39	2.71	9.48	12.24	2.45	0.26	0.025	Abnormal
As	1.51	0.74	11.31	18.85	4.49	0.40	0.118	Normal

CV: Coefficient variation; SD; Standard deviation
* Standard deviation; ** Coefficient of variation; † Kolmogorov–Smirnov normality test; †† Background values.

Correlation between roadside dust heavy metals

Correlation measures the linear relationship between variables. The Pearson correlation coefficients and their significance levels between all of the variables are presented in table 4.

Strong positive correlations were observed between Cd, and As and Zn, indicating that they were closely related to each other. A significant correlation was also observed between Zn, Pb, and As.

Contamination assessment by Igeo

The maximum, minimum, and mean values of I_{geo} for each element are shown in table 5. Based on the I_{geo} data and Muller's classifications listed in table 1, the mean I_{geo} value for Cd was in the range of class 1, which indicates that roadside dust in Sanandaj was uncontaminated to moderately contaminate with Cd. The mean I_{geo} values for Cr, Ni, and Pb were in the range of class 2, which indicates that roadside dust was moderately contaminated with the mentioned heavy metals. The element of Zn, according to I_{geo} classification, was in the range of class 3, which shows that roadside dust was moderately to heavily contaminate with Zn. The highest I_{geo} mean value in Sanandaj roadside dust was observed for As that was in the range of class 4, which indicates heavy contamination. The maximum I_{geo} value for each element (Table 5) also showed that roadside dust was moderately contaminated with Ni and Cr, moderately to heavily contaminated with Pb and Cd, and heavily to extremely contaminated with As and Zn. These results may suggest that As, Zn, Pb, and Cd, in roadside dust, are most significantly impacted by anthropogenic pollution sources.

Contamination assessment by IPI

The PIs of the considered heavy metals in urban roadside dust were calculated according to the background value (B_n) of each metal (Table 5). The mean PI values for Cd (1.07), Cr (1.46), Ni (1.77), and Pb (2.16) were in the range of class 2, indicating a moderate pollution level. However, Ni from sampling site 21 and Cd from sampling sites 2 and 35 were highly polluted. On the other hand, the mean PI values for Zn (4.09) and As (7.47) were classified as high pollution levels (class 3), indicating the presence of problematic Zn and As pollution of roadside dust in Sanandaj. The IPIs of all the analyzed dust samples varied from 1.59 to 5.05. Figure 1 represents the spatial distributions of IPIs in Sanandaj.

The assessment of the data shows that 92% of all roadside dust samples had moderate pollution levels with an IPI of higher than 2, indicating that the roadside dust quality of Sanandaj is moderately polluted by anthropogenic emissions. In addition, heavy metal concentrations would have the highest possibility of being influenced by non-point anthropogenic sources such as traffic emissions (including vehicle exhaust particles, tire and brake lining wear particles, and weathered street asphalt particles).[11]

Table 4. Pearson correlation coefficients of Sanandaj roadside dust heavy metals

Heavy metals	As	Cd	Cr	Ni	Pb	Zn
As	1					
Cd	0.363[**]	1				
Cr	0.197	0.053	1			
Ni	0.206	0.173	0.027	1		
Pb	0.186	0.187	-0.204	0.006	1	
Zn	0.358[*]	0.536[**]	-0.273	0.205	0.376[**]	1

[*] Correlation significance in the level of 0.05; [**] Correlation significance in the level 0.01

Table 5. Geoaccumulation index (I_{geo}) and pollution index (PI) of urban roadside dust in Sanandaj

Heavy metals	Background values	Igeo			PI			Max.
		Min.	Mean	Max.	Min.	Mean	Max.	
Cd	105.00	-1.55	0.37	2.25	0.23	1.07	3.18	
Cr	1.23	-1.86	1.02	1.88	0.18	1.46	2.46	
Zn	100.54	0.96	2.45	4.23	1.30	4.09	12.53	
Ni	1.56	0.04	1.33	1.96	0.68	1.77	3.11	
Pb	4.39	-0.11	1.63	2.06	0.62	2.16	2.79	
As	1.51	-0.44	3.30	4.22	0.49	7.47	12.46	

I_{geo}: Geoaccumulation index; PI: Pollution index

Moreover, some of the dust samples with high pollution levels (IPI of higher than 4) such as sampling sites 26, 32, 35, and 38 were in crowded areas influenced by high traffic density. Sampling sites 34, 40, and 41, with high pollution levels, were affected by industrial emissions such as auto repairs and car washes. Finally, sampling sites with low pollution levels (IPI of lower than 2) were estimated for about 8% of all samples, located in new urban areas and the countryside.

Spatial distribution of heavy metals

The spatial distribution of heavy metal concentrations is an effective visual method to evaluate the possible sources of enrichment and to identify hotspots with high metal concentrations.[16,29] In the present study, the spatial distribution patterns of the considered elements were analyzed by GIS methods. The maps of Zn, Cr, Pb, Cd, Ni, and As concentrations in the entire urban area of Sanandaj are presented in figure 2. It was observed that the spatial distributions of Pb and Zn have similar patterns, they had relatively less spatial variability, and the scope of pollution for Zn was relatively small. Their hotspots were mainly associated with main roads at the North and Northwest edge of the city, where high traffic density was identified. The features suggest the existence of these metals in rodeside dust is probably due to vehicular emission. From the map of As and Ni spatial distribution, the highest concentration area was located in the Northern and central part of the city. For these elements, they had relatively high spatial variability. Furthermore, 2 different hotspots were identified, i.e., in the Eastern part of the city for As, and in the Southern part of the study area for Ni. The most contaminated roadside dust samples by As and Ni are in the proximity of the local industrial park and streets with high traffic flows. The distribution pattern of Cd concentration presented relatively high spatial variability. One of the hotspots was located in the city center close to the old urban area that was mainly a commerce center. Other hotspots for Cd were located in the Eastern part of the city. In the studied region, anthropogenic emission sources of Cd in the roadside dust may be attributed to industrial activities and application of organic manures as well as phosphate fertilizer in farming practices. Several studies reported that activities, such as smelting, waste disposal, waste water irrigation, and phosphate fertilizer application resulted in the emission of significant quantities of Cd into the environment.[16,30-33] The spatial distribution pattern of Cr concentration was different from those of the metals mentioned above, and Cr presented moderate variability. The hotspots were located in the center and Northwest of the study area close to the old residential area. Cr and As were used to preserve wooden instruments like door, window, sofa, and cabinets.

Conclusion

Heavy metals created by human activity are among the main factors affecting the human health in residential areas. In this paper, roadside dust was analyzed to determine the effect of traffic density and industrial centers on heavy metal concentrations in an urban area. using a GFAAS, 50 samples of roadside dust collected from Sanandaj were analyzed for Cd, Cr, Ni, Pb, Zn, and As. The concentrations of these elements were generally higher than their background values. I_{geo} showed that most of the heavy metals including As, Zn, Pb, and Cd have high or moderate level concentrations. The highest PI index was observed for Zn (4.09) and As (7.47) that indicate hazardous levels of Zn and As pollution in Sanandaj. Surface maps of heavy metals, drawn in GIS environment helped show similar patterns of heavy metal distributions which indicted the same sources. Surface maps also helped identify the different sources of heavy metals by presenting the individual distribution of metals like Cd which may be attributed to industrial activities,

application of organic manures, and phosphate fertilizers in farming practices. From the results of this study, we conclude that GIS is an excellent tool for studying the variables which can affect the concentration of heavy metals in urban areas.

Conflict of Interests

Authors have no conflict of interests.

Acknowledgements

References

1. United Nations. World urbanization prospects: 2009 revisions. New York, NY: United Nations Department of Economic and Social Affairs; 2010.

2. Madrid L, Diaz-Barrientos E, Madrid F. Distribution of heavy metal contents of urban soils in parks of Seville. Chemosphere 2002; 49(10): 1301-8.

3. Imperato M, Adamo P, Naimo D, Arienzo M, Stanzione D, Violante P. Spatial distribution of heavy metals in urban soils of Naples city (Italy). Environ Pollut 2003; 124(2): 247-56.

4. Li X, Poon Cs, Liu PS. Heavy metal contamination of urban soils and street dusts in Hong Kong. Applied Geochemistry 2001; 16(11□12): 1361-8.

5. Maas S, Scheifler R, Benslama M, Crini N, Lucot E, Brahmia Z, et al. Spatial distribution of heavy metal concentrations in urban, suburban and agricultural soils in a Mediterranean city of Algeria. Environ Pollut 2010; 158(6): 2294-301.

6. Apeagyei E, Bank MS, Spengler JD. Distribution of heavy metals in road dust along an urban-rural gradient in Massachusetts. Atmospheric Environment 2011; 45(13): 2310-23.

7. Cambra K, Martinez T, Urzelai A, Alonso E. Risk Analysis of a Farm Area Near a Lead- and Cadmium-Contaminated Industrial Site. Journal of Soil Contamination 1999; 8(5): 527-40.

8. Moreno T, Karanasiou A, Amato F, Lucarelli F, Nava S, Calzolai G, et al. Daily and hourly sourcing of metallic and mineral dust in urban air contaminated by traffic and coal-burning emissions. Atmospheric Environment 2013; 68: 33-44.

9. Sinclair AH, Tolsma D. Associations and lags between air pollution and acute respiratory visits in an ambulatory care setting: 25-month results from the aerosol research and inhalation epidemiological study. J Air Waste Manag Assoc 2004; 54(9): 1212-8.

10. Adriano DC. Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability, and Risks of Metals. Berlin, Germany: Springer Science & Business Media; 2001.

11. Sezgin N, Ozcan HK, Demir G, Nemlioglu S, Bayat C. Determination of heavy metal concentrations in street dusts in Istanbul E-5 highway. Environ Int 2004; 29(7): 979-85.

12. De MiguelE, Iribarren I, Chacon E, Ordonez A, Charlesworth S. Risk-based evaluation of the exposure of children to trace elements in playgrounds in Madrid (Spain). Chemosphere 2007; 66(3): 505-13.

13. Lim HS, Lee JS, Chon HT, Sager M. Heavy metal contamination and health risk assessment in the vicinity of the abandoned Songcheon Au-Ag mine in Korea. Journal of Geochemical Exploration 2008; 96(2-3): 223-30.

14. Christoforidis A, Stamatis N. Heavy metal contamination in street dust and roadside soil along the major national road in Kavala's region, Greece. Geoderma 2009; 151(3-4): 257-63.

15. Garcia R, Millaín E. Assessment of Cd, Pb and Zn contamination in roadside soils and grasses from Gipuzkoa (Spain). Chemosphere 1998; 37(8): 1615-25.

16. Wei B, Jiang F, Li X, Mu S. Spatial distribution and contamination assessment of heavy metals in urban road dusts from Urumqi, NW China. Microchemical Journal 2009; 93(2): 147-52.

17. Bretzel F, Benvenuti S, Pistelli L. Metal contamination in urban street sediment in Pisa (Italy) can affect the production of antioxidant metabolites in Taraxacum officinale Weber. Environ Sci Pollut Res Int 2014; 21(3): 2325-33.

18. Liu E, Yan T, Birch G, Zhu Y. Pollution and health risk of potentially toxic metals in urban road dust in Nanjing, a mega-city of China. Sci Total Environ 2014; 476-477: 522-31.

19. Banerjee AD. Heavy metal levels and solid phase speciation in street dusts of Delhi, India. Environ Pollut 2003; 123(1): 95-105.

20. Duzgoren-Aydin NS, Wong CS, Aydin A, Song Z, You M, Li XD. Heavy metal contamination and distribution in the urban environment of Guangzhou, SE China. Environ Geochem Health 2006; 28(4): 375-91.

21. Amato F, Pandolfi M, Viana M, Querol X, Alastuey A, Moreno T. Spatial and chemical patterns of PM10 in road dust deposited in urban environment. Atmospheric Environment 2009; 43(9): 1650-9.

22. Amanollahi J, Kaboodvandpour S, Abdullah AM, Rashidi P. Effect of the influence of heat and moisture changes of desert area around the Euphrates on the recent dust storms in Iran using Landsat satellite images processing. International journal of physical sciences 2012; 7(5): 827-30.

23. Bourlinos AB, Simopoulos A, Boukos N, Petridis D. Magnetic Modification of the External Surfaces in the MCM-41 Porous Silica:? Synthesis, Characterization, and Functionalization. J Phys Chem B 2001; 105(31): 7432-37.

24. United state Environmental Protection Agency. Acid digestion of sediments sludges and soils [Online]. [cited1996]; Available from: URL: http://www.epa.gov/waste/hazard/testmethods/sw846/pdfs/3050b.pdf

25. Muller G. Index of geoaccumulation in sediments of the Rhine river. Geol J 1969; 2(3): 108-18.

26. Ji Y, Feng Y, Wu J, Zhu T, Bai Z, Duan C. Using geoaccumulation index to study source profiles of soil dust in China. J Environ Sci (China) 2008; 20(5): 571-8.

27. Chen TB, Zheng YM, Lei M, Huang ZC, Wu HT, Chen H, et al. Assessment of heavy metal pollution in surface soils of urban parks in Beijing, China. Chemosphere 2005; 60(4): 542-51.

28. Wei B, Yang L. A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China. Microchemical Journal 2010; 94(2): 99-107.

29. Cao S, Duan X, Zhao X, Ma J, Dong T, Huang N, et al. Health risks from the exposure of children to As, Se, Pb and other heavy metals near the largest coking plant in China. Sci Total Environ 2014; 472: 1001-9.

30. Li Y, Wang YB, Gou X, Su YB, Wang G. Risk assessment of heavy metals in soils and vegetables around non-ferrous metals mining and smelting sites, Baiyin, China. J Environ Sci (China) 2006; 18(6): 1124-34.

31. Sharma RK, Agrawal M, Marshall FM. Heavy metal (Cu, Zn, Cd and Pb) contamination of vegetables in urban India: a case study in Varanasi. Environ Pollut 2008; 154(2): 254-63.

32. Zeng Xb, Li Lf, Mei Xr. Heavy Metal Content in Chinese Vegetable Plantation Land Soils and Related Source Analysis. Agricultural Sciences in China 2008; 7(9): 1115-26.

33. Song B, Lei M, Chen T, Zheng Y, Xie Y, Li X, et al. Assessing the health risk of heavy metals in vegetables to the general population in Beijing, China. J Environ Sci (China) 2009; 21(12): 1702-9.

Removal of Reactive Green 19 dye from synthetic wastewater using electrocoagulation and aluminum electrodes

Mostafa Alizadeh[1], Esmaeil Ghahremani[2], Shahram Sadeghi[3]

1 Department of Environmental Health, Zahedan University of Medical Sciences, Zahedan, Iran
2 Environmental Health Research Center, Kurdistan University of Medical Sciences, Sanandaj, Iran
3 Student Research Committee, Kurdistan University of Medical Sciences, Sanandaj, Iran

Original Article

Abstract

Textile dyeing is considered to be one of the major industrial sources of high rates of organic and aromatic compounds. Conversely, these compounds have become a significant environmental problem. Many methods have been investigated for color removal from dye-containing wastewater. In this research, the efficiency of the electrocoagulation (EC) process with aluminum electrodes in the removal of Reactive Green 19 (RG-19) dye from synthetic solutions was studied. The experiments were conducted in a batch reactor equipped with 4 aluminum electrodes with a volume of 2 l. Dye concentrations were measured (λ_{max} = 630 nm). The effects of operating parameters, such as voltage, reaction time, initial dye concentration, energy consumption, pH, KCl concentration, and inter-electrode distance, on removal efficiency were investigated. The highest removal efficiency of RG-19 was found to be 33.49, 60.32, 72.43, 93.63, and 94.91 percent for initial voltage of 10, 20, 30, 40 and 50 v, respectively, in optimum conditions (pH = 11, KCL concentration = 0.005 M, and distance = 1 cm). The removal was effectively reduced to less than 99.88% when the initial dye concentration increased from 25 to 150 mg/l. In addition, by increasing KCl concentration and decreasing electrode distance, removal efficiency increased considerably. Based on the results, EC process by aluminum electrodes is an efficient and suitable method for reactive dye removal from wastewater.

KEYWORDS: Aluminum, Electrodes, Electrocoagulation, Textile Wastewater

Citation: Alizadeh M, Ghahremani E, Sadeghi Sh. **Removal of Reactive Green 19 dye from synthetic wastewater using electrocoagulation and aluminum electrodes.** J Adv Environ Health Res 2015; 3(1): 42-8.

Introduction

Textile dyeing creates large volumes of effluent and is considered as one of the major industrial polluters. The large quantity of aqueous waste generated by textile industries has become a significant environmental problem.[1,2] The production of dyes-containing wastewater is common in industries like textile, paper, plastic, food, and mineral processing industries ;

furthermore, azo dyes constitute over 50% of all textile dyes used in the industry.[3,4] In developed countries, these types of wastewater are normally treated through traditional methods, but in developing countries, they are discharged into natural streams and/or any river. This causes serious problems as well as biological changes, consuming dissolved oxygen (DO) and demolishing aquatic life. Some dyes are carcinogenic, mutagenic, and toxic.[5] Therefore, it is necessary to treat dye effluents prior to their discharge into streams. Many methods have been investigated for color removal from dye-

---

Corresponding Author:
Shahram Sadeghi
Email: shahram.snna@yahoo.com

containing wastewater. In general, several techniques are used for the treatment of textile effluents including physiochemical methods of dye removal [such as filtration, chemical coagulation, activated carbon adsorption, ultrafiltration, ozonation, and electrocoagulation (EC)], chemical methods of dye removal (such as reduction, oxidation, ion exchange, and neutralization), and dye removal by means of biodegradation.[6-9] Some of these methods are effective, although they are quite expensive and have many disadvantages and limitations. In chemical oxidation or coagulation, added chemical substances lead to secondary pollution. Biological methods cannot be applied for most textile wastewater types, because most commercial dyes are toxic to the organisms used in the process.[5,10,11] In recent years, the successful EC treatment of various organic effluents has been reported by many authors.[9-13] The EC process provides a simple, reliable, and cost-effective method for the treatment of wastewater without any additional chemicals and secondary pollution. It also reduces the amount of disposed sludge and requires simple equipment and easy operation.[9,14] The dye is coagulated by aluminum hydrates or hydroxides produced from the sacrificial anode.[15,16] Reactive Orange 19 (RG-19) dye belongs to a class of organic compounds known as azo dyes, which are abundantly used in textile industries for dyeing.[5]

The present work was carried out to study the removal of RG-19 dye by EC with aluminum electrodes from synthetic wastewater. Wastewater parameters, such as dye adsorption, high salt concentration, voltage, initial concentration of dye, and pH, were also investigated to examine their effects on the dye.

Materials and Methods

All chemicals used in this study were obtained from the Merck Company (Germany). The chemical structure of RG-19 is $C_{40}H_{23}Cl_2N_{15}Na_6O_{19}S_6$ with a molecular weight of 1418.93 g/mol. The pH was adjusted using either 0.15 M NaOH or 0.1 M H_2SO_4 as necessary.

Figure 1 illustrates the batch reactor apparatus used in the study. It consisted of 4 bipolar aluminum electrodes; 2 anodes and 2 cathodes of the same dimensions (10 × 15 cm) placed 1 cm apart. A digital DC power apparatus (ADAK PS808 model, Iran) was used in all experiments.
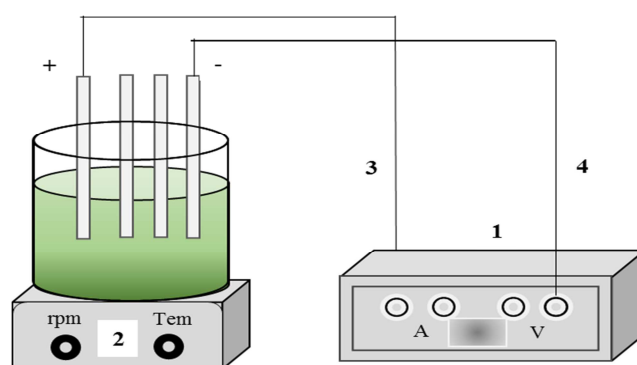

Figure 1. An electrocoagulation cell apparatus: (1) digital DC power apparatus; (2) magnetic stirrer bar; (3) anode; (4) cathode (bipolar electrodes in parallel connection)

RG-19 dye solutions were prepared by dissolving stock solution in distilled water and used without any further treatment. In each run, 1000 ml of the dye solution was added to the reactor. The pH of the solution was measured before and after each experiment. The electrodes were connected to a digital direct current (DC) power supply to measure the current and the potential between the two electrodes. All runs were performed at the constant temperature of 22 ± 2 °C. In each run, 2 l of the wastewater solution was added to the electrolytic cell. At the end of EC, the solution was filtered and the filtrate was centrifuged at 4000 rpm for 5 minutes, and then, was analyzed. Before each run, the electrodes were washed by dipping for 5 minutes in a solution freshly prepared by HCl solution (35%) to remove impurities on the surface of the aluminum electrodes.[17] Finally, the electrodes were washed thoroughly with diluted

water to remove any solid residues on the surfaces, dried, and re-weighted. Moreover, in the EC method, as a treatment technology with aluminum electrodes, some factors such as initial pH, contact time, voltage, energy consumption rate, and initial concentration of dyes were studied. Table 1 shows the range used for these experiments.

The concentration of dye remnants were measured (λ_{max} = 630 nm) using a spectrophotometer (Shimadzu, Tokyo, Japan; Model 1601). The efficiency of dye (RG-19) removal, % Removal, after EC treatment was calculated as follows:

$$RE(\%) = \frac{(C_0 - C)}{C_0} \times 100 \qquad (1)$$

Where C_0 is the initial concentration (mg/l) and C is the final dye concentration (mg/l). Electric energy consumption was also calculated using the commonly used equation[18]:

$$E = \frac{UIt_{EC}}{V}$$

Where E is electric energy (kWh/m³), U the cell voltage in volt (V), I the current in ampere (A), V is the volume of solution (m³), and t_{EC} is the duration of EC process (minute).

Results and Discussion

Effect of initial pH and voltage
The pH of the solution is one of the most important parameters in EC process and dye removal from aqueous solutions. Using the EC process at its optimum pH results in maximum pollutant removal.[19] To achieve an optimum voltage and pH, dye removal percentage should be evaluated. Figures 2–6 and the results show that an increase in voltage from 10 to 50 v caused an increase in dye removal efficiency at

different pH values; maximum color removal was achieved at a pH of 11. The highest removal percentages were found to be 33.49, 60.32, 72.43, 93.63, and 94.91% for initial voltages of 10, 20, 30, 40, and 50 v, respectively, at a pH of 11.

The mechanism of the electrochemical process in aqueous systems is complex. With an increase in voltage, the amount of aluminum ion produced increased. Therefore, there was an increase in flock production, and hence, an improvement in dye removal efficiency.[20] In addition, the results showed that the EC process with aluminum electrodes had greater effect on the pH of the samples and caused an increase in final solution pH. AcIn the study performed by by Sengil and Ozacar on the decolorization of C.I. Reactive Black 5 in aqueous solution in 2009, the results showed that by increasing pH, the dye removal efficiency increased.[21] In another research by Basiri Parsa et al. on the removal of acid brown 14 from aqueous media, the findings proved that, in time, the final pH solution enhanced.[22] The investigation by Daneshvar et al. illustrated that with increasing the primary voltage in EC process, the removal efficiency increased.[23]

Effect of initial concentration of dye
The effect of initial concentration of dye on the removal efficiency and energy consumption (E) has been presented in table 2. The results showed that with increasing initial concentration of dye, both energy consumption and dye removal increased.

By using aluminum as sacrificial anode, the removal efficiency of RG-19 dye reduced dramatically to less than 99.88%, when the initial dye concentration increased from 25 to 150 mg/l. This is because of the decrease in aluminum ions in high concentration.

Table 1. The ranges of experimental parameters

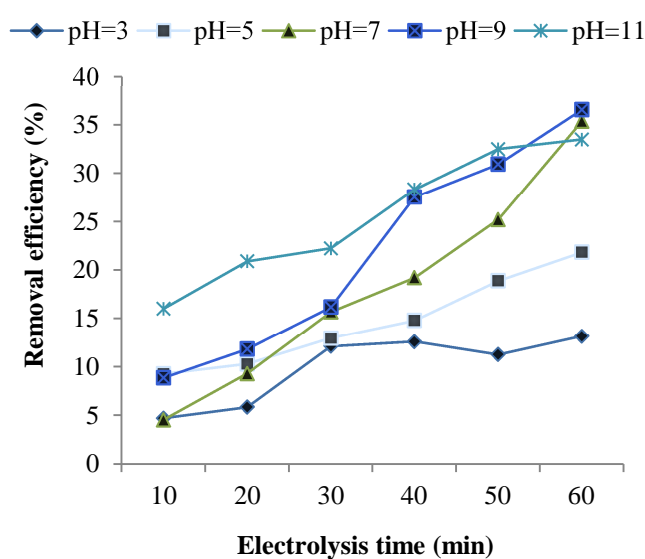| pH	Voltage (v)	Dye concentration (mg/l)	Time of reaction (min)	KCl concentration (M)	electrode distance (cm)
3,5,7,9,11	10,20,30,40,50	25,50,75,100,150	10,20,30,40,50,60	0.0025,0.005,0.0075,0.01	1,2,3

Figure 2. Effect of initial pH on removal efficiency of Reactive Green 19 (RG-19) dye
(Voltage = 10 v, C_0 = 50 mg/l, d = 1 cm, KCl = 0.005 M, T = 22 ± 2 $^\circ$C)
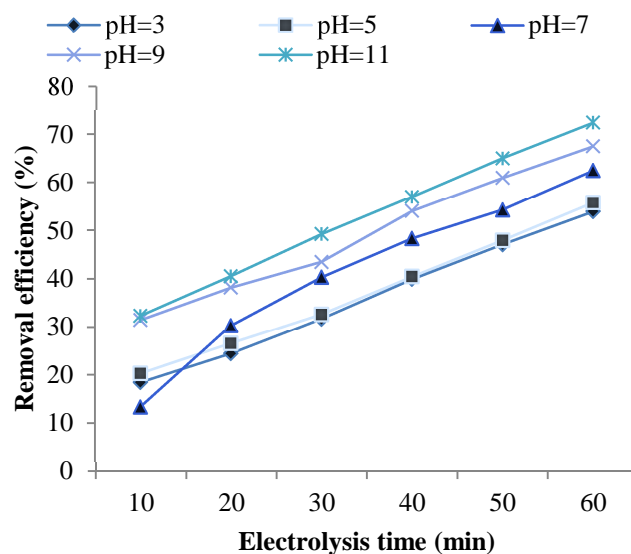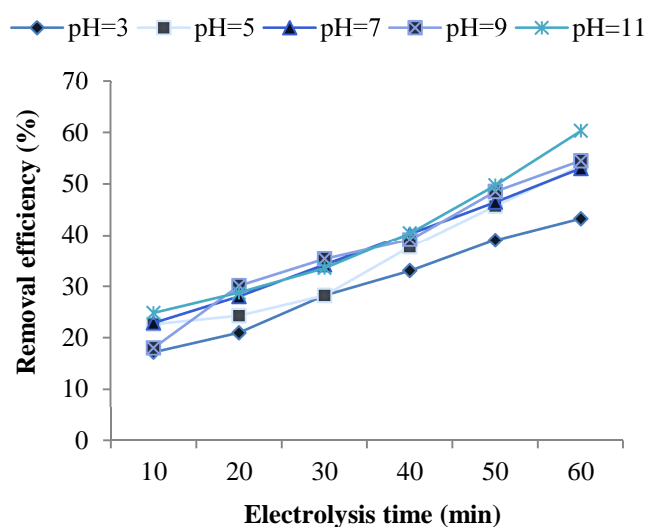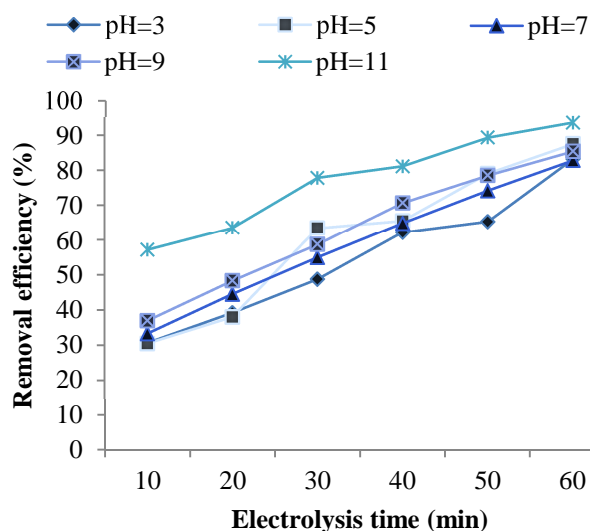

Figure 4. Effect of initial pH on removal efficiency of Reactive Green 19 (RG-19) dye
(Voltage = 30 v, C_0 = 50 mg/l, d = 1 cm, KCl = 0.005 M, T = 22 ± 2 $^\circ$C)

Figure 3. Effect of initial pH on removal efficiency of Reactive Green 19 (RG-19) dye
(Voltage = 20 v, C_0 = 50 mg/l, d = 1 cm, KCl = 0.005 M, T = 22 ± 2 $^\circ$C)

Figure 5. Effect of initial pH on removal efficiency of Reactive Green 19 (RG-19) dye
(Voltage = 40 v, C_0 = 50 mg/l, d = 1 cm, KCl = 0.005 M, T = 22 ± 2 $^\circ$C)

At concentrations of higher than 50 mg/l (99.27%) the no reduction was observed in color removal rate and it was relatively constant. However, increasing initial dye concentration caused a steady increase in decolorization capacity.[22]

Moreover, up to the concentration of 50 mg/l, the energy consumption was constant, but above this amount, it increased. When initial concentration of the dye was raised from 25 to 150 mg/l at the electrolysis time of 60 minutes, the efficiency decreased from 99.88 to 99.56%.

On the contrary, the energy consumption increased from 10.25 to 13.18 kWh/(kg m³). Furthermore, the study by Daneshvar et al. has also proven the fact that an increase in initial concentration of dye can enhance energy consumption and increase dye removal from solution.[23]
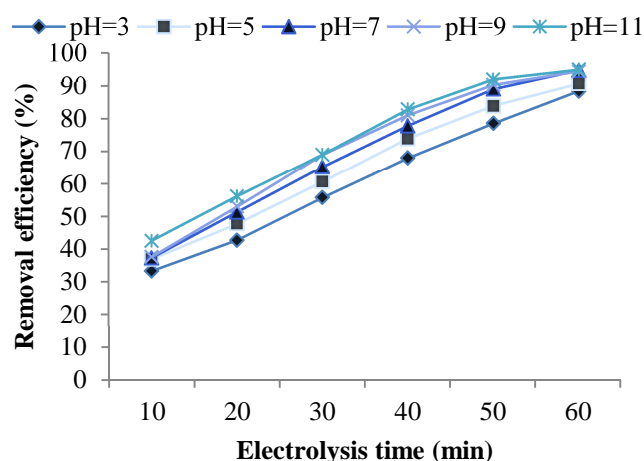

Figure 6. Effect of initial pH on removal efficiency of Reactive Green 19 (RG-19) dye
(Voltage = 50 v, C_0 = 50 mg/l, d = 1 cm, KCl = 0.005 M, T = 22 ± 2 °C)

Effect of KCL concentration

The effect of KCl concentration on removal efficiency and electrode consumption has been shown in figures 7 and 8. With an increase in the concentration of KCl in solution, the conductivity of the solution and the current density also increased. The cell voltage decreased with increasing wastewater conductivity at constant current density.[24] According to the results, high color removal

with low energy consumption occurred at around 0.01 M of KCl, but electrode consumption ratio increased at this concentration. The results of the study by Sengil and Ozacar showed that high color removal percentage with low cell voltages and low energy consumption could be obtained in dye solutions containing around 3 g⁻¹ of NaCl.[21]

Effect of electrode distance

Figures 9 and 10 show the percentage of color removal against distance between the electrodes. The effect of inter-electrode distance on removal efficiency was examined at 1-3 cm. the efficiency decreased slightly, when the inter-electrode distance increased. The distance of 1 cm was selected as the optimum point. Moreover, low energy was consumed at this distance. The reason for this observation is thought to be the fact that when inter-electrode distance increases, the produced ions move more slowly in the solution. Hence, the voltage and energy consumption increase.[24]

Conclusion

EC is one of the most effective techniques for removing color and organic pollutants from wastewater. In this research, the removal efficiency of EC process by means of aluminum electrodes for decolorization of RG-19 in batch system was studied. The results showed that the highest dye removal efficiency was 99.88%, at the optimized conditions of pH of 11, initial dye concentration of 25 mg/l, voltage of 50 v, electrolysis time of 60 minutes, and electrode

Table 2. Effect of initial dye concentration on removal efficiency and energy consumption

Time	Concentration of dye									
	25 mg/l		50 mg/l		75 mg/l		100 mg/l		150 mg/l	
	RE (%)	E (Kw.h/m³)	RE (%)	E (Kw.h/m³)	RE (%)	E (Kw.h/m³)	RE (%)	E (Kw.h/m³)	RE (%)	E (Kw.h/m³)
10	24.21	1.04	15.40	2.13	36.39	2.64	46.11	2.80	63.45	4.62
20	48.60	2.83	49.14	3.24	53.71	3.84	65.46	4.11	63.75	5.36
30	68.85	4.38	68.69	4.40	80.08	4.46	81.42	5.29	66.89	7.33
40	92.10	5.92	84.91	6.17	98.48	7.33	94.71	6.53	91.77	9.75
50	95.68	7.38	90.44	7.93	99.51	9.06	99.49	9.94	99.50	11.08
60	99.88	10.25	91.66	10.27	99.62	12.41	99.57	11.87	99.56	13.18

RE: Removal; E: Energy Consumption

distance of approximately1 cm. The removal efficiency increased with the increase in inter-electrode distance to 1 cm and KCl concentration to 0.01 M. It can be concluded that the EC process by aluminum electrodes is an efficient method for reactive dye removal from colored solutions.
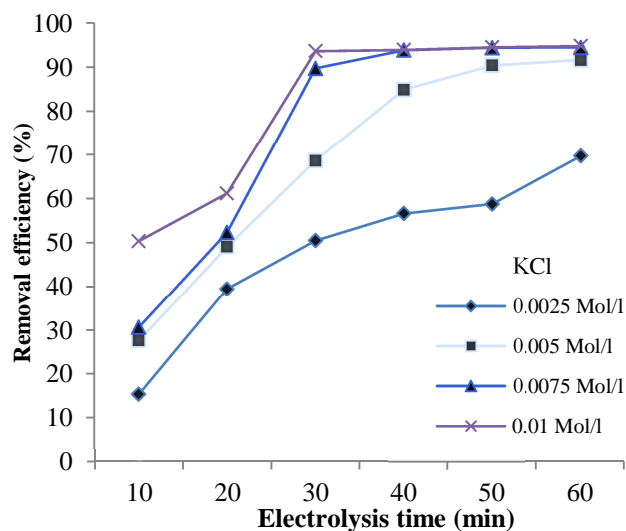

Figure 7. Effect of KCl concentration on the removal efficiency of Reactive Green 19 (RG-19) dye
(Voltage = 50 v, C_0 = 50 mg/l, d = 1 cm, pH =11, T = 22 ± 2 $^\circ$C)

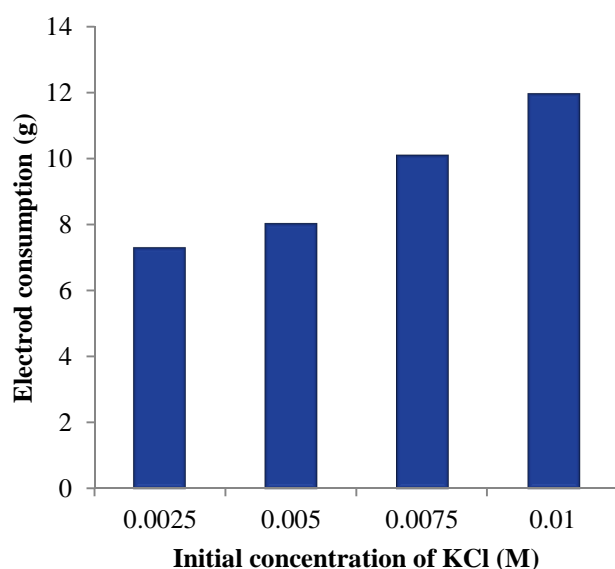**Figure 8. Effect of KCl concentration on electrode consumption**
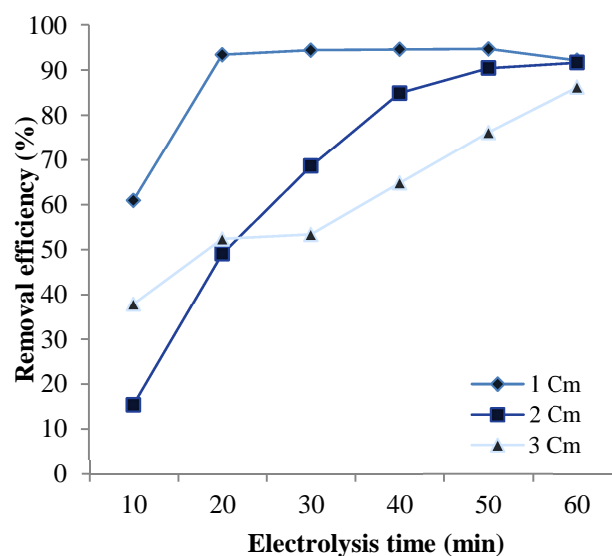(Voltage = 50 v, C_0 = 50 mg/l, d = 1 cm, pH =11, T= 22 ± 2 $^\circ$C)

Figure 9. Effect of distance between electrodes on removal efficiency of Reactive Green 19 (RG-19) dye
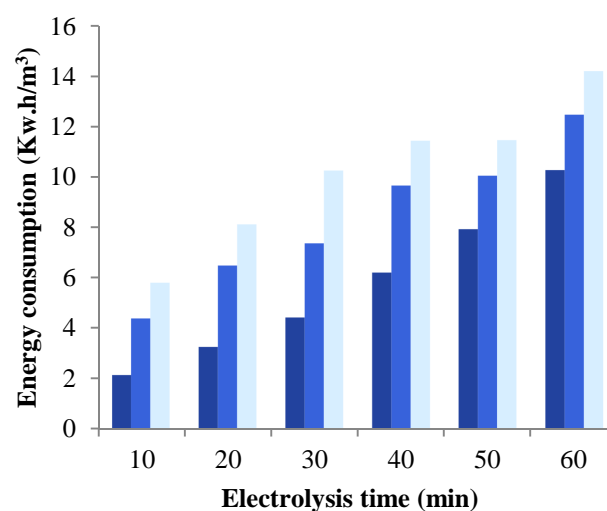(Voltage = 50 v, C_0 = 50 mg/l, KCl = 0.01 M, pH = 11, T = 22 ± 2 $^\circ$C)

Figure 10. Effect of distance between electrodes on energy consumption
(Voltage = 50 v, C_0 = 50 mg/l, KCl = 0.01 M, pH = 11, T = 22 ± 2 $^\circ$C)

Conflict of Interests

Authors have no conflict of interests.

Acknowledgements

References

1. Correia VM, Stephenson T, Judd SJ. Characterisation of textile wastewaters-a review. Environmental Technology 1994; 15(10): 917-29.
2. Daneshvar N, Ashassi-Sorkhabi H, Tizpar A. Decolorization of orange II by electrocoagulation method. Separation and Purification Technology 2003; 31(2): 153-62.
3. Golder AK, Hridaya N, Samanta AN, Ray S. Electrocoagulation of methylene blue and eosin yellowish using mild steel electrodes. J Hazard Mater 2005; 127(1-3): 134-40.
4. Tang WZ, Huren A. UV/TiO2 photocatalytic oxidation of commercial dyes in aqueous solutions. Chemosphere 1995; 31(9): 4157-70.
5. Mollah MYA, Pathak SR, Patil PK, Vayuvegula M, Agrawal TS, Gomes JAG, et al. Treatment of orange II azo-dye by electrocoagulation (EC) technique in a continuous flow cell using sacrificial iron electrodes. Journal of Hazardous Materials 2004; 109(1–3): 165-71.
6. An H, Qian Y, Gu X, Tang WZ. Biological treatment of dye wastewaters using an anaerobic-oxic system. Chemosphere 1996; 33(12): 2533-42.
7. Buitron G, Quezada M, Moreno G. Aerobic degradation of the azo dye acid red 151 in a sequencing batch biofilter. Bioresource Technology 2004; 92(2): 143-9.
8. Lin SH, Peng CF. Treatment of textile wastewater by electrochemical method. Water Research 1994; 28(2): 277-82.
9. Slokar YM, Majcen Le Marechal A. Methods of decoloration of textile wastewaters. Dyes and Pigments 1998; 37(4): 335-56.
10. Nadi H, Alizadeh M, Ahmadabadi M, Yari AR, Hashemi S. Removal of reactive dyes (green, orange, and yellow) from aqueous solutions by peanut shell powder as a natural adsorbent. Arch HygSci 2012; 1(2): 41-7.
11. Low KS, Lee CK. Quaternized rice husk as sorbent for reactive dyes. Technology 1997; 61(2): 121-5.
12. Szpyrkowicz L, Naumczyk J, Zilio-Grandi F. Electrochemical treatment of tannery wastewater using TiPt and Ti/Pt/Ir electrodes. Water Research 1995; 29(2): 517-24.
13. Lin SH, Peng CF. Continuous treatment of textile wastewater by combined coagulation, electrochemical oxidation and activated sludge. Water Research 1996; 30(3): 587-92.
14. Barrera-Diaz C, Urena-Nunez F, Campos E, Palomar-Pardave M, Romero-Romo M. A combined electrochemical-irradiation treatment of highly colored and polluted industrial wastewater. Radiation Physics and Chemistry 2003; 67(5): 657-63.
15. Can OT, Kobya M, Demirbas E, Bayramoglu M. Treatment of the textile wastewater by combined electrocoagulation. Chemosphere 2006; 62(2): 181-7.
16. Bayramoglu M, Eyvaz M, Kobya M. Treatment of the textile wastewater by electrocoagulation: Economical evaluation. Chemical Engineering Journal 2007; 128(2–3): 155-61.
17. Do JS, Chen ML. Decolourization of dye-containing solutions by electrocoagulation. Journal of Applied Electrochemistry 1994; 24(8): 785-90.
18. Ghosh D, Medhi CR, Solanki H, Purkait K. Decolorization of Crystal Violet Solution by Electrocoagulation. Journal of Environmental Protection Science 2008; 2(1): 25-35.
19. Wang CT, Chou WL, Kuo YM. Removal of COD from laundry wastewater by electrocoagulation/electroflotation. J Hazard Mater 2009; 164(1): 81-6.
20. Moreno-Casillas HA, Cocke DL, Gomes JAG, Morkovsky P, Parga JR, Peterson E. Electrocoagulation mechanism for COD removal. Separation and Purification Technology 2007; 56(2): 204-11.
21. Sengil IA, Ozacar M. The decolorization of C.I. Reactive Black 5 in aqueous solution by electrocoagulation using sacrificial iron electrodes. J Hazard Mater 2009; 161(2-3): 1369-76.
22. Basiri Parsa J, Rezaei Vahidian H, Soleymani AR, Abbasi M. Removal of Acid Brown 14 in aqueous media by electrocoagulation: Optimization parameters and minimizing of energy consumption. Desalina 2011; 278(1-3): 295-302.
23. Daneshvar N, Oladegaragoze A, Djafarzadeh N. Decolorization of basic dye solutions by electrocoagulation: an investigation of the effect of operational parameters. J Hazard Mater 2006; 129(1-3): 116-22.
24. Daneshvar N, Khataee AR, Amani Ghadim AR, Rasoulifard MH. Decolorization of C.I. Acid Yellow 23 solution by electrocoagulation process: investigation of operational parameters and evaluation of specific electrical energy consumption (SEEC). J Hazard Mater 2007; 148(3): 566-72.

http://jaehr.muk.ac.ir

The effect of climatic parameters on air pollution in Sanandaj, Iran

Hamzeh Ahmadi[1], Taleb Ahmadi[2], Behzad Shahmoradi[3], Shahab Mohammadi[4], Shadi Kohzadi[5]

1 Department of Climatology, Hakim Sabzevari University, Sabzevar, Iran
2 Department of Architecture and Urban Planning, School of Engineering, University of Kurdistan, Sanandaj, Iran
3 Kurdistan Environmental Health Research Center, Kurdistan University of Medical Sciences, Sanandaj, Iran
4 Department of Environmental Protection, Sanandaj, Iran
5 Department of Environmental Health Engineering, Student Research Committee, Kurdistan University of Medical Sciences, Sanandaj, Iran

Original Article

Abstract

Air pollution is one of the emerging environmental issues of the western cities of Iran. Daily data (2009-2012) on air pollutants in Sanandaj, Iran, were collected from the Department of Environmental Protection, Kurdistan Province, Iran. Climatic parameters were collected from the Kurdistan Meteorological Bureau. The quality of air was assessed based on the air quality index (AQI). The relationship between climatic parameters was analyzed using the Pearson correlation coefficient and multiple regression analysis. AQI indicated that the air quality in Sanandaj is under normal conditions. However, Particulate Matter (PM_{10}) was at medium and critical level, requiring precautionary measures for the health of the elderly and children. The concentration of PM_{10} has increased in recent years during the months of April to June (reached an unhealthy level in the warm days of the year). The highest pollutant concentration (CO and SO_2) was observed during cold days of the year (December to February). The highest concentration of NO_2, NO, O_3, and PM_{10} were observed in summer and spring, whereas the lowest concentrations were observed in cold seasons. The Pearson correlation analysis revealed a significant correlation between air pollutants and climatic parameters. The multiple regression analysis and R^2 analysis showed the influence of climatic factors on pollutant concentration. ANOVA indicated Factors which cause the most significant variability in pollutant concentration are air temperature, relative humidity, and wind speed.

KEYWORDS: Air Pollution, Analysis of Variance, Humidity, Iran, Regression Analysis, Temperature

Introduction

Air quality is strongly dependent on weather and is, therefore, sensitive to climate change.[1] Air pollution in urban areas is often the result of exhaust gases from vehicles, and combustion in industries and for domestic purposes.[2] Anthropogenic air pollutants caused by technological progress, industrialization, and urban overpopulation have led to the deterioration of environmental air quality.[3] Air quality has become an important environmental problem throughout the world because of the dramatic increase in emission of pollutants resulted from the economic and industrial growth in the last century.[4] Today, vehicles are the main cause of air pollution in developing countries such as Iran.[5] Urban air pollution has different characteristics because of the variability of meteorological factors depending on the geographical and topographical peculiarities of the urban area.[6] To understand the influence of the climate on pollution,

Corresponding Author:
Behzad Shahmoradi
Email: bshahmorady@gmail.com

regional and local climatic parameters must be taken into account. Atmospheric visibility degradation is a key issue in climatology and air pollution studies. It exerts adverse effects on human lives, such as on highway crowding and restricted aircraft movements.[7] The concentration of air pollutants varies depending on meteorological factors, the source of pollutants, and the local topography.[8] The air quality index (AQI) is one of the main indices used to show the overall quality of the environment. With the variation in weather, from day to day, the air quality also changes. Urbanization is a spreading phenomenon throughout the world. Urban environments are often characterized by higher mean temperature, concentration of greenhouse gases, and atmospheric pollutants compared with surrounding rural areas.[9] In such areas, human health is affected by air pollution. The most significant air pollutants are nitrogen dioxide, sulfur dioxide, polycyclic aromatic hydrocarbons (PAHs), and particulate matter (PM) including dust, soot, and smoke.[10] The most abundant components of air pollution in urban areas are nitrogen dioxide (NO_2), ozone (O_3), and PM. SO_2 is particularly abundant in industrial areas.[11] Urban air pollution issues are of increasing concern to urban planners and policymakers. Air quality in most urban areas can reach levels high enough to have some health impacts. Initially, urban air pollution was considered as a problem mainly associated with domestic heating and industrial emissions.[12] However, the concentration of air pollutants is not only affected by sources of emission, but also by meteorological variables. Meteorological variables play an important role in the dispersion, transportation, and photochemical reactions of air pollutants, and secondary pollutant formation including O_3 and NO_2.[13]

Venegas and Mazzeo estimated horizontal distributions of CO and NOx background concentrations in Buenos Aires City, Argentina.[12]

Alkasassbeh et al. assessed Particulate Matter (PM_{10}) concentration prediction, and total suspended particles (TSP) using autoregressive artificial neural networks and external input models. They used climatic parameters (temperature, relative humidity, and wind) for model input and developed two autoregressive artificial neural networks with external input models (ANNARX) to provide high performance modeling for PM_{10} and TSP parameters.[10] Stamatelos analyzed data from ambient PM_{10} concentration monitoring in Volos during 2005-2010. The results showed that PM_{10} concentration had a negative correlation with temperature and a positive correlation with relative humidity.[14] Marcazzan et al. considered the characterization of PM_{10} and $PM_{2.5}$ in the ambient air of Milan (Italy). They simulated $PM_{2.5}$ and PM_{10} in September 1997 and 1998 in the city center of Milan. The multivariate analysis of elements, gaseous pollutants, and concentration data led to the identification of four main sources contributing to PM_{10} and $PM_{2.5}$ composition; vehicle exhaust emissions, suspended crustal dust, secondary sulfates, and industrial emissions.[15] Akpinar et al. performed statistical analysis of meteorological factors and air pollution during winter months in Elazig, Turkey.[6] They observed a relationship between pollutant concentrations (SO_2 and TSP) and climatic factors from October to March 2003 to 2005. They found a medium and weak relationship between pollutant concentrations and meteorological factors in Elazig.[6]

Iran is one of the top ten disastrous countries in the world and it will soon become one of the most polluted countries in the world. According to the World Health Organization (WHO) report in 2013, Sanandaj, Iran, was the most polluted city regarding PM_{10} concentration. Hence, this research was performed with the aim to identify and evaluate Sanandaj City air pollution for six major pollutants (SO_2, CO, NO_2, NO, O_3, and PM_{10}) and establish its relationship with climatic parameters (temperature, precipitation, relative humidity, frost days, and wind speed).

Materials and Methods

Sanandaj City, Kurdistan Province, Iran, is located on the geographic coordinates of 35°20' north latitude and 47°18' east longitude of the prime meridian (Figure 1). Height average of Sanandaj is 1535 m above sea level (the lowest and highest points are 600 and 2550 m, respectively). The city has a semi-arid Mediterranean climate.

This was a statistical-analytical research. Daily, monthly, and annual (from 2009 to 2012) data on climatic parameters (minimum temperature, maximum temperature, daily temperature (T °C), precipitation (mm), relative humidity (RH%), wind speed (Knot), and frost days of Sanandaj) were collected from the Kurdistan Meteorological Bureau. Then, the air quality data on pollutants (SO_2, CO, NO, NO_2, O_3, and PM_{10}) collected from the Kurdistan Environmental Protection Agency were adjusted for the same period. The Pearson correlation and multiple regression analysis were used to find and interpret the relationship between pollutants and meteorological parameters. Moreover, AQI was used to assess the air quality.

Results and Discussion

Climatic conditions

Sanandaj has a Mediterranean climate (Figure 2). Most of the total precipitation occurs between November and May, and the dry period is from June to October. The maximum, minimum, and daily mean temperature recorded for Sanandaj City is shown in figure 3. As figure 3 indicates, the coldest (-4.6 °C) and warmest (38 °C) months are January and June, respectively. Climatic parameters, such as relative humidity, wind speed, and frost days, are crucial factors in dispersing air pollutants. Figure 4 shows that the highest amount of relative humidity and frost days are observed in the winter (late December to late February), whereas the highest wind speed of the area occurs in spring to late summer. In fact, from late winter, wind speed increases due to the change of season and gradual increase in heat.
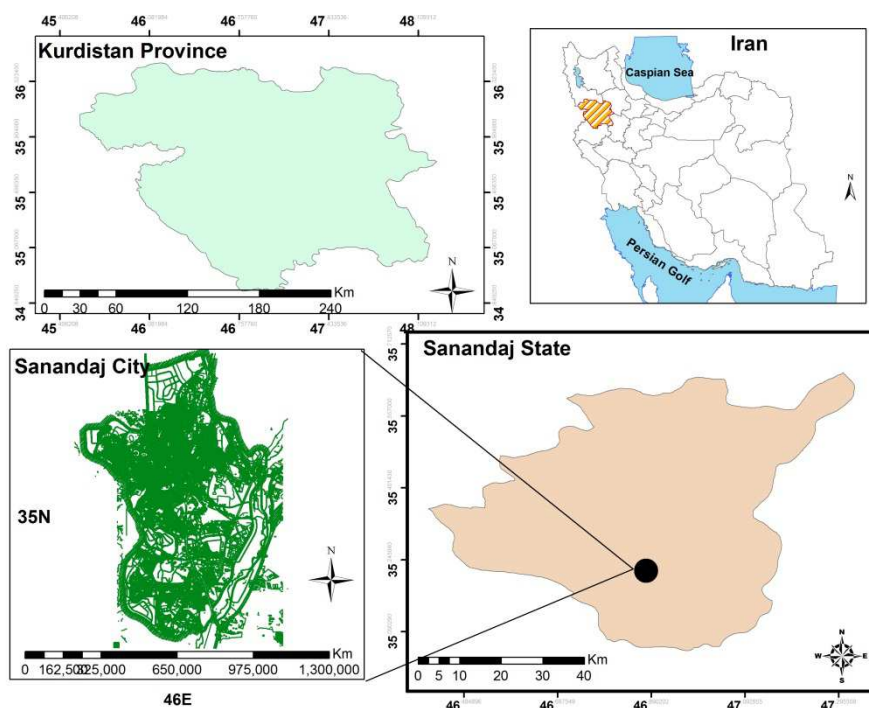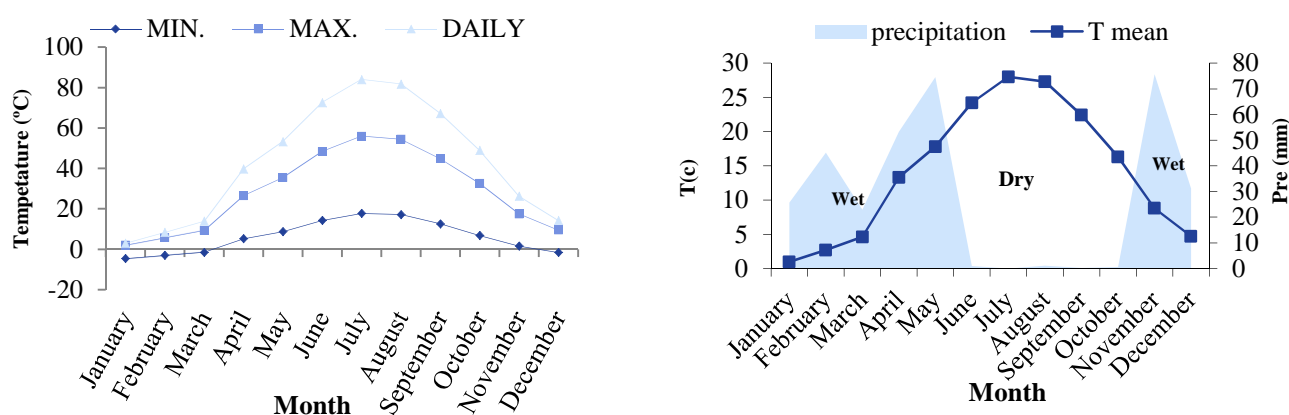

Figure 1. Geographical location of Sanandaj City

Figure 2. Climatic diagram of Sanandaj for 2009-2012

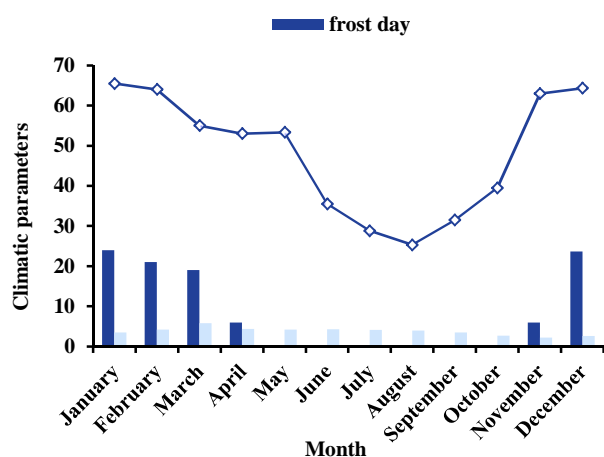T mean: mean daily air temperature; pre: monthly total precipitation

Figure 3. The mean frost days, humidity (%), and wind speed (m/s) in Sanandaj City from 2009 to 2012

Pollutant concentration

The monthly and seasonal, and diurnal concentrations of SO_2, NO, NO_2, CO, O_3, and PM_{10} during the period of the study are represented graphically in figure 4 and figure 5, respectively. The monthly variation of pollutants shows that CO and SO_2 have reached their maximum amount during December to February and NO, NO_2, and O_3 during June to August. The two main maximum concentrations of PM_{10} were observed during April to May and in July. The seasonal variation of pollutants shows that CO and SO_2 reached their maximum amount in winter, NO, NO_2, and O_3 in summer, and PM_{10} in spring.

Akpinar et al. reported that the highest concentration of SO_2 was observed during January-February, which are the coldest months of the year in Elaziğ City, Turkey.[6] Al-Awadhi observed that Kuwait experienced higher concentration of NO and SO_2 during winter, while higher O_3 values were recorded in summer.[16] In another study conducted in Daegu, Korea, Jo and Park reported that the maximum levels of CO and SO_2 were obtained in cold seasons, while NO_2 and O_3 had the highest level during warm seasons.[17] Moreover, AL-Jeelani showed that low values of O_3 and NO_2 appear in late autumn and winter (colder periods), while the high values appeared in late spring, summer, and early autumn (warmer periods).[3]

The high level of some pollutants during cold seasons can be attributed to the increased consumption of fuels caused by heat sources and vehicles along with meteorological conditions such as increased atmospheric pressure, air stability, and temperature inversion. Moreover, the seasonal maximum heat season could be contributed to the gradually increasing ground surface temperature, and decreasing precipitation and relative humidity. One of the main factors of an increase in ozone during spring and summer is

the increase of photochemical reactions, and thus, ozone production. Factors effective on the high level of PM_{10} during summer might be air dryness, and increase in temperature and wind speed during this season.[18]

There is no heavy industry in Sanandaj or its neighboring areas. However, these high concentrations of pollutants could be attributed to the high number of old model vehicles, low quality petrol, and tendency to use private cars instead of public transportation.

Because of the importance of PM_{10} in the study area, the AQI was calculated for this pollutant based on daily data from 2012. Although mathematical equations could be used to convert air pollutant concentration into AQI values, many websites are available online which convert pollutant concentrations into AQI values.[19,20] As table 1 indicates, citizens of Sanandaj City and its surrounding areas experienced different concentrations of PM_{10} for 240 days, 38 days of which, the concentration exceeded 950 µg/m³ (very dangerous class).

It was found that the frequency and occurrence of sand and dust storms has continuously and drastically increased in the last decade in Iraq. Hence, the high concentration of PM_{10} could be attributed to the uncontrolled formation and occurrence of dust phenomenon in neighborhood countries like Iraq (Figure 6).[21]
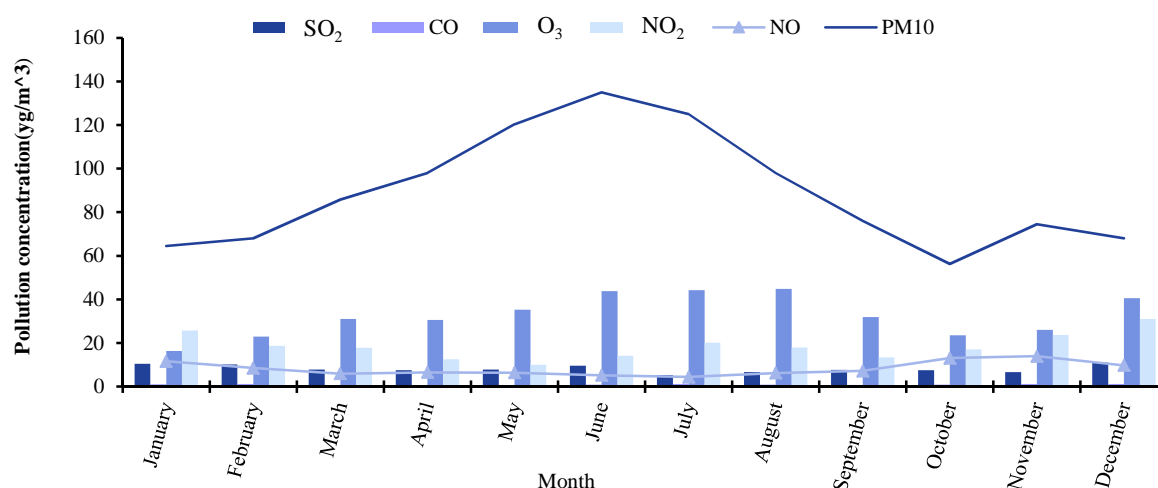

Figure 4. The mean monthly concentration of pollutants in Sanandaj City from 2009 to 2012
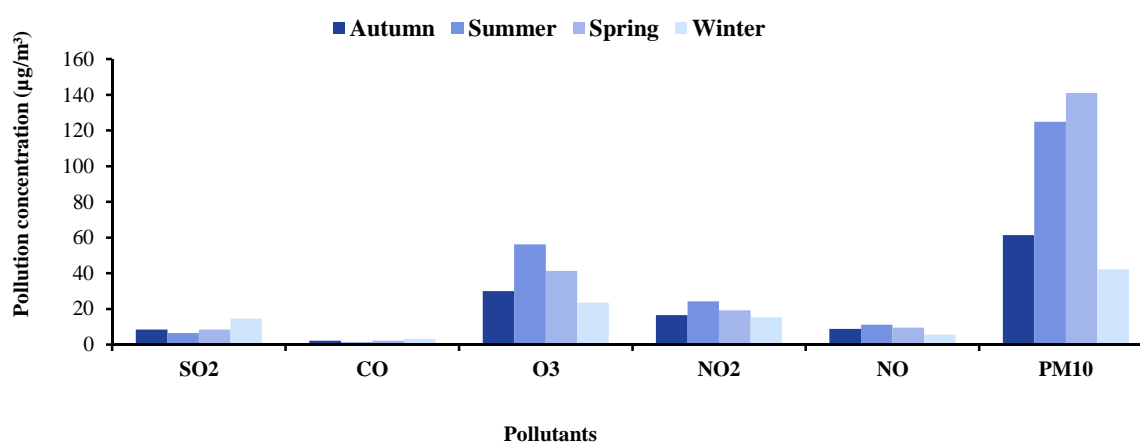

Figure 5. The mean seasonal concentration of pollutants in Sanandaj City from 2009 to 2012

Influence of climatic parameters on pollutant concentration

Climatic parameters have direct effect on dispersion or accumulation of pollutants. The minimum temperature during the cold period of the year caused increasing CO and SO_2 concentrations, while the concentrations of NO, NO_2, O_3, and PM_{10} decreased (Figure 7). On the other hand, gradually increasing temperature during warm days of the year caused a decrease in CO and SO_2 concentrations and increase in O_3, NO, NO_2, and PM_{10} (Figure 8). Decrease in relative humidity during the year caused an increase in pollutant concentration. There is a reverse relationship between CO, SO_2, O_3, NO, and NO_2, and increase in wind speed. The latter resulted in the decreasing of pollutant concentration because of air turbulence on

ground surface with high atmospheric levels.

However, a direct relationship was observed between wind speed and PM_{10}. Similar findings have been reported in literature.[23,24]

AQI

Table 2 shows the results of AQI for pollutants during 2009-2012 at Sanandaj station. Except for PM_{10}, all pollutants were within good level (green color), indicating compliance with standards and no need for cautionary instruction. PM_{10} may be the only cause for concern in the city. Its elevated values could be attributed directly to natural dust fallout, which is a natural common phenomenon in Sanandaj, especially in the summer. Al-Awadhi reported that except for PM_{10}, the yearly average AQI of SO_2, NO_2, CO, and O_3 concentrations were within the category of good and moderate in Kuwait.[16]

Table 1. Diurnal concentration and classification of PM_{10} ($\mu g/m^3$) based on air quality index (AQI) in 2012

PM_{10} Concentration Class	50-100 ($\mu g/m^3$)	100-150 ($\mu g/m^3$)	150-200 ($\mu g/m^3$)	200-400 ($\mu g/m^3$)	> 400 ($\mu g/m^3$)
Number of days	158.00	51	12.0	10.0	16
Mean concentration	91.76	140	162.7	265.2	951
Time distribution	April to May	May to June	April to June	May to June	May to July
AQI	68 (Moderate)	93 (Moderate)	104 (Unhealthy for sensitive groups)	155 unhealthy	> 605[*] (out of range)

[*] The maximum calculable PM_{10} concentration to AQI is $\mu g/m^3$; hence, the authors considered values greater than this value as very hazardous; AQI: Air quality index

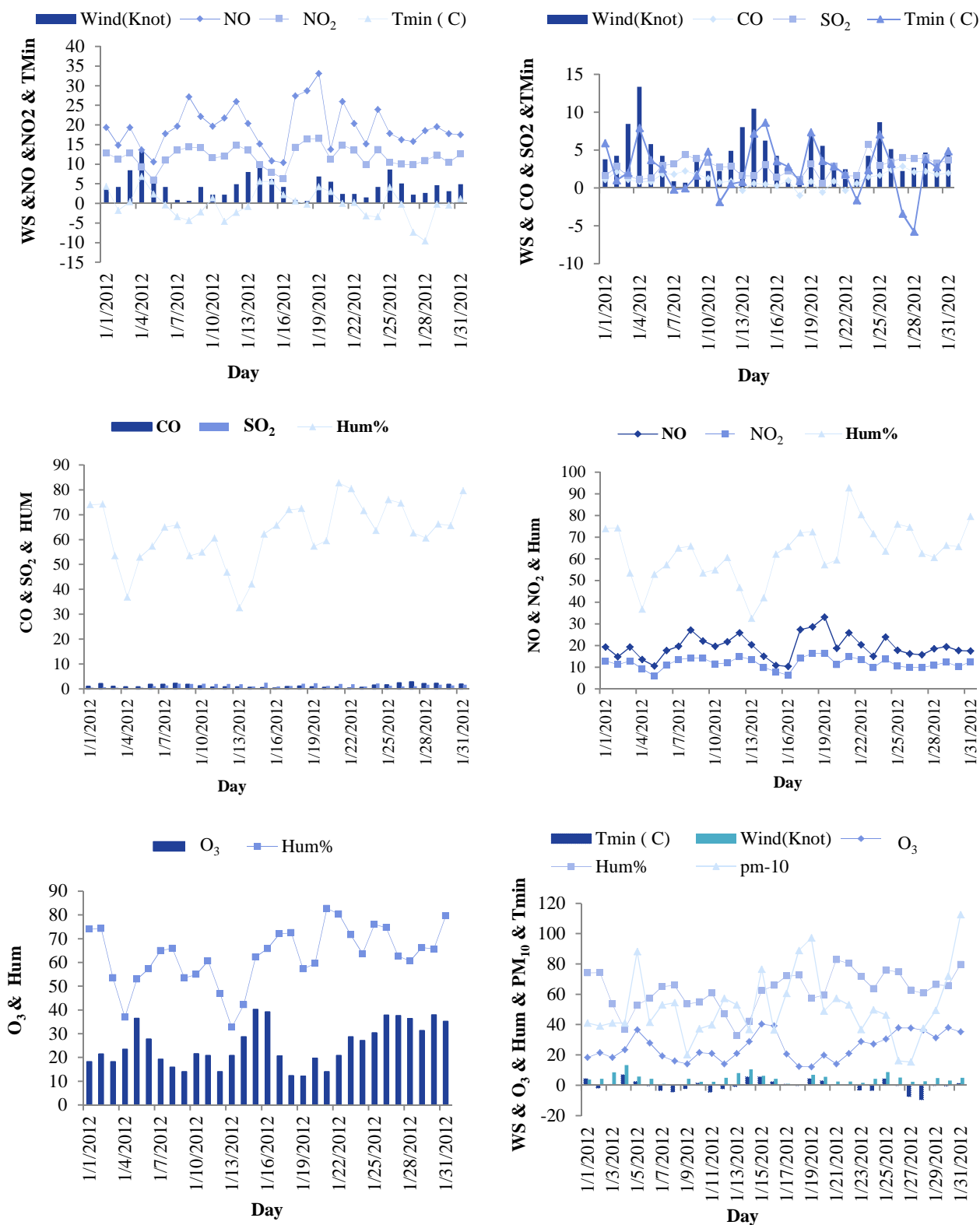**Figure 6. Satellite image of dust phenomenon in Western Iran[22]**

Figure 7. Relationship between pollutant concentration and climatic parameters during cold days
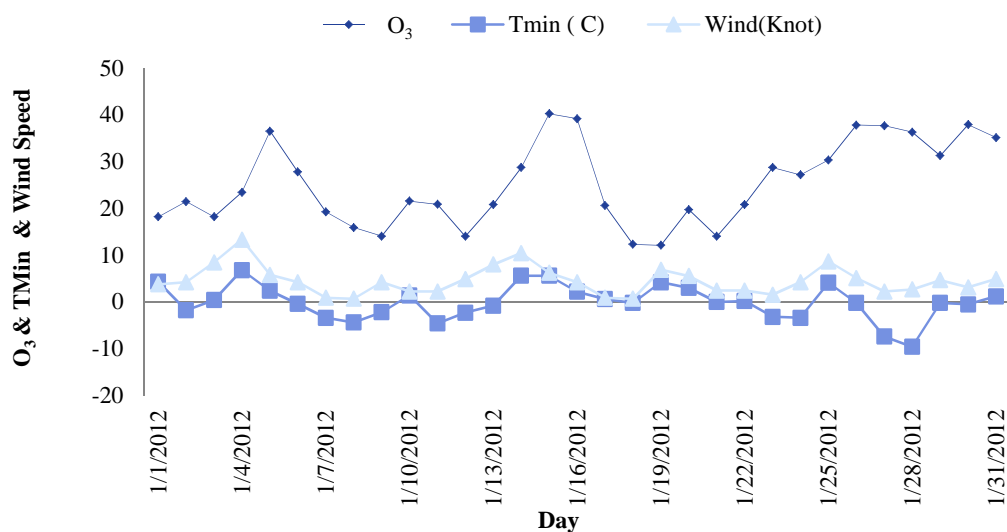
Figure 7. Relationship between pollutant concentration and climatic parameters during cold days (continue)
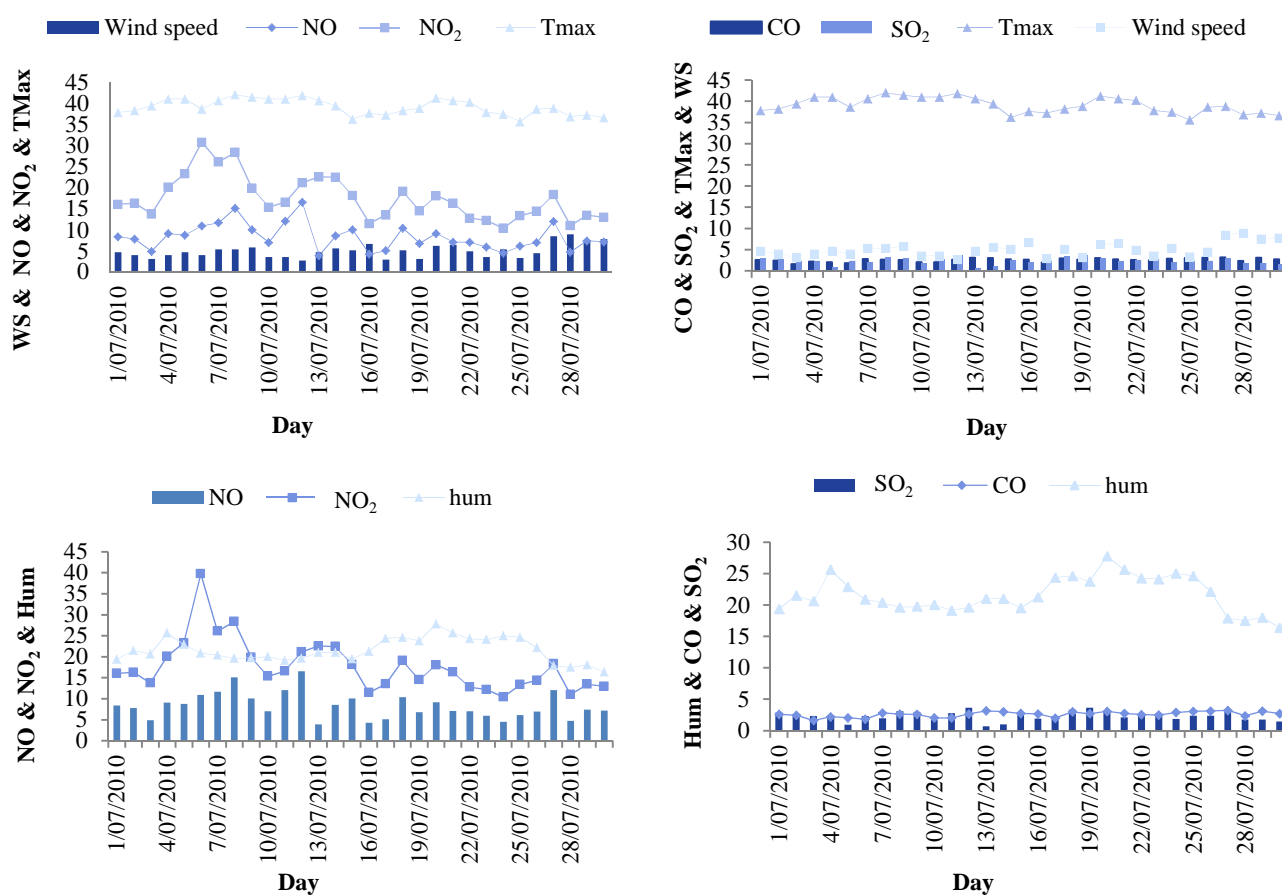

Figure 8. Relationship between pollutant concentration and climatic parameters during warm days
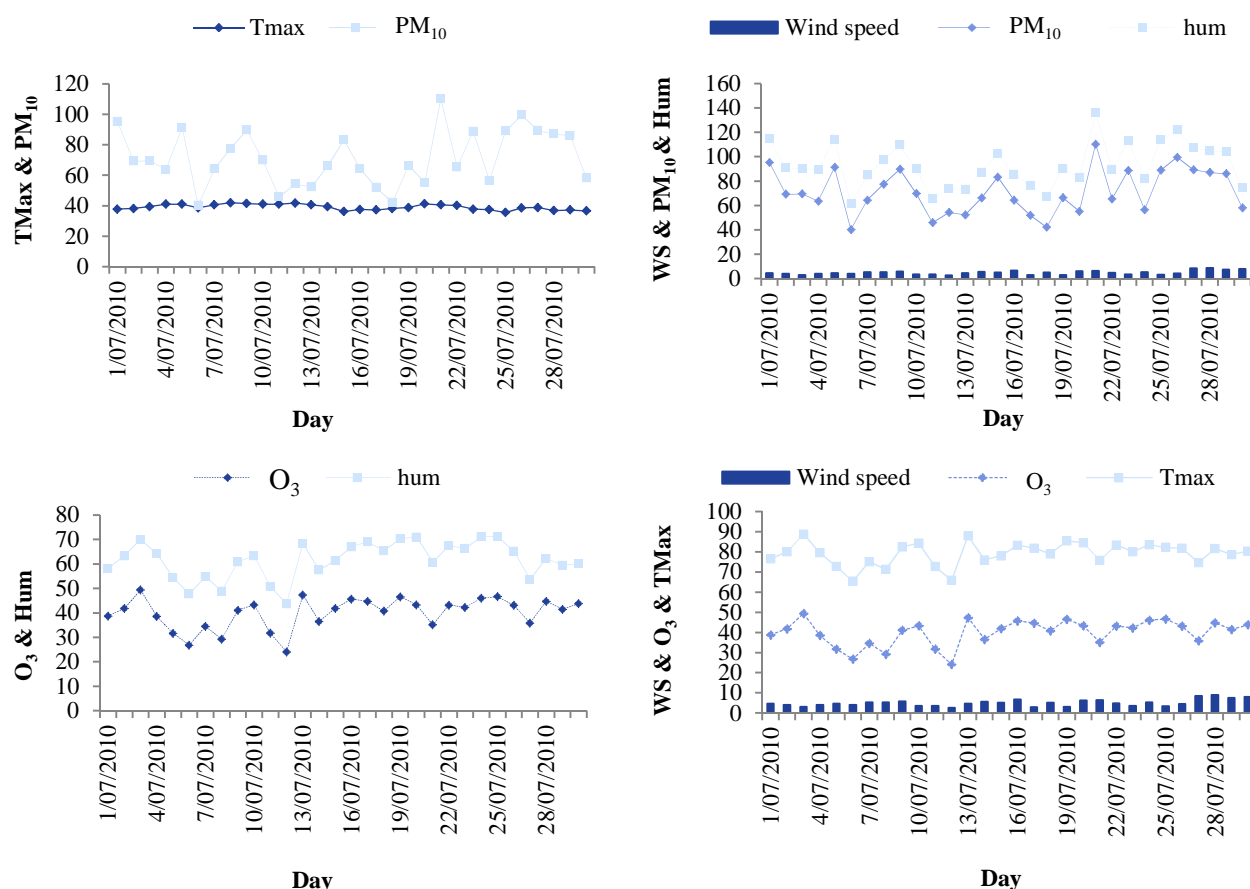
Figure 8. Relationship between pollutant concentration and climatic parameters during warm days (continue)

Data Analysis

Correlation Analysis

The relationships between air pollutant concentrations and meteorological indicators were analyzed based on the Pearson correlation coefficient (Table 3). The results showed that there is a significant relationship between climatic parameters and pollutant concentration. T_{min} had direct relationship with CO ($r = 0.66$, $P < 0.05$) and SO_2 concentrations ($r = 0.75$, $P < 0.05$). Nevertheless, it had a reverse relationship with O_3, NO_2, NO, and PM_{10} concentrations ($r = -0.55$, $P < 0.01$). Moreover, with increasing temperature, the concentration of PM_{10}, NO_2, NO, and O_3 also increased. Relative humidity showed negative and reverse relationship with most of the pollutants, especially PM_{10} ($r = -0.96$, $P < 0.01$). Wind speed had a controlling effect on pollutant dispersion (for example, in the case of NO, $r = -0.77$ and $P < 0.01$). The exception was PM_{10}, which could be attributed to the transferring and dispersing property of the wind. Precipitation, as an important climatic parameter, plays an effective role in this respect. There is a reverse relationship between precipitation and concentration of CO ($r = -0.68$, $P < 0.05$), SO_2 ($r = -0.88$, $P < 0.01$), O_3 ($r = -0.71$, $P < 0.05$), NO ($r = -0.67$, $P < 0.05$), NO_2 ($r = -0.69$, $P < 0.05$), and PM_{10} ($r = -0.97$, $P < 0.01$). Precipitation is a pollution reducer. As it is expected to have clean air during precipitation, data analysis also revealed that precipitation has a reverse relationship with pollutant concentration.

ANOVA Analysis

The relationship between climatic parameters and

pollutant concentration was analyzed using multiple regression technique. Pollutant concentration and climatic parameters were used in regression techniques as a dependent variable and independent variables, respectively. The results of regression analysis are presented in table 4. The research found a significant relationship (P< 0.05) between air pollutant concentration and climatic parameters; the highest relationship with O_3 (r = 80, P < 0.05) and the lowest relationship with PM_{10} (r = 68, P < 0.05). Therefore, there is a significant relationship between climatic parameters and pollutant concentration.

The coefficient of determination (R^2, from 0.46 to 0.87%) between different factors indicates that the highest amount of pollutant concentration is directly influenced by climatic conditions in different days of the year. The lowest R^2 (0.46) is related to PM_{10}, whereas, the highest (R^2 = 0.78%) is related to O_3, followed by CO, and NO_2. The lower R^2 in PM_{10} reveals that particulate matters in the air of the study area originated from another area such as Iraq that is an external source. Therefore, climatic condition has the lowest role in this regard.

Generally, the results showed that there is a significant relationship and correlation between climatic parameters and pollutant concentration (SO_2, CO, O_3, NO_2, NO, and PM_{10}). Temperature and wind speed are the parameters which have a role in relative increasing of pollutant concentration, but precipitation and relative humidity are effective on decreasing of pollutant concentration (Table 4).

It should be noted that R^2 represents the fraction of the variance in air pollution levels due to the variability of the correlated meteorological parameters. Multiple regression analysis confirmed that meteorological parameters are important for pollutant concentration. Hence, it can be concluded that meteorology plays an important role on pollutant concentration. Temperature, relative humidity, and wind speed seem to be the most important parameters influencing the behavior of air pollutants.

Elminir found that temperature changes did not significantly influence SO_2 concentration, but relative humidity was the most important meteorological parameter influencing the behavior of air pollutants.[25]

Table 2. Air quality index (AQI) for different pollutants in Sanandaj City during 2009-2012

PM_{10}	NO	NO_2	O_3	CO	SO_2	Year
Unhealthy(Orange)	Good (green)	Good (green)	Good (green)	Good (green)	Good (green)	2009
Unhealthy (Orange)	Good (green)	Good (green)	Good (green)	Good (green)	Good (green)	2010
Critica l(Red)	Good (green)	Good (green)	Good (green)	Good (green)	Good (green)	2012

Table 3. Pearson correlation analysis for climatic parameters and pollutant concentration

	CO (ppm)	O_3 (ppm)	SO_2 (ppm)	NO_2 (ppm)	NO (ppm)	PM_{10} ($\mu g\ m^{-3}$)
Min T (°C)	0.75*	-0.6*	0.66*	-0.50	-0.52	-0.54
Max T (°C)	-0.48	0.71**	-0.51	0.59	0.6*	0.87**
Relative humidity (%)	0.62	-0.61*	-0.79**	-0.66*	-0.62*	-0.96**
Wind speed (knot)	-0.77**	-0.56	-0.59	-0.68*	-0.77**	0.68*
Rainfall (mm)	-0.68*	-0.71*	-0.88**	-0.69*	-0.67*	-0.97**

* Correlation is significant at the 0.05 level (2-tailed); ** Correlation is significant at the 0.01 level (2-tailed); PM_{10}: Particulate Matter

Table 4. ANOVA for pollutants and meteorological parameters

Pollutant	Coefficients					
	R^2	Regression square sum	df	F	T	P
SO_2	0.67	676.171	6	6.39	T_{min} = 1.8 Frost day = 1.18 Wind speed = 3.2 Precipitation = -2.8	< 0.05
CO	0.77	333.910	6	3.82	Relative humidity = - 2.32 T_{min} = 3.2	
O_3	0.78	757.232	6	5.97	T_{max} 2.3 T_{min} 0.96 Rh = -2.23 Precipitation = -1.6	
NO_2	0.77	303.967	6	3.80	T_{max} = 4.2 Min T = 2.1 Precipitation = -1.9	
NO	0.63	619.390	6	4.43	Frost day = -1.7 T_{max} = 2.3 Wind speed -2.1	
PM_{10}	0.46	1037.098	6	4.71	T_{max} = 2.2 Relative humidity = -2.23 Precipitation = -1.6	

df: Degree of freedom

Grinn-Gofron et al. reported contrary results; they found close relationship between SO_2 concentrations and meteorological conditions in Poland.[26] However, Carreras and Pignata found no relationship between climatic parameters and pollutant concentration in the Cordoba region, Argentina.[27]

The trend of urbanization in Sanandaj has been increasing during the last decade; many new suburban areas have been built by scaling down free areas surrounding the city. With the continuous and rapid urbanization process, more people become exposed to high levels of air pollution. Sanandaj has a natural hole-like structure surrounded by mountains. The main platform of the city is located on semi-flat lands and there is height difference among the city areas. Hence, natural conditions and city environmental constraints are the potential barriers for pollutant dispersion and the created inversion heightens this issue in the city.

Conclusion

This research considered the daily, monthly, and seasonal variations of pollutants in Sanandaj, and assessed the relationship between climatic parameters and pollutant concentration using the Pearson correlation and regression analysis. To indicate healthy days, the AQI was determined. It was observed that, during very cold days, the concentrations of CO and SO_2 were higher compared with other pollutants. However, during the warm days of July with the highest temperature, the concentrations of NO, NO_2, O_3, and PM_{10} were high. The monthly variations of pollutants showed that the maximum concentrations of CO and SO_2 were observed during December-February and that of NO, NO_2, and O_3 during June-August. Nevertheless, the maximum concentration of PM_{10} was observed during April-May. NO, NO_2, O_3, and PM_{10} reached their maximum concentration in the summer. Maximum and minimum temperatures have an effective role in increasing pollutant concentration during the year. However, relative humidity causes a reduction in pollutant concentration. Except for PM_{10}, wind speed reduced the concentration of other studied pollutants. In

recent years, PM_{10} has become one of the most dominant pollutants of the area, with its highest concentration in April, May, and June. It is affected by the Arabic dust phenomenon from the deserts of neighboring countries in Western Iran. The Pearson correlation analysis indicated a significant correlation between air pollutants and climatic parameters. Results from AQI determination showed that pollutant concentrations, except PM_{10}, were within good (green color) level, indicating compliance with standards and no need for cautionary instruction. R^2 showed that climatic parameters play an important role in pollutant concentration. The multiple regression analysis indicated the influence of climatic factors on pollutant concentration. ANOVA analysis revealed that variables with the most significant effect on pollutant concentration were air temperature, relative humidity, and wind speed. There is no heavy industry in Sanandaj or its surrounding areas. However, traffic was observed as the main source of high concentrations of pollutants. Air pollution has very negative impacts on society; thus, the survey of climatic parameters and pollutant concentration may help the government to adopt necessary preventive measures to ensure better living conditions.

Conflict of Interests

Authors have no conflict of interests.

References

1. Jacob DJ, Winner DA. Effect of climate change on air quality. Atmospheric Environment 2009; 43(1):51-63.
2. Banan N, Talib Latif M, Juneng L. An Assessment of Ozone Levels in Typical Urban Areas in the Malaysian Peninsular. International Journal of Environmental, Ecological, Geological and Geophysical Engineering 2013; 7(2): 60-4.
3. Al-Jeelani HA. Diurnal and Seasonal Variations of Surface Ozone and Its Precursors in the Atmosphere of Yanbu, Saudi Arabia. Journal of Environmental Protection 2014; 5: 408-22.
4. Sportisse B. Fundamentals in Air Pollution: From Processes to Modelling. Berlin, Germany: Springer Science & Business Media; 2009.
5. Yousefi Kebria D, Darvishi G, Haghighi F. Estimation of Air Pollution in Urban Streets by Modeling of PM10, O3 and CO Pollutants according to Regression Method (Case study-Yadegar and Azadi streets intersection, Tehran, Iran). Research Journal of Recent Sciences 2013; 2(4): 36-45.
6. Akpinar E, Akpinar S, Oztop H. Statistical analysis of meteorological factors and air pollution at winter months in Elazig, Turkey. Ebru, Sinan, Hakan. Journal of Urban and Environmental Engineering 2009; 3(1): 7-16.
7. Mansouri B, Hoshyari E, Mansouri A. Study on ambient concentrations of air quality parameters (O3, SO2, CO and PM10) in different months in Shiraz city, Iran. International Journal of Environmental Sciences 2011; 1(7): 1440-7.
8. Dominick D, Juahir H, Latif MT, Zain SM, Aris AZ. Spatial assessment of air quality patterns in Malaysia using multivariate analysis. Atmospheric Environment 2012; 60(0): 172-81.
9. Paoletti E, Bardelli T, Giovannini G, Pecchioli L. Air quality impact of an urban park over time. Procedia Environmental Sciences 2011; 4(0): 10-6.
10. Alkasassbeh M, Sheta AF, Faris H, Turabieh H. Prediction of PM10 and TSP Air Pollution Parameters Using Artificial Neural Network Autoregressive, External Input Models: A Case Study in Salt, Jordan. Middle-East Journal of Scientific Research 2013; 14(7): 999-1009.
11. D'Amato G, Cecchi L, D'Amato M, Annesi-Maesano I. Climate change and respiratory diseases. Eur Respir Rev 2014; 23(132): 161-9.
12. Venegas LE, Mazzeo NA. Modelling of urban background pollution in Buenos Aires City (Argentina). Environmental Modelling & Software 2006; 21(4): 577-86.
13. Habeebullah TM. An investigation of the effects of meteorology on air pollution in makkah. Ass Univ Bull Environ Res 2013; 16(1): 63-85.
14. Stamatelos ZO. Analysis of Data From Ambient PM10 Concentration Monitoring in Volos in the Period 2005-2010 . American Journal of Environmental Engineering 2012; 2(4): 97-108.
15. Marcazzan GM, Vaccaro S, Valli G, Vecchi R.

Characterisation of PM10 and PM2.5 particulate matter in the ambient air of Milan (Italy). Atmospheric Environment 2001; 35(27): 4639-50.

16. Al-Awadhi J. Measurement of Air Pollution in Kuwait City Using Passive Samplers. Atmospheric and Climate Sciences 2014; 4(2): 253-71.

17. Jo WK, Park JH. Characteristics of roadside air pollution in Korean metropolitan city (Daegu) over last 5 to 6 years: temporal variations, standard exceedances, and dependence on meteorological conditions. Chemosphere 2005; 59(11): 1557-73.

18. Shariepour Z. Seasonal and daily variation of air pollutants and their relation to meteorological parameters. Journal of the Earth and Space Physics 2009; 35(2): 119-37. [In Persian].

19. North Carolina Department of Environment and Natural resources. Division of Air Quality [Online]. [cited 2008 Jun 8]; Available from: URL: http://daq.state.nc.us/airaware/forecast/pm_codecalc.shtml

20. US EPA Scale convertor. AQI calculator [Online]. [cited 2015 Feb 02]; Available from: URL: http://aqicn.org/calculator

21. Sissakian V, Al-Ansari NS. Sand and dust storm events in Iraq. Natural Science ed. 2015.

22. Earth System Research Laboratory. PSD Map Room Climate Products [Online]. [cited 2015 May 22]; Available from: URL: http://www.esrl.noaa.gov/psd/map/clim/gsdm.composites.shtml

23. Cuhadaroglu B, Demirci E. Influence of some meteorological factors on air pollution in Trabzon city. Energy and Buildings 1997; 25(3): 179-84.

24. Duenas C, Fernandez MC, Canete S, Carretero J, Liger E. Assessment of ozone variations and meteorological effects in an urban area in the Mediterranean Coast. Sci Total Environ 2002; 299(1-3): 97-113.

25. Elminir HK. Dependence of urban air pollutants on meteorology. Sci Total Environ 2005; 350(1-3): 225-37.

26. Grinn-Gofron A, Strzelczak A, Wolski T. The relationships between air pollutants, meteorological parameters and concentration of airborne fungal spores. Environ Pollut 2011; 159(2): 602-8.

27. Carreras HA, Pignata ML. Comparison among air pollutants, meteorological conditions and some chemical parameters in the transplanted lichen Usnea amblyoclada. Environ Pollut 2001; 111(1): 45-52.

Optimization of temperature and supporting electrolyte for ammonium removal using bioelectrochemical systems

Hooshyar Hossini[1], Abbas Rezaee[1], Bita Ayati[2], Amir Hossein Mahvi[3], Reza Barati Roshvanlou[1]

1 Department of Environmental Health, School of Medical Sciences, Tarbiat Modares University, Tehran, Iran
2 Department of Environmental Engineering, School of Civil and Environmental Engineering, Tarbiat Modares University, Tehran, Iran
3 Center for Solid Waste Research, Institute for Environmental Research, Tehran AND School of Public Health, Tehran University of Medical Sciences, Tehran, Iran

Original Article

Abstract

High concentrations of ammonium in drinking water can cause many diseases and environmental problems such as eutrophication. Therefore, high-performance and eco-friendly methods for purification are of great importance and must be considered. Recently, bioelectrochemical systems have been successfully applied for the removal of many pollutants from water and wastewater. In the present work, ammonium was treated using the bioelectrochemical process. The two effective factors of temperature and supporting electrolyte dose were optimized using response surface methodology (RSM). The optimal conditions were electrolyte dosage of 250 mg/l and temperature of 26.5 °C. Under optimized conditions, the maximum ammonia removal percentage was 99.6%. Analysis of variance indicated a reasonable correlation coefficient (R^2) between the predicted and actual values. R^2 (0.8913), adjusted R^2 (0.8137), and coefficient of variation (8.32 %) were calculated based on statistical analysis. The results indicate that the bioelectrochemical process is the most useful and effective method for the removal of ammonium from wastewater.

KEYWORDS: Ammonium Treatment, Waste Water, Bioelctrochemical, Response Surface Methodology

Introduction

Ammoniacal nitrogen is an essential element for living organisms, but it can contribute to dissolved oxygen depletion, accelerated eutrophication of lakes and rivers, and fish toxicity in water bodies.[1,2] High concentrations of ammonia have been reported in the wastewater of various industries such as coke plant, landfill leachate, textile, and tannery, and municipal and domestic wastewater, urban water run-off, and agriculture drainage.[3,4] The commonly used processes for nitrogen removal are biological process, chemical treatment, ion exchange, and ammonia volatilization by air stripping.[5] Among treatment methods, biological processes are more sustainable approaches due to their lower impact on the surrounding environment and lower cost compared to other physical and chemical processes.[6] The combination of biological processes and electrochemistry in a bioelectrochemical system is a novel approach to the treatment of various contaminants and

Corresponding Author:
Abbas Rezaee
Email: rezaee@modares.ac.ir

pollutants of water and wastewater. The bioelectrochemical system is composed of an electrochemical reactor and microorganism agents (biocatalyst) that are placed on the electrode surface. In recent years, this process has been widely applied for the removal of many pollutants such as organic carbon, metal, and nutrient compounds.[7-13] The 2 most common bioelectrochemical systems are the microbial fuel cell (MFC) and the microbial electrolysis cell (MEC). In the MFC, energy can be obtained, but in the MEC, electrical energy must be supplied using a power supply.[14] Among nutrient compounds, the treatment of nitrogen compounds (ammonia/ammonium, nitrite, and nitrate) are considered in the present work. Depending on treatment goals, many successful studies have been reported on bioelectrochemical systems' removal of nitrogen compounds from water and wastewater. For example, using a MFC reactor, Xie et al. were successfully able to remove about 97.4% ammonium from synthetic wastewater.[15] In a similar study that was performed by Yan et al., simultaneous nitrification and denitrification without extra energy input was reported.[16] In this case, more than 96.8% ammonia removal was reported.[16]

Various statistical experimental design techniques have been proposed in the optimization of experimental studies. In recent years, response surface methodology (RSM) has been applied successfully in many scientific fields such as chemistry, biology, medicine, and economy.[17] It was originally developed in the 1950s.[18] RSM is based on the experimental design with the final goal of evaluating optimal functioning of industrial facilities using minimum experimental effort.[17] RSM was described by Wilson as an experimental approach to identifying the optimum conditions for a multivariable system using minimum experimental samples.[18] Nitrifying bacteria are sensitive to temperature which is a key influential parameter in ammonium removal rates in bioreactor systems.[19] On the other hand, the

amount of salt or supporting electrolyte dose can affect the electrochemical/bioelectrochemical reaction progress. However, in the present study, the 2 factors of temperature and supporting electrolyte dose were optimized using RSM.

Materials and Methods

All chemicals used in this study were analytical reagent grade and were used without further purification. An aqueous stock solution of ammonia (from NH_4Cl salt) was prepared in deionized distilled water. Different concentrations of ammonia were obtained by diluting the stock solution.

Inoculum mass for growth and enrichment of denitrifying bacteria was collected from the Shahrak Gharb Wastewater Treatment Plant, Tehran, Iran. The sludge was added to a 1 l flask containing synthetic wastewater. For enrichment, synthetic wastewater was prepared by dissolving (in terms of g/l) 0.3 KH_2PO_4, 1 $Na_2HPO_4.12H_2O$, 0.1-0.5 NaCl, 0.1 $MgSO_4.7H_2O$, and 0.1-0.4 NH_4Cl. $NaHCO_3$. NH_4Cl was added into the reactor to achieve a carbon/nitrogen ratio of equal to 2:1. In order to supply the required oxygen, an aerator with constant flow rate (0.9 l/minute) was used. During this period, nitrifying bacteria were enriched and used in the bioelectrochemistry reactor.[20]

A 2 l glass vessel (with effective volume of 1.8 l) was utilized for bioelectrochemical nitrification. The schematic of bioelectrochemical cell (BEC) system with its related parts is illustrated in figure 1. The anode and cathode were placed vertically at a fixed distance of 5.5 cm without any separated membrane. A DC power supply (TEK-8051, 30 V, and 5 A double) was set for startup process. Flow rate and hydraulic retention time (HRT) were maintained at approximately 0.9 l/minute and 24 hours, respectively. Batch bioelectrochemical nitrification system (BNS) was operated for 3 weeks and ammonia concentration was determined daily. Growth medium was inoculated to reactor with a mixed liquor suspended solids (MLSS) of about 3000 mg/l. Startup was operated using an electric current of 5 mA/cm^2 and ammonium

concentration of 38.88 mg-N/l (50 mg-NH_4^+/l). The BNS was fed with growth medium containing 0.45 g/l Na_2HPO_4, 0.15 g/l KH_2PO_4, 0.1 g/l $MgSO_4$ $7H_2O$, and 0.015 g/l $CaCl_2$ $7H_2O$. In addition, 1 ml/l trace nutrients solution consisted of 1.5 g/l $FeCl_3$ $6H_2O$, 0.15 g/l H_3BO_3, 0.03 g/l $CuSO_4$ $5H_2O$, 0.18 g/l KI, 0.12 g/l $MnCl_2$ $4H_2O$, 0.06 g/l Na_2MoO_4 $2H_2O$, 0.12 g/l $ZnSO_4$ $7H_2O$, 0.15 g/l $CoCl_2$ $6H_2O$, and 10 mM acetate.[21]
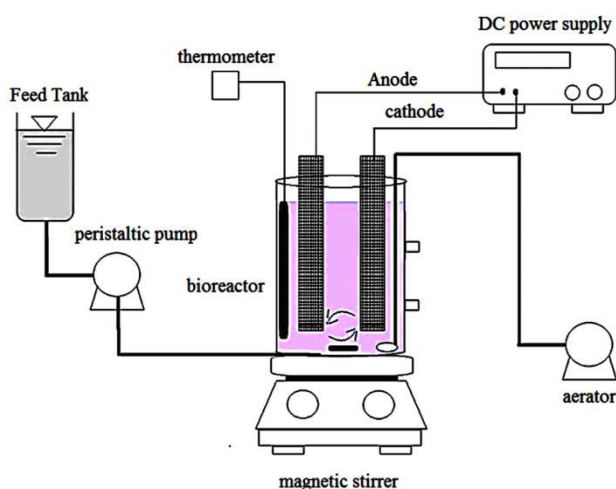

Figure 1. Schematic plan of bioelectrochemical nitrification system (BNS)

Samples were analyzed according to standard methods for water and wastewater. To determine the ammonium content, the phenate method at λ_{max} 640 nm was used. Nitrate concentration was determined using a spectrophotometer at λmax 220 and 275 nm. The nitrite content was analyzed through the colorimetric method using sulfanilamide and naphthylethylenediamine dihydrochloride regents at λ_{max} 543 nm.[11]

The coefficients of the response functions for different dependent variables were determined through correlating the experimental results using the Design-Expert regression software. The central composite design (CCD) was used to introduce this model as a specific design.[10] The CCD of the main parameters (x_1: supporting electrolyte of 100-500 mg/l and x_2: wastewater temperature of 22-32 ˚C) have been displayed in table 1. According to the design proposed by the Design-Expert software (version 7.0, Stat-Ease, Inc., Minneapolis, MN, USA), 13 experiments were conducted that is presented in table 2. Total number of experiments in CCD method was calculated based on $2k + n_\alpha + n_0$, where k is the number of independent variables, n_α axial points, and n_0 center points.[12,13] In this study, a 4 (2^2) factorial design, 4 (2 × 2) axial points, and 5 central points were selected. In order to ensure the validation of the obtained model, an experiment was performed at optimal factor levels and the result was compared with that predicted by the model.

Results and Discussion

Startup and optimum time

Primary startup of the bioelectrochemical process was performed in certain conditions for about 3 weeks and ammonium removal efficiency was controlled daily. A quasi-steady state was reached at the end of this period, and 78% ammonium removal was achieved (data are not shown). Scanning electron microscope (SEM) images of biofilm-electrode are illustrated in figure 2. The performance of the ammonium removal in the bioelectrochemical nitrification process at HRT of 0-72 hours is shown in figure 3. According to this figure, ammonium removal efficiency was about 80% in HRT of 24 hours. This was considered as optimized condition due to the lack of a significant difference in ammonium removal efficiency at the greater amount of 38.88 mg-N/l.

Table 1. Experimental range and levels of variables

Variable	Low axial (-1.41) $-\alpha$	Low factorial (-1)	Center point (0)	High factorial (+1)	High axial (+1.41) $+\alpha$
x_1 (mg/l)	100	160	300	440	500
x_2 (˚C)	22	24	27	30	32

x1: Supporting electrolyte; x2: Temperature

ANOVA

In order to determine responses, 13 experimental conditions of the runs proposed by the CCD were conducted in the laboratory. The response surface models were validated statistically for adequacy using ANOVA. Table 3 presents ANOVA of regression parameters of the predicted response surface quadratic model for bioelectrochemical ammonium removal efficiency. The high F value (11.48) and a low P value (0.0029) that is lower than 0.05 show that the ammonium removal model was significant.

The final second-order polynomial regression in terms of coded and actual factors is shown by equations 1 and 2.

Final equation in terms of coded factors:

$$\text{Ammonia Removal} = 95.6 - (9.24 \times x_1) - (3.5 \times x_2) - (2.35 \times x_1 \times x_2) - (13.69 \times x_1^2) - (10.17 \times x_2^2) \quad (1)$$

Final equation in terms of actual factors:

$$\text{Ammonia Removal} = -550.805 + (0.4724 \times \text{Supporting Electrolyte}) + (44.34879 \times \text{Temperature}) - (4.70E - 03 \times \text{Supporting Electrolyte} \times \text{Temperature}) - (6.85E - 04 \times \text{Supporting Electrolyte}^2) - (0.8135 \times \text{Temperature}^2) \quad (2)$$

Table 2. Central composite design (CCD) consisting of 13 experiments for the study of two experimental factors in coded units along with observed values

Run	x_1	x_2	Ammonium removal efficiency (%)	
			Actual	Predicated
1	1.00	1.00	65.7	56.65
2	0	-1.41	83.0	80.21
3	1.00	-1.00	72.1	68.35
4	0	0	98.6	95.60
5	1.41	0	46.5	55.15
6	0	0	96.6	95.60
7	0	0	94.0	95.60
8	-1.41	0	88.0	81.29
9	0	0	95.4	95.60
10	-1.00	-1.00	75.0	82.13
11	0	0	93.4	95.60
12	-1.00	1.00	78.0	79.83
13	0	1.41	65.6	70.31

x_1: Supporting electrolyte; x_2: Temperature
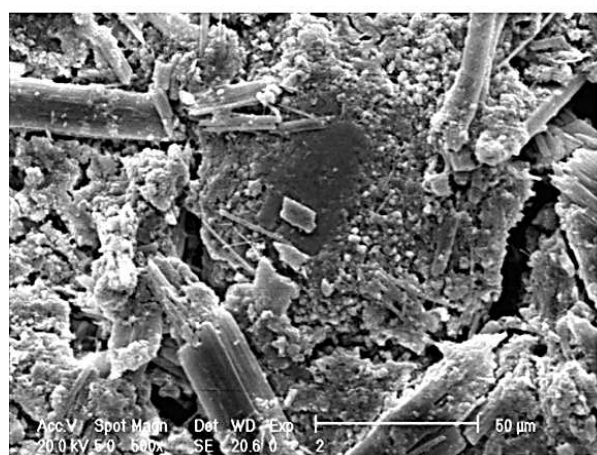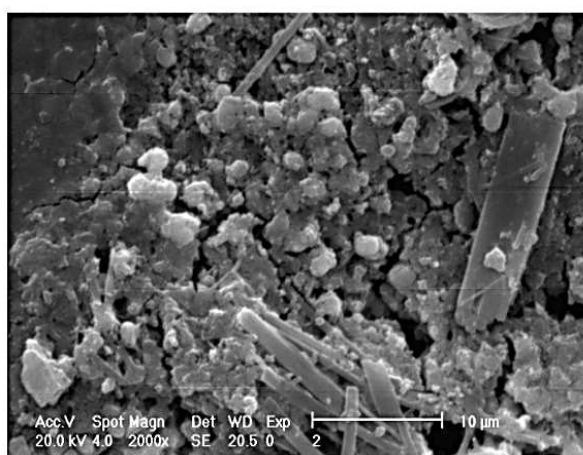
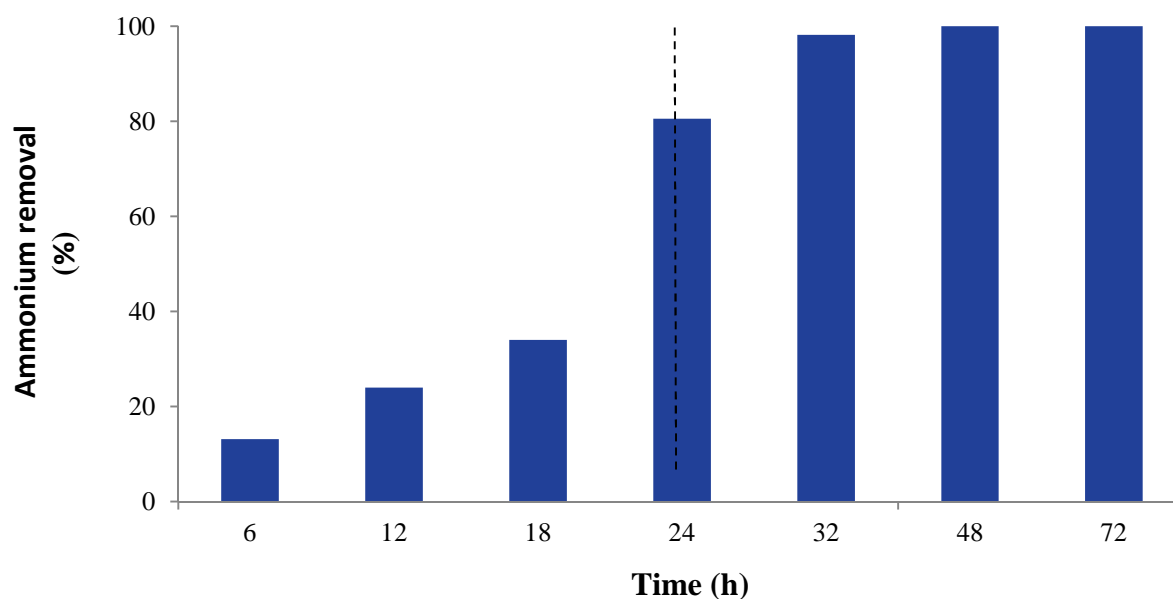**Figure 2. Scanning electron microscope (SEM) images of bio-electrode**

Figure 3. Ammonium variation via reaction time

Table 3. Analysis of variance (ANOVA) for quadratic model

Source	df	F	P Probability > F
Model	5	11.48	0.0029
x_1-Supporting Electrolyte	1	15.05	0.0061
x_2-Tempreature	1	2.16	0.1849
$x_1 x_2$	1	0.49	0.5078
x_1^2	1	28.76	0.0010
x_2^2	1	15.86	0.0053
Residual	7		
Lack of fit	3	22.94	0.0056
Pure error	4		
Cor total	12		
Standard Deviation		6.73	
Mean		80.92	
C.V. %		8.32	
R^2		0.89	
Adjusted R^2		0.81	

Df: Degree of freedom; x_1: Supporting electrolyte; x_2: Temperature; CV: Coefficient of variation

According to R^2 and adjusted R^2, the experimental analysis value indicates a good agreement with the predicted values. The predicted R^2 of 0.8913 is in reasonable agreement with the adjusted R^2 of 0.8137. In addition, the coefficient of variation (CV) is the value of the reproducibility of the model and should be lower than 10%. Accordingly, CV of 8.32% indicates reliability and high precision of the experimental data. Adequate precision is the ratio of signal to noise, and it should be greater than 4 to be desirable. Adequate precision of about 8.78 was obtained in the present study. In figure 4 a, predicted versus actual ammonia removal efficiency are observed. The predicted values were calculated from the final coded model equation (Equation 1). The respective R^2 (0.8137) and its fitted equation indicate the reasonability

of experiments. Usually, the adequacy of the model can be evaluated by diagnostic plots, such as a normal probability plot of the studentized residuals and a plot of predicted versus actual values. The normal probability plots of the studentized residuals for bioelectrochemical ammonium removal are presented in figure 4. This plot indicates that residuals follow a normal distribution and in this case the points will fall along a straight line.[22]

Effects of main parameters

Figure 5 illustrates the three-dimensional and related contour plot of response surface. Accordingly, the interaction between temperature and supporting electrolyte on ammonium removal efficiency is observed. It is clear that the increase in temperature and supporting electrolyte dosage promotes an increase in ammonium removal efficiency. The maximum observed removal of ammonium (optimum point for nitrification) was around center point (300 mg/l of NaCl and 27 ˚C). According to plot, the ammonium removal percentage decreased to a minimum with the increase in supporting electrolyte dosage to 500 mg/l. It is clear that the higher NaCl dose has adverse effects on biological population.

Bacterial activity is improved by increasing of ambient temperature. The oxidation rates of specific ammonium and its byproducts were also highly dependent on solution or ambient temperature. The variations of ammonia-oxidizing bacteria (β-Proteobacterial AOB) and nitrite-oxidizing bacteria (NOB) (Nitrobacter spp.) are sensitive and affected by temperature changes.[19] Zhang et al. suggested that the activity of AOB increased more than that of NOB by the increasing of temperature from 7.2 to 28.3 ˚C, but was inhibited more below 5.0 ˚C.[19] Moreover, Xiao et al. reported that increase in temperature could benefit the anode microbes when heat is transferred into the anode compartment through electrolyte.[23] In temperatures higher than 26.5 ˚C, nitrification rate declined. This can be due to the decreasing of ohmic resistance. As a result, electric current increased and this can have adverse effects on nitrifying bacteria. On the other hand, this phenomenon is intensified by the increasing of supporting electrolyte dosage. Dincer and Kargi reported that in a continuous flow nitrification/denitrification system, rates of nitrification/denitrification dropped significantly with salt dosage of more than 1000 mg/l.[24]
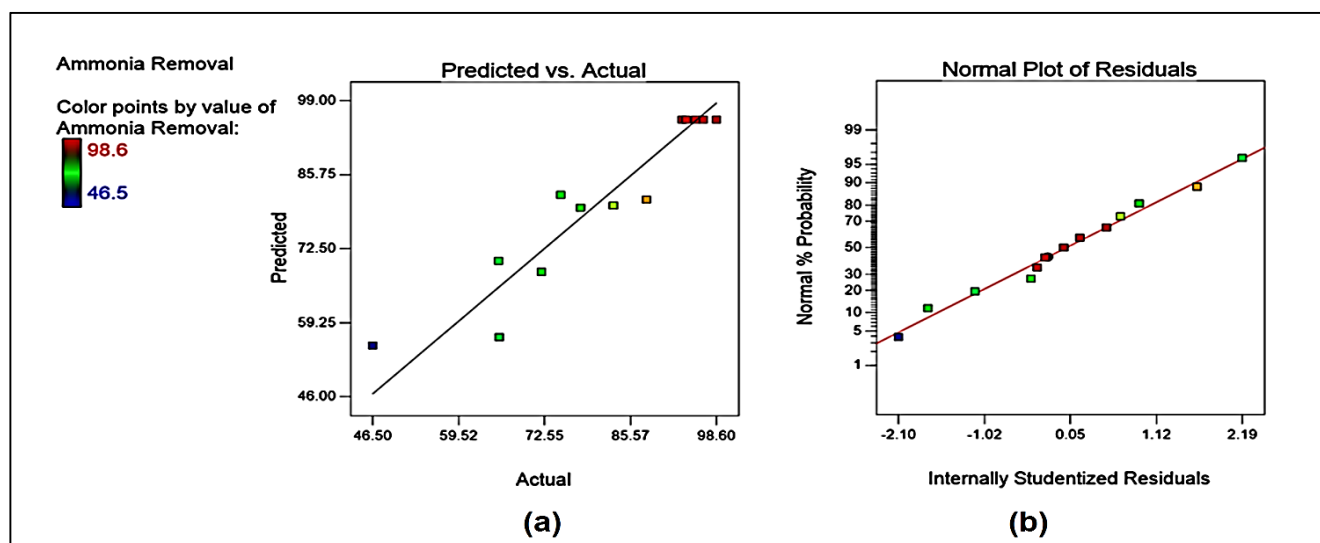

Figure 4. Predicted versus actual values plot (a) and normal probability plot (b) of the studentized residual for bioelectrochemical ammonium removal
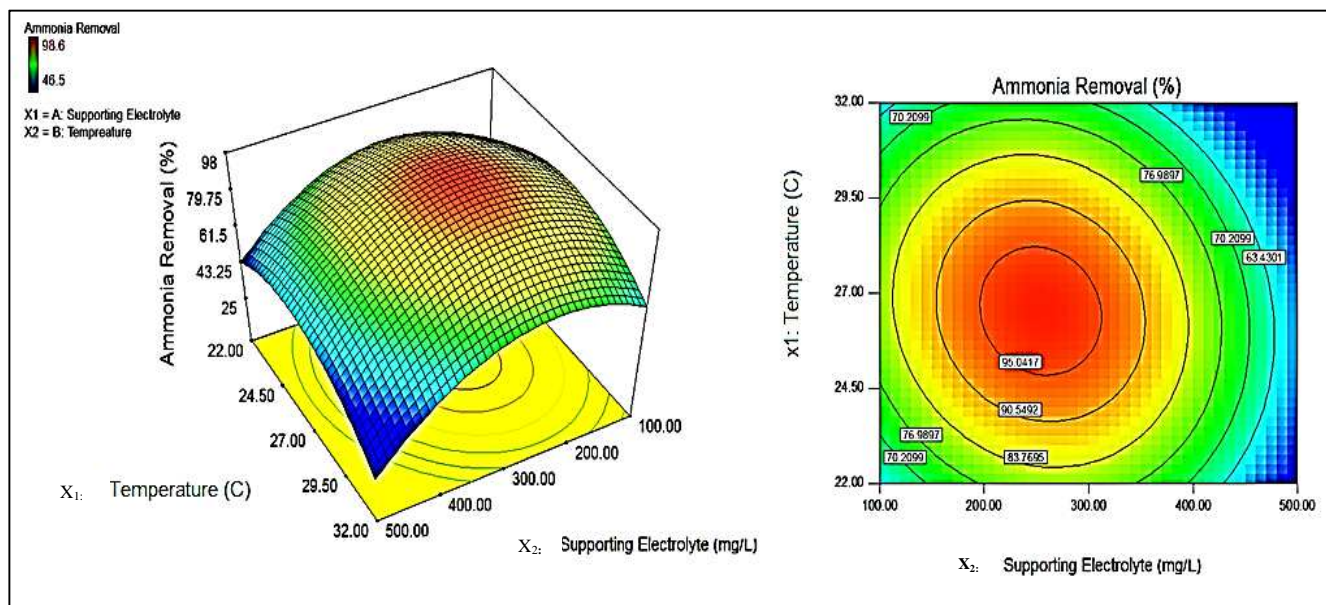
Figure 5. Three-dimensional and related contour graphics of response surface for bioelectrochemical ammonium removal

Optimization and confirmatory experiment

To achieve optimal nitrification, the desired goal for desired parameters was considered to be the "within the range" status, while for ammonium efficiency percentage it was "maximum". Therefore, the optimal values of working conditions and predicated removal efficiencies of ammonium were established. Figure 6 and table 4 indicate the optimal processing conditions and verification actual test. Regarding figure 6 that shows the overlay plot, optimal acquired condition for nitrification was about 250 mg/l of NaCl and 26.5 °C. Figure 7 shows the removal efficiency of ammonium in time. According to this figure, the experimental analysis value (99.6% at 24 hours) represents a good compatibility with the predication values (97.34%) and is in close agreement at a 95% confidence and prediction interval. The generation rate of nitrate and nitrite were determined. Nitrite is an unstable form of nitrogen which can be converted into other nitrogen compounds. This fact can be seen in figure 7 in which nitrite is converted to nitrate. Final concentrations of nitrite and nitrate were determined around 9.8 and 103 mg/l, respectively.

Conclusion

The present study showed that a desirable rate of ammonium removal from aqueous solution could be achieved using bioelectrochemical nitrification method. Effects of the two operational parameters of temperature and supporting electrolyte dosage were evaluated to obtain the maximum efficiency using RSM. Accordingly, the optimal amounts of desired parameters were 250 mg/l of NaCl and 26.5 °C. Under these conditions, a 99.6% experimental value was obtained.

Conflict of Interests

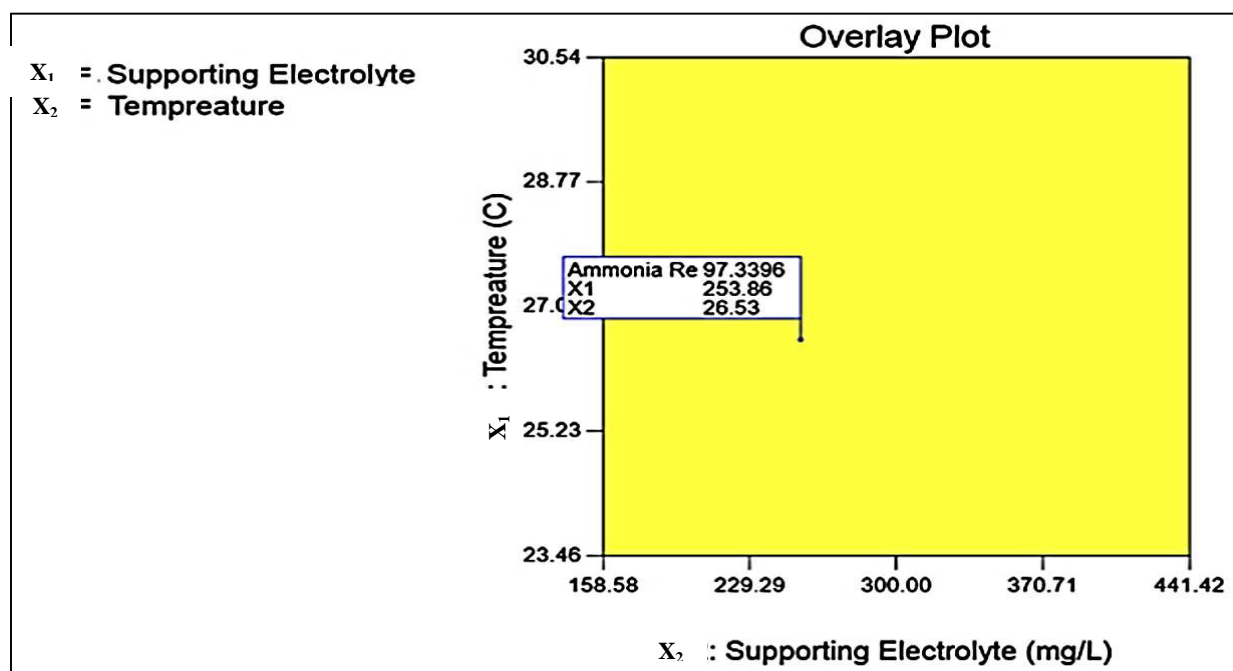Authors have no conflict of interests.

Acknowledgements

Figure 6. Overlay plot for ammonium removal

Table 4. Optimum condition verification and additional experiments

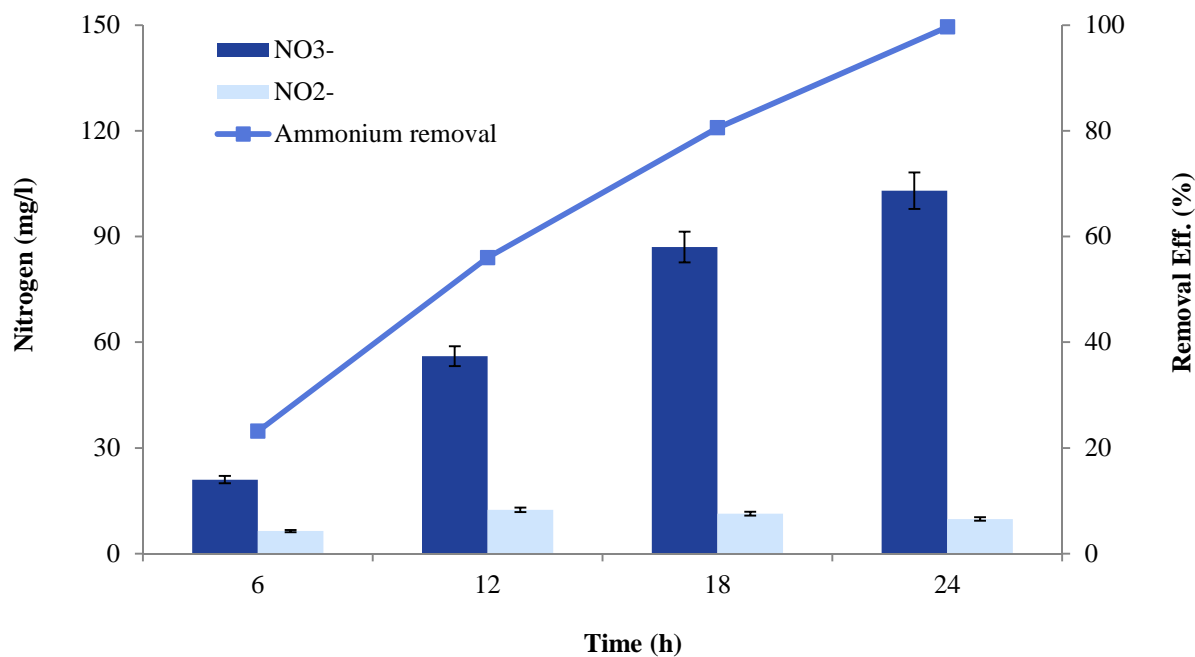| Response	Prediction	95% CI		95% PI		Conformity experiment
		Low	High	Low	High	
Ammonia removal	97.34%	90.34	100	79.94	100	99.6%

CI: Confidence interval; PI: Predicted interval

Figure 7. Variation of nitrogenous compounds during ammonia removal

References

1. Lai CL, Chen SH, Liou RM. Removing aqueous ammonia by membrane contactor process. Desalination and Water Treatment 2013; 51(25-27): 5307-10.
2. Foley B, Jones ID, Maberly SC, Rippey B. Long-term changes in oxygen depletion in a small temperate lake: effects of climate change and eutrophication. Freshwater Biology 2012; 57(2): 278-89.
3. Budzianowski WM. Mitigating NH3 Vaporization from an Aqueous Ammonia Process for CO2 Capture. Information: International Journal of Chemical Reactor Engineering 2011; 9(1).
4. Haule AT, Pratap HB, Katima HJ, Mugittu K, Mbwette TS. Potential Macrophytes for Nitrogen Removal from Domestic Wastewater in Horizontal Subsurface Flow Constructed Wetlands in Tanzania. The Open Environmental Engineering Journal 2013; 6: 14-21.
5. Sarioglu M. Removal of ammonium from municipal wastewater using natural Turkish (Dogantepe) zeolite. Separation and Purification Technology 2005; 41(1): 1-11.
6. Nguyen VK, Hong S, Park Y, Jo K, Lee T. Autotrophic denitrification performance and bacterial community at biocathodes of bioelectrochemical systems with either abiotic or biotic anodes. Journal of Bioscience and Bioengineering 2015; 119(2): 180-7.
7. Clauwaert P, Desloover J, Shea C, Nerenberg R, Boon N, Verstraete W. Enhanced nitrogen removal in bioelectrochemical systems by pH control. Biotechnol Lett 2009; 31(10): 1537-43.
8. Sayess RR, Saikaly PE, El-Fadel M, Li D, Semerjian L. Reactor performance in terms of COD and nitrogen removal and bacterial community structure of a three-stage rotating bioelectrochemical contactor. Water Res 2013; 47(2): 881-94.
9. Feleke Z, Sakakibara Y. A bio-electrochemical reactor coupled with adsorber for the removal of nitrate and inhibitory pesticide. Water Res 2002; 36(12): 3092-102.
10. Mousavi SA, Ibrahim Sh. Application of response surface methodology (RSM) for analyzing and modeling of nitrification process using sequencing batch reactors. Desalination and Water Treatment 2015; 1-10.
11. Rezaee A, Safari M, Hossini H. Bioelectrochemical denitrification using carbon felt/multiwall carbon nanotube. Environ Technol 2015; 36(8): 1057-62.
12. Varia J, Silva Martinez S, Velasquez Orta SB, Bull S, Roy S. Bioelectrochemical metal remediation and recovery of Au3+, Co2+ and Fe3+ metal ions. Electrochimica Acta 2013; 95: 125-31.
13. Jia YH, Tran HT, Kim DH, Oh SJ, Park DH, Zhang RH, et al. Simultaneous organics removal and bioelectrochemical denitrification in microbial fuel cells. Bioprocess Biosyst Eng 2008; 31(4): 315-21.
14. Rozendal RA, Hamelers HV, Rabaey K, Keller J, Buisman CJ. Towards practical implementation of bioelectrochemical wastewater treatment. Trends Biotechnol 2008; 26(8): 450-9.
15. Xie S, Liang P, Chen Y, Xia X, Huang X. Simultaneous carbon and nitrogen removal using an oxic/anoxic-biocathode microbial fuel cells coupled system. Bioresour Technol 2011; 102(1): 348-54.
16. Yan H, Saito T, Regan JM. Nitrogen removal in a single-chamber microbial fuel cell with nitrifying biofilm enriched at the air cathode. Water Res 2012; 46(7): 2215-24.
17. Jiménez-Contreras E, Torres-Salinas D, Bailón Moreno R, Baños RR, López-Cózar ED. Response Surface Methodology and its application in evaluating scientific activity. Scientometrics 2008; 79(1): 201-18.
18. Wilson KB. On the Experimental Attainment of Optimum Conditions. Journal of the Royal Statistical Society Series B (Methodological) 1951; 13(1): 1-45.
19. Zhang S, Wang Y, He W, Wu M, Xing M, Yang J, et al. Impacts of temperature and nitrifying community on nitrification kinetics in a moving-bed biofilm reactor treating polluted raw water. Chemical Engineering Journal 2014; 236: 242-50.
20. Zhao Y, Zhang B, Feng C, Huang F, Zhang P, Zhang Z, et al. Behavior of autotrophic denitrification and heterotrophic denitrification in an intensified biofilm-electrode reactor for nitrate-contaminated drinking water treatment. Bioresour Technol 2012; 107: 159-65.
21. Lu H, Oehmen A, Virdis B, Keller J, Yuan Z. Obtaining highly enriched cultures of Candidatus Accumulibacter phosphates through alternating carbon sources. Water Res 2006; 40(20): 3838-48.
22. Muhamad MH, Sheikh Abdullah SR, Mohamad AB, Abdul RR, Hasan Kadhum AA. Application of response surface methodology (RSM) for optimisation of COD, NH3-N and 2,4-DCP removal from recycled paper wastewater in a pilot-scale granular activated carbon sequencing batch biofilm reactor (GAC-SBBR). J Environ Manage 2013; 121: 179-90.
23. Xiao L, Young EB, Berges JA, He Z. Integrated photo-bioelectrochemical system for contaminants removal and bioenergy production. Environ Sci Technol 2012; 46(20): 11459-66.
24. Dincer AR, Kargi F. Salt inhibition of nitrification and denitrification in saline wastewater. Environ Technol 1999; 20: 1147-53.

http://jaehr.muk.ac.ir