Journal of Advances in Environmental Health Research
Kurdistan University of Medical Sciences
Kurdistan Environmental Health Research Center

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

JAEHR. Authors agree to execute copyright transfer forms as requested with respect to their *Journal of Advances in Environmental Health Research* has the right to use, reproduce, transmit, derive works from, publish, and distribute the contribution, in the *Journal* or otherwise, in any form or medium. Authors will not use or authorize the use of the contribution without the Journal Office' written consent

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**

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

Table of Contents

Original Article(s)

Journal of Advances in Environmental Health Research

Correlation of air pollutants with land use and traffic measures in Tehran, Iran: A preliminary statistical analysis for land use regression modeling

Hassan Amini[1], Seyed-Mahmood Taghavi-Shahri[2], Kazem Naddafi[3], Ramin Nabizadeh[4], Masud Yunesian[3]

1 Kurdistan Environmental Health Research Center, Kurdistan University of Medical Sciences, Sanandaj AND Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran
2 Research Center for Environmental Pollutants, Qom University of Medical Sciences, Qom AND Department of Epidemiology and Biostatistics, School of Public Health, Isfahan University of Medical Sciences, Isfahan, Iran
3 Center for Air Pollution Research (CAPR), Institute for Environmental Research (IER), Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran
4 Department of Environmental Health Engineering, School of Public Health, Tehran University of Medical Sciences, Tehran, Iran

Original Article

Abstract

Land use regression (LUR) models have been globally used to estimate long-term air pollution exposures. The present study aimed to analyze the association of different land use types and traffic measures with air pollutants in Tehran, Iran, as part of the future development of LUR models. Data of the particulate matter (PM_{10}), sulfur dioxide (SO_2), and nitrogen dioxide (NO_2) were extracted from 23 Tehran's air quality monitors for 2010. The data of different land use types and traffic measures within the circular buffer radii 100 to 1000 meters and distances to them were calculated using Geographic Information System (GIS). Thereafter, the association of the mentioned air pollutants was evaluated with land use types and traffic measures. The annual average concentrations of PM_{10}, SO_2 and NO_2 were 100.8 μg/m³, 38 parts per billion (ppb), and 53.2 ppb, respectively. The PM_{10} was associated with transportation area, other areas, and with distance to the other nearest land use ($P < 0.05$). The SO_2 concentration was associated with official or commercial land use, and with other area land use ($P < 0.05$). Noteworthy, the NO_2 concentration was associated with official or commercial land use, and with other areas ($P < 0.05$). The air pollutant concentrations was analyzed with different land use types and traffic measures as a preliminary work for development of LUR models in Tehran. It is hoped these analyses lead to successful development of LUR models in the near future.

KEYWORDS: Land Use Regression, Land Use Types, Traffic Measures, Particulate Matter, Sulfur Dioxide, Nitrogen Dioxide

Date of submission: 18 Mar 2013, ***Date of acceptance:*** 20 May 2013

Citation: Amini H, Taghavi-Shahri SM, Naddafi K, Nabizadeh R, Yunesian M. **Correlation of air pollutants with land use and traffic measures in Tehran, Iran: A preliminary statistical analysis for land use regression modeling.** J Adv Environ Health Res 2013; 1(1): 1-8.

Introduction

Recently, extensive epidemiological studies have linked the indoor and outdoor short and long-term air pollution exposures to the considerably significant acute and chronic adverse health effects,[1,2] particularly studies on development of asthma,[3] respiratory and cardiovascular diseases,[4]

Corresponding Author:
Masud Yunesian
Email: yunesian@tums.ac.ir

birth outcomes and developmental effects,[5] leukemia,[6] mortality,[7,8] and even neighborhood walkability.[9] Generally, albeit these studies collected a very large datasets on health outcomes, air pollution exposure assessment has been a challenge in the majority of the epidemiological studies.[10-12] Though personal monitoring through several consecutive days in studies with less than hundreds of subjects has assessed short-term exposures, it has still been a serious challenge as the study population increases. However, since epidemiological studies on long-term air pollution exposures need only annual (or any other long-term average) exposure concentrations, and ideally as close to the individual-level as possible, and even more because their study population mainly comprises several hundreds to thousands of subjects, the mere monitoring will not be feasible.[12-15] Initial epidemiological surveys have assigned only one average exposure to all the participants in a large geographical area, and assumed that the concentration of the pollutant of interest is homogeneous throughout the whole such an area. However, various investigations have now demonstrated that there is a considerable difference on a very small-scale in the ambient air pollution concentrations.[16-18] Consequently, individual-scale exposure assessment is warranted to minimize exposure misclassification in epidemiological studies.[19] Hence, various approaches have been used in recent years to capture small-scale spatial variations of outdoor air pollution, which are described elsewhere.[20-22] More recently, land use regression (LUR) modeling -which is classified as geospatial modeling techniques- has been developed and emerged as a successful approach to predict neighborhood-scale air pollution exposures, even better than kriging and dispersion models.[21,23,24] Initially, this technique was applied in Europe,[25] but recently several applications have been reported in North America,[26-28] China,[29] and Japan.[19] As part of the future LUR models development, this study aimed to analyze the association of different land use and traffic measures with air pollutant concentrations in Tehran, Iran.

Materials and Methods

The study area encompassed Tehran, Iran, with approximately 613 square kilometers study area (Figure 1). Tehran is the largest city in Iran and suffers from extreme air pollution concentrations. The population of the city is about 9 million people, albeit it would be much higher during daily time hours.[30]

The data of air pollutant concentrations for 2010 were extracted from 23 air quality monitors belong to Air Quality Control Company (AQCC) and Department of Environment (DOE). These included particulate matter with aerodynamic diameter of 10 micrometer or smaller (PM_{10}), sulfur dioxide (SO_2), and nitrogen dioxide (NO_2). Data were purified in Microsoft Office Excel and then were imported to the R statistical software.[31] The missing data were imputed using AMELIA program.[32]

The data of land use and traffic measures have been originated from a study on seismic micro-zoning of Greater Tehran area.[33] The land use was in ten categories including: 1. residential, 2. green space, 3. urban facilities, 4. industrial or workshop, 5. official or commercial, 6. transportation, 7. military, 8. arable, 9. arid or undeveloped and finally 10. other land use areas. The total length of the land use types were considered for analyses within circular buffer radii 100 to 500 meters and distances of the air quality monitors toward them. The traffic measure variables were surrogates of traffic including length of the streets, highways, bridges, and all roads within the circular buffer radii 100 to 1000 meters around the air quality monitoring stations and distances away (Figure 2) (Table 1). All these variables were calculated and analyzed in Geographic Information System (GIS) using ArcGIS® 9.3 (ESRI®, Redlands, CA, USA).

Descriptive statistics including annual average of the air pollutant concentrations were calculated and reported. Meanwhile, the

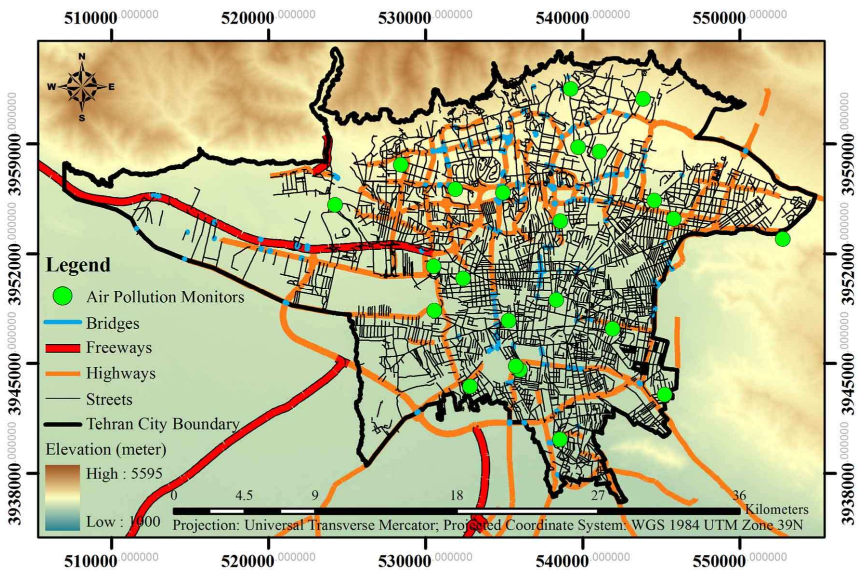


Figure 1. Study area of Tehran, Iran

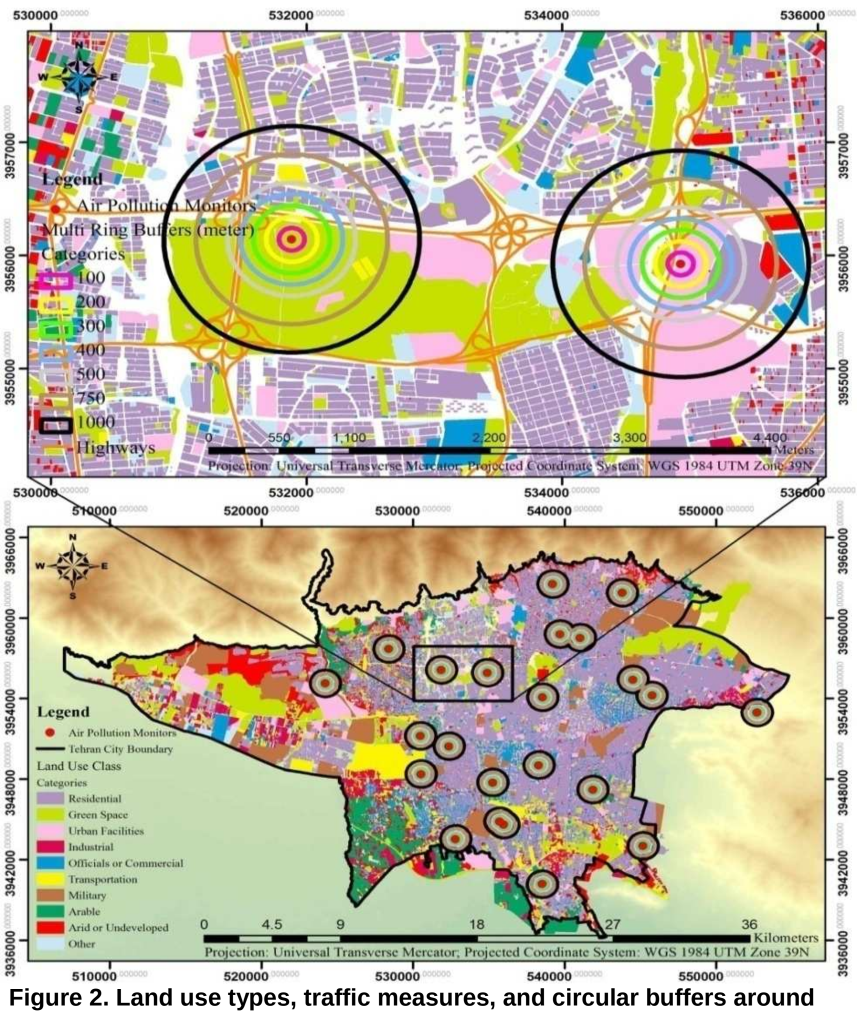


Figure 2. Land use types, traffic measures, and circular buffers around the air quality monitoring stations with different radii

Table 1. Summary of the traffic measures variables

Variable name	Buffer radii (m) around monitors
Length of streets	100, 200, 300, 400, 500
Length of highways	100, 200, 300, 400, 500
Length of bridges	400, 500
Length of all road types	100, 200, 300, 400, 500, 750, 1000
Distance to streets	-
Distance to highways	-
Distance to bridges	-
Distance to all road types	-

maximum, minimum and median of which were plotted by the box plots. Descriptive statistics were also calculated for all the traffic measures and land use type variables. Thereafter, the correlations of the measured air pollutant concentrations were calculated with all the land use types and traffic surrogate measures. The p-value less than 0.05 set as a significant level in all the statistical analyses. All the statistical analyses were performed by Stata Statistical Software, Release 12.0 (Stata Corporation, College Station, TX, USA) and R statistical software.

Results and Discussion

In this study, it was tried to analyze the associations of different land use and traffic measures with air pollutant concentrations as part of the future land use regression models development in Tehran, Iran. The annual average concentrations of PM_{10}, SO_2 and NO_2 were 100.8 μg/m^3, 38 parts per billion (ppb), and 53.2 ppb, respectively. Meanwhile, descriptive statistics of the air pollutants concentrations are shown in figure 3. Moreover, descriptive statistics of all traffic measures are tabulated in table 2. In addition, descriptive statistics of all the land use variables are tabulated in table 3.

The air pollutant concentration in Tehran is much higher than other contexts of the world where land use regression models have been

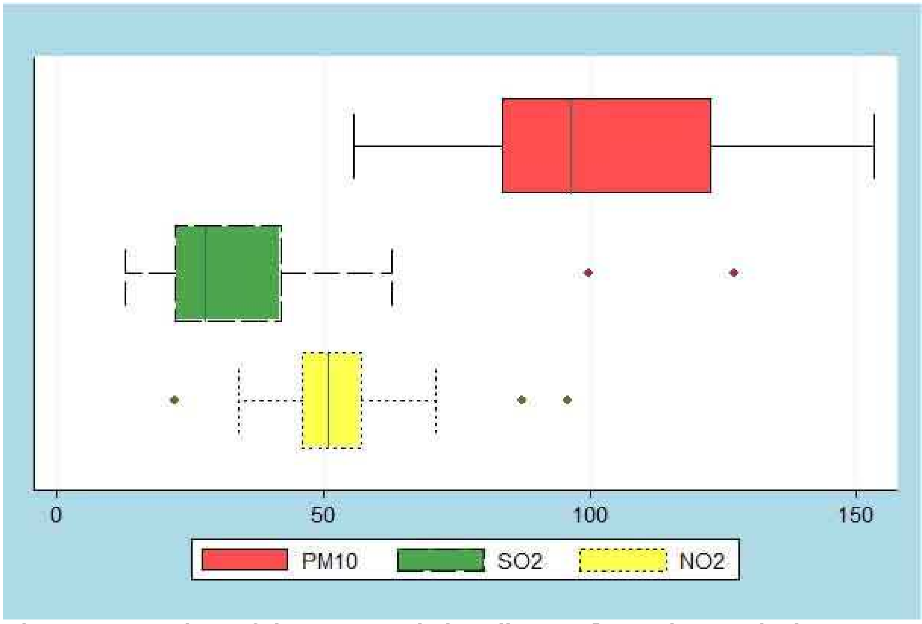


Figure 3. Box plots of the measured air pollutants [Note that particulate matter (PM10) units is in µg/m3, sulfur dioxide (SO2) and nitrogen dioxide (NO2) units are in ppb]

Table 2. Summary of the traffic surrogates variables

Variable name (buffer radii in meter)	Minimum	Maximum	Mean	Standard deviation
Length of streets (100)	0	280	92.83	96.5
Length of streets (200)	0	1130	438.04	352.8
Length of streets (300)	0	2505	1006.09	624.1
Length of streets (400)	0	3880	1705.00	969.3
Length of streets (500)	0	5180	2698.48	1276.9
Length of all road types (100)	0	905	388.48	232.8
Length of all road types (200)	0	3840	1752.61	986.7
Length of all road types (300)	440	7595	3906.52	2015.7
Length of all road types (400)	825	13870	7055.87	3588.7
Length of all road types (500)	1260	21325	11370.43	5196.3
Length of all road types (750)	3350	48995	26045.00	11401.6
Length of all road types (1000)	4985	83030	46360.87	20103.9
Length of highways (100)	0	235	31.30	71.4
Length of highways (200)	0	760	97.61	204.4
Length of highways (300)	0	1100	209.57	363.0
Length of highways (400)	0	1635	389.57	570.8
Length of highways (500)	0	2810	666.96	871.3
Length of bridges (400)	0	690	66.09	169.4
Length of bridges (500)	0	1535	123.04	330.5
Distance to the nearest street	4	511	119.36	117.2
Distance to the nearest all road type	10	211	43.09	47.4
Distance to the nearest highway	21	2258	649.60	597.3
Distance to the nearest bridge	39	6032	1367.00	1244.0

reported.[10,27,34-36] In Tehran, the PM_{10} pollutant was associated with transportation area within buffer radii 100, 200, 300, 400 and 500 meters; with other area land use within buffer of 500 meters; and with distance to the other nearest land use ($P < 0.05$). The SO_2 concentration was associated with official or commercial land use area within buffer radii 300, 400, and 500 meters; and with other area land use within buffer of 100, 200, 300, 400 and 500 meters ($P < 0.05$). Noteworthy, the NO_2 concentration was associated with official or commercial land use area within buffer radii 200, 300, 400, and 500 meters; and with other area land use within buffer of 100 meters ($P < 0.05$).

These variables have been studied in other cities of the world. In other parts of the world, these pollutants have been associated mainly with traffic counts or surrogates of the traffic.[12] As shown in figure 2, the official or commercial land use areas are mainly located close to streets, roads, and highways where they are highly correlated with traffic counts. Thus, the significant associations of SO_2 and NO_2 with official or commercial land use areas demonstrated that traffic, indirectly, is the origin of these pollutants. This is in line with the results of other studies around the globe.[12,21]

In conclusion, some air pollutant concentrations in this research were analyzed with different within-city land use types and traffic measures as a preliminary work for development of the land use regression models in Tehran. It is hoped this analyses lead to successful development of land use regression models in the near future.

Table 3. Summary of all the land use variables

Variable Name (buffer radii in meter)	Minimum (m^2)	Maximum (m^2)	Mean (m^2)	Standard deviation (m^2)
Residential area (100)	0	16275	6811	5735
Residential area (200)	0	74250	31878	23586
Residential area (300)	0	184025	75405	52749
Residential area (400)	0	309975	140676	89313
Residential area (500)	0	485975	232904	133962
Green space area (100)	0	31425	4989	8207
Green space area (200)	0	115100	18452	27013
Green space area (300)	0	236650	35172	52847
Green space area (400)	0	385175	54657	83057
Green space area (500)	0	531450	71021	111868
Urban facilities area (100)	0	22200	3634	5618
Urban facilities area (200)	0	77500	15541	20204
Urban facilities area (300)	0	151050	33985	41399
Urban facilities area (400)	0	251750	55903	65748
Urban facilities area (500)	75	373250	80625	88154
Industrial area (100)	0	1600	203	439
Industrial area (200)	0	2750	530	885
Industrial area (300)	0	15175	2443	4271
Industrial area (400)	0	52975	8197	15044
Industrial area (500)	0	104500	14827	27268
Official or commercial area (100)	0	19200	2935	4813
Official or commercial area (200)	0	36975	7211	9718
Official or commercial area (300)	0	87925	14404	19743
Official or commercial area (400)	0	154425	23959	33034
Official or commercial area (500)	0	258775	38432	53712
Transportation area (100)	0	14725	1461	3734
Transportation area (200)	0	60575	5397	13239
Transportation area (300)	0	130075	14760	30261
Transportation area (400)	0	212625	28141	54161
Transportation area (500)	0	308150	45684	83081
Military area (100)	0	13575	872	2922
Military area (200)	0	54250	4107	12517
Military area (300)	0	111350	9477	26033
Military area (400)	0	190000	18220	45361
Military area (500)	0	307775	30455	73689
Arable area (100)	0	0	0	0
Arable area (200)	0	4850	210	1011
Arable area (300)	0	19125	1013	4005
Arable area (400)	0	33675	2061	7077
Arable area (500)	0	64550	4805	14842
Arid or undeveloped area (100)	0	9550	1477	3057
Arid or undeveloped area (200)	0	33700	5029	9158
Arid or undeveloped area (300)	0	77450	11469	21663
Arid or undeveloped area (400)	0	130050	20630	38153
Arid or undeveloped area (500)	0	179125	29328	52120
Other areas (100)	0	75	3	15
Other areas (200)	0	6550	431	1425
Other areas (300)	0	19475	1516	4748
Other areas (400)	0	31775	2829	7278

Table 3. Summary of all the land use variables (Continues)

Variable name (buffer radii in meter)	Minimum (m^2)	Maximum (m^2)	Mean (m^2)	Standard deviation (m^2)
Other areas (500)	0	45100	5108	10681
Distance to nearest residential land use	0	622	96	153
Distance to nearest green space land use	0	1351	161	299
Distance to nearest urban facilities land use	0	482	95	107
Distance to nearest industrial or workhouse land use	36	990	345	277
Distance to nearest commercial or official land use	0	710	124	178
Distance to nearest transportation land use	0	1716	435	460
Distance to nearest military land use	7	3934	984	1041
Distance to nearest arable land use	130	4235	1478	1184
Distance to nearest arid or undeveloped land use	0	1906	335	433
Distance to nearest other land use	47	6831	1719	2022

Conflict of Interests

Authors have no conflict of interests.

Acknowledgements

This study was part of the MSPH thesis completed by Hassan Amini in Environmental Health Engineering, and has been supported by Tehran University of Medical Sciences (grant number 89-10-18-240.3646) and Tehran Urban Planning and Research Center. The authors acknowledged the following for assistance in various parts of the project: Majid Ramezani Mehrian, Mohammad Sadegh Hassanvand, Meinolf Drueeke, Ali Hosseini, Hossein Nasiri, Mohammad Ali Najafi, Arash Atri, Mohammad Hossein Sowlat, and numerous other contributors. Hereby, many thanks go to the Air Quality Control Company and Department of Environment for providing air pollution data. Noteworthy, we extend our sincerest gratitude to Drs. Gerard Hoek, Michael Brauer, and Sarah B. Henderson for their extensive help and guidance during the work and comments on previous versions of the paper. The authors acknowledged reviewers for their valuable feedback.

References

1. Brunekreef B, Holgate ST. Air pollution and health. Lancet 2002; 360(9341): 1233-42.
2. Yunesian M, Asghari F, Vash JH, Forouzanfar MH, Farhud D. Acute symptoms related to air pollution in urban areas: a study protocol. BMC Public Health 2006; 6: 218.
3. Clark NA, Demers PA, Karr CJ, Koehoorn M, Lencar C, Tamburic L, et al. Effect of early life exposure to air pollution on development of childhood asthma. Environ Health Perspect 2010; 118(2): 284-90.
4. Hosseinpoor AR, Forouzanfar MH, Yunesian M, Asghari F, Naieni KH, Farhood D. Air pollution and hospitalization due to angina pectoris in Tehran, Iran: a time-series study. Environ Res 2005; 99(1): 126-31.
5. Malmqvist E, Rignell-Hydbom A, Tinnerberg H, Bjork J, Stroh E, Jakobsson K, et al. Maternal exposure to air pollution and birth outcomes. Environ Health Perspect 2011; 119(4): 553-8.
6. Amigou A, Sermage-Faure C, Orsi L, Leverger G, Baruchel A, Bertrand Y, et al. Road traffic and childhood leukemia: the ESCALE study (SFCE). Environ Health Perspect 2011; 119(4): 566-72.
7. Hoek G, Fischer P, Van Den Brandt P, Goldbohm S, Brunekreef B. Estimation of long-term average exposure to outdoor air pollution for a cohort study on mortality. J Expo Anal Environ Epidemiol 2001; 11(6): 459-69.
8. Hoek G, Brunekreef B, Goldbohm S, Fischer P, van den Brandt PA. Association between mortality and indicators of traffic-related air pollution in the Netherlands: a cohort study. Lancet 2002; 360(9341): 1203-9.
9. Marshall JD, Brauer M, Frank LD. Healthy neighborhoods: walk ability and air pollution. Environ Health Perspect 2009; 117(11): 1752-9.
10. Molter A, Lindley S, de Vocht F, Simpson A, Agius R. Modeling air pollution for epidemiologic research--Part I: A novel approach combining land use regression and air dispersion. Sci Total Environ 2010; 408(23): 5862-9.
11. Marshall JD, Nethery E, Brauer M. Within-urban variability in ambient air pollution: Comparison of estimation methods. Atmospheric Environment 2008;

42(6): 1359-69.
12. Hoek G, Beelen R, de Hoogh K, Vienneau D, Gulliver J, Fischer P, et al. A review of land-use regression models to assess spatial variation of outdoor air pollution. Atmospheric Environment 2008; 42(33): 7561-78.
13. Brook RD, Shin HH, Bard RL, Burnett RT, Vette A, Croghan C, et al. Exploration of the rapid effects of personal fine particulate matter exposure on arterial hemodynamics and vascular function during the same day. Environ Health Perspect 2011; 119(5): 688-94.
14. Liao D, Peuquet DJ, Duan Y, Whitsel EA, Dou J, Smith RL, et al. GIS approaches for the estimation of residential-level ambient PM concentrations. Environ Health Perspect 2006; 114(9): 1374-80.
15. Naghizadeh A, Mahvi AH, Jabbari H, Derakhshani E, Amini H. Exposure assessment to dust and free silica for workers of Sangan iron ore mine in Khaf, Iran. Bull Environ Contam Toxicol 2011; 87(5): 531-8.
16. Beelen R, Voogt M, Duyzer J, Zandveld P, Hoek G. Comparison of the performances of land use regression modelling and dispersion modelling in estimating small-scale variations in long-term air pollution concentrations in a Dutch urban area. Atmospheric Environment 2010; 44(36): 4614-21.
17. Kingham S, Briggs D, Elliott P, Fischer P, Erik L. Spatial variations in the concentrations of traffic-related pollutants in indoor and outdoor air in Huddersfield, England. Atmospheric Environment 2000; 34(6): 905-16.
18. Lebret E, Briggs D, van Reeuwijk H, Fischer P, Smallbone K, Harssema H, et al. Small area variations in ambient NO2 concentrations in four European areas. Atmospheric Environment 2000; 34(2): 177-85.
19. Kashima S, Yorifuji T, Tsuda T, Doi H. Application of land use regression to regulatory air quality data in Japan. Sci Total Environ 2009; 407(8): 3055-62.
20. Vienneau D, de Hoogh K, Beelen R, Fischer P, Hoek G, Briggs D. Comparison of land-use regression models between Great Britain and the Netherlands. Atmospheric Environment 2010; 44(5): 688-96.
21. Jerrett M, Arain A, Kanaroglou P, Beckerman B, Potoglou D, Sahsuvaroglu T, et al. A review and evaluation of intraurban air pollution exposure models. J Expo Anal Environ Epidemiol 2005; 15(2): 185-204.
22. Dijkema MB, Gehring U, van Strien RT, van der Zee SC, Fischer P, Hoek G, et al. A comparison of different approaches to estimate small-scale spatial variation in outdoor NO(2) concentrations. Environ Health Perspect 2011; 119(5): 670-5.
23. Su JG, Jerrett M, Beckerman B, Wilhelm M, Ghosh JK, Ritz B. Predicting traffic-related air pollution in Los Angeles using a distance decay regression selection strategy. Environ Res 2009; 109(6): 657-70.
24. Clougherty JE, Wright RJ, Baxter LK, Levy JI. Land use regression modeling of intra-urban residential variability in multiple traffic-related air pollutants. Environ Health 2008; 7: 17.
25. Briggs DJ, Collins S, Elliott P, Fischer P, Kingham S, Lebret E, et al. Mapping urban air pollution using GIS: a regression-based approach. International Journal of Geographical Information Science 1997; 11(7): 699-718.
26. Ryan PH, Lemasters GK, Levin L, Burkle J, Biswas P, Hu S, et al. A land-use regression model for estimating microenvironmental diesel exposure given multiple addresses from birth through childhood. Sci Total Environ 2008; 404(1): 139-47.
27. Ross Z, Jerrett M, Ito K, Tempalski B, Thurston GD. A land use regression for predicting fine particulate matter concentrations in the New York City region. Atmospheric Environment 2007; 41(11): 2255-69.
28. Novotny EV, Bechle MJ, Millet DB, Marshall JD. National satellite-based land-use regression: NO2 in the United States. Environ Sci Technol 2011; 45(10): 4407-14.
29. Chen L, Baili Z, Kong S, Han B, You Y, Ding X, et al. A land use regression for predicting NO2 and PM10 concentrations in different seasons in Tianjin region, China. J Environ Sci (China) 2010; 22(9): 1364-73.
30. Statistical Centre of Iran. Estimated Population of Country Cities for 2010 [Online]. 2012 [cited 2012 Aug 1]; Available from: URL: http://www.amar.org.ir/Default.aspx?tabid=339&agentType=View&PropertyID=1130 [In Persian].
31. R Development Core Team. R: A Language and Environment for Statistical Computing. Vienna, Austria: R Foundation for Statistical Computing; 2009.
32. Honaker J, King G, Blackwell M. Amelia II: A Program for Missing Data. Journal of Statistical Software 2011; 45(7): 1-47.
33. JICA and CEST. The study on seismic micro-zoning of the greater Tehran area in the Islamic Republic of Iran [Online]. 2001; Available from: URL: http://www.vojoudi.com/earthquake/jica [In Persian].
34. Henderson SB, Beckerman B, Jerrett M, Brauer M. Application of land use regression to estimate long-term concentrations of traffic-related nitrogen oxides and fine particulate matter. Environ Sci Technol 2007; 41(7): 2422-8.
35. Sangrador JL, Nuñez MC, Villarreal A B, Cadena LH, Jerrett M, Romieu I. A Land Use Regression Model for Predicting PM2.5 in Mexico City. Epidemiology 2008; 19(6): 259.
36. Hystad P, Setton E, Cervantes A, Poplawski K, Deschenes S, Brauer M, et al. Creating national air pollution models for population exposure assessment in Canada. Environ Health Perspect 2011; 119(8): 1123-9.

Journal of Advances in Environmental Health Research

Assessment of ultrasound irradiation on inactivation of gram negative and positive bacteria isolated from hospital in aqueous solution

Afshin Maleki[1], Behzad Shahmoradi[1], Hiua Daraei[1], Enayatollah Kalantar[2]

1 Kurdistan Environmental Health Research Center, Kurdistan University of Medical Sciences, Sanandaj, Iran
2 Department of Microbiology, School of Medicine, Alborz University of Medical Sciences, Karaj, Iran

Original Article

Abstract

Microbial contamination of water poses a major threat to public health. With the emergence of microorganisms resistant to multiple antimicrobial agents, there is increased request for promotion of disinfection methods. Since ultrasound wave (US) exhibits antibacterial activities on bacteria, the aim of this study was to evaluate the antimicrobial effect of low frequency (37 kHz) ultrasound on *Pseudomonas aeruginosa* and *Staphylococcus aureus* as a model for gram-negative and gram-positive bacteria, respectively. Sonolysis experiment was carried out in a laboratory-scale batch sonoreactor equipped with plate type transducer at 400 W of acoustic power in the presence and absence of ampicillin as an antibiotic on the both *Pseudomonas aeruginosa* and *Staphylococcus aureus*. All of the bacteria were affected by the ultrasound and an increase in percent kill for both bacteria occurred with increasing duration of exposure and intensity of ultrasound. It was found that gram-negative bacteria were more susceptible to the ultrasonic treatment rather than gram-positive bacteria. In addition, the combination of US with an antibiotic (ampicillin) enhanced killing of both bacteria over the use of US alone. The rate of bactericide effect of US wave was increased in samples containing ampicillin. This process was influenced by the chemical and microbiological characteristics of aqueous media. Therefore, with further research about its practicality for treatment of wastewater, it may become a possible substitute process for wastewater disinfection.

KEYWORDS: Ultrasonic Irradiation, Pseudomonas Aeruginosa, Staphylococcus Aureus, Antibiotic, Ultrasonic Frequency

Date of submission: 17 Mar 2013, ***Date of acceptance:*** 18 May 2013

Citation: 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.

Introduction

Having many pathogenic, opportunistic microorganisms, and laboratory and pharmaceutical residues, hospital wastewaters are considered as a threat to the public health and environment compared to the municipal wastewater. Therefore, to provide the community health and to prevent the environmental contamination, such wastewaters should be collected in accordance with technical and sanitary regulations, and be properly treated, disinfected and discharged. However, due to the indiscriminate and inappropriate use of different types of disinfectants and the incidence of resistant strains in such centers, not only specific problems have been created (for example nosocomial infections, which is one of the very important health issues[1,2]), but also problems related to the wastewater treatment operations and assurance of an effluent safe and free from microbial agents have been formed. Therefore, disinfection of such types of wastewater and specific look to the new and efficient disinfection methods has always been emphasized.

During recent years, application of ultrasound

Corresponding Author:
Afshin Maleki
Email: maleki43@yahoo.com

(US) as an efficient and powerful technology has been considered in different disciplines of environmental engineering including water and wastewater disinfection. US results in inactivation of bacteria through the physical, mechanical and chemical mechanisms. During the bubbles explosion, a considerable energy is generated. As a result, the pressures and pressure gradients will cause mechanically weakening and finally destroys bacteria cell wall. Of course, the generated radicals have impact on the biological agents. These free radicals attack to the chemical structure of bacterial cell wall and cause cell wall weakening and destruction.[3] But the most effective way for killing biological agents is the mechanical effects resulted from the bubbles exploding. The microorganisms' cell membrane is decayed because of the pressure intensity produced. These effects include complete destroy or death of microorganisms or bigger organisms and lysis of cell membrane, which results in cell death.[4] On the other hand, application of antibiotics is always considered; not only because of creating antibiotic resistance, but also because of their antimicrobial properties. Therefore, since both US and antibiotics destroy the microbial agents, there is a possibility that their simultaneous application has synergetic effect so that the resistant strains become more sensitive to US and their removal efficiency be increased. Thus, the main objective of the present study was to study the effect of US alone and combined with antibiotic on Pseudomonas aeruginosa (P. aeruginosa) and Staphylococcus aureus (S. aureus), which are among the most important and common infectious agents shown resistance against a wide range of antibiotics.[5,6].

Materials and Methods

It is an experimental-applied study conducted at lab scale at Faculties of Health and Medicine of Kurdistan University of Medical Sciences, Sanandaj, Iran, in 2011. Based on the study aims, the methodology consisted of two parts. In the first part, we handled the P. aeruginosa and S. aureus bacteria obtained from the hospital environment. Therefore, first water samples from different parts of Sanandaj's hospitals (burn, dialysis, operating room, members exchange wards, etc.) were collected and in order to conduct the required tests (temperature, water pH and chlorine content and culturing), they were transferred to the Faculties of Health and Medicine. Then, the loop was cultured on MacConkey and blood agar medium. We used gram strain to identify the microorganisms grown on culture media.[7,8] According to standard methods, oxidase test for gram negative and catalase test for gram-positive bacteria were performed. Differential test was done to detect the Enterobacteriaceae family.[8] After identification of P. aeruginosa and S. aureus, different concentrations [10^2, 10^4, 10^6, and 10^8 colony forming units (CFU)/ml] of both bacteria were prepared and at different time intervals (including 25, 50, 75, and 100 minutes) and in presence of a blank, they were exposed US. The irradiation source of US was a sonoreactor device (Elmasonic P30H, Germany), equipped with a 37 kHz plate adapter with maximum 400 watts power at the laboratory scale. In order to determine the type of antibiotic to be used, the antibiotic susceptibility test was performed using nine antibiotic discs (including amikacin, cotrimoxazole, ampicillin, tetracycline, amoxicillin and vancomycin). Finally, ampicillin was selected and antibiotic doses of 10, 20, and 40 µg were prepared using its 1 g vial. Later, each one was evaluated for its effect on desired bacteria surveillance individually and combined with US for 100 minutes.

In the second part, first strains of P. aeruginosa (PTCC1074) and S. aureus (PTCC1112) were prepared from the Collection Center for Industrial and Infectious Fungi and Bacteria of Iran (Organization of Scientific and Industrial Research of Iran) and cultured according to standard recipes. All stages of the ultrasonic and antibiotics effects on the standard strains were performed according to the first part of study on the isolated strains from hospital environment.

Results and Discussion

In this study, ultrasonic wave's efficiency on degradation of P. aeruginosa and S. aureus and also effect of these waves on effectiveness and improvement of ampicillin on eradication of the resistant strains to this antibiotic has been investigated. Table 1 shows the results of the ultrasonic wave's effect on the strains obtained from environment and on the standard strains of P. aeruginosa and S. aureus over 100 minutes irradiation at different concentrations of each bacteria. As table 1 indicates, the effect of US on reducing the number of P. aeruginosa was more than S. aureus. After 100 minutes, removal of standard strain of P. aeruginosa and S. aureus became 72% and 63% at initial concentration of 10^8 CFU/ml, respectively. These results match well with findings of Villamiel and De Jong.[9] They observed that P. fluorescens (gram negative bacterium) was more sensitive to US compared with S. thermophilus (gram negative bacterium).[9]

Alliger has expressed similar results in the gram-positive bacteria more resistant to US.[10] This difference is due to the characteristics of the bacterial cell wall. Gram-positive bacteria usually contain a dense, strong and thick layer of peptidoglycan compared with gram-negative bacteria so that makes gram-positive bacteria more resistance to US.[11] However, it is believed that the effects of US on the gram-positive and gram-negative bacteria is not yet completely clear.[9] Even some researchers did not observe a significant difference with reference to the effect of US between gram-positive and gram-negative bacteria. In this regard, Scherba et al. studied the effect of US on P. aeruginosa and E. coli (gram-negative bacteria) and S. aureus and B. subtilis (gram positive bacteria) and did not notice any difference between gram positive or gram negative bacteria in terms of the efficiency of ultrasonolysis process.[12] They argued that the main cause of bacteria destroying was the effect of US on the bacterial cytoplasmic membrane; and cell wall is less affected.[12] No significant difference between gram-positive and gram-negative bacteria was observed.

Another notable factor was the effect of process time and bacteria concentration on the removal yield. As table 1 indicates, the bactericide effect of US has increased with time; the concentration of P. aeruginosa and S. aureus from 22 and 19 percent at t = 25 minutes was increased to 69 and 60 percent at t =100 minutes, respectively. These results are consistent with Scherba et al. findings, as they also observed the same trend during their research.[12] However, the linear relationship between contact time and removal percentage of bacteria is logic, and as exposure time of microbial agent with bactericide agent increases, definitely opportunity for the effect of antimicrobial agent increases and removal yield increases. Hence, our results revealed that reducing bacteria concentration enhanced the removal efficiency because reducing number of bacteria results in increasing the possibility of exposure to the ultrasonic wave's irradiation, which in turn, their destroying percent would increase. Therefore, it is noted that reducing the concentration from 10^8 CFU/ml to 10^2 CFU/ml in 100 minutes caused increasing removal efficiency of P. aeruginosa and S. aureus from 69 to 88 percent and from 60 to 77 percent, respectively.

All of the abovementioned experimental procedures were repeated for the standard strains of those bacteria obtained from the media as there is possibility that different bacteria manifest different resistant against ultrasonic irradiation (Table 1). It is noteworthy that no tangible and significant difference was observed between the removal efficiency of standard and media bacteria strains. Although the media strain has shown resistant to some types of antibiotics, this resistant did not have any influence on the efficiency of US in bacteria elimination. Considering that the resistance is a genetic trait and concerns with plasmid,[13] it is concluded that the mechanisms leading to drug resistance or in other words a bacteria resistance, does not cause any change in the sensitivity of bacteria against the US.

Table 1. Removal percentage of P. aeruginosa and S. aureus using ultrasonolysis process under different conditions

Bacteria strain	Bacteria concentration (CFU/ml)	Contact time (min)				
		0	25	50	75	100
P. aeruginosa (isolated from hospital)	10^2	0	38	61	77	88
	10^4	0	33	55	68	80
	10^6	0	25	44	64	74
	10^8	0	22	35	59	69
P. aeruginosa (standard strain)	10^2	0	41	66	82	92
	10^4	0	35	58	72	86
	10^6	0	28	41	69	81
	10^8	0	25	32	61	72
S. aureus (isolated from hospital)	10^2	0	34	48	63	77
	10^4	0	27	44	53	69
	10^6	0	22	37	49	62
	10^8	0	19	32	43	60
S. aureus (standard strain)	10^2	0	35	52	65	79
	10^4	0	30	47	55	71
	10^6	0	24	41	53	65
	10^8	0	20	34	45	63

CFU: Colony forming units; P. aeruginosa: Pseudomonas aeruginosa; S. aureus: Staphylococcus aureus

Considering the genetic origin of acquiring resistance in bacteria, they manifest different response against the different antibiotics. Therefore, we evaluated the studied bacteria resistance in presence of nine different antibiotics and it was revealed that the studied bacteria were resistant against co-trimoxazole, ampicillin, amoxicillin, and tobramycin and ultimately the effect of ampicillin along with US was studied (Table 2).

The results achieved from this research indicated that the removal efficiency against bacteria is more when combined antibiotic and ultrasonic irradiation is used; this efficiency was less when only the ultrasonolysis process was applied (Figure 1 and 2).

This difference has been contributed to the increase in release of antibiotics from the cell wall liposaccharide layer and its penetration into cell because of the exposure with ultrasonic irradiation. Similar results have been reported by other researchers; for example Johnson et al. studied the combined effect of ultrasonic 70 kHz frequency and the gentamicin antibiotic on reducing E. coli and observed 97 percent reduction in number of bacteria within 2 hours.[14] In another study, Rediske et al. has reported a 2-log increase in mortality of P. aeruginosa by combined process of ultrasonic irradiation and erythromycin antibiotic.[15] It is noteworthy that this efficiency increase cannot be only attributed to antibiotic constituents and in general, ultrasonic irradiation increase bacteria sensitivity to bactericidal agents.[16]

Table 2. Antibiotic resistance of isolated bacteria from hospital

Antibiotic Type	P. aeruginosa	S. aureus
Amoxicillin	Resistance	Resistance
Tobramycin	Resistance	Intermediate
Amikacin	Sensitive	Resistance
Co-trimoxazole	Resistance	Sensitive
Ampicillin	Resistance	Resistance
Tetracycline	Intermediate	Sensitive
Carbenicillin	Resistance	Sensitive
Vancomycin	Resistance	Resistance
Ciprofloxacin	Sensitive	Intermediate

P. aeruginosa: Pseudomonas aeruginosa; S. aureus: Staphylococcus aureus:

Conclusion

In this study, the destruction of P. aeruginosa and S. aureus was assessed using US in the presence of ampicillin. Our results showed that first, US had ability to destroy both bacteria and second, compared to S. aureus, P. aeruginosa bacteria are

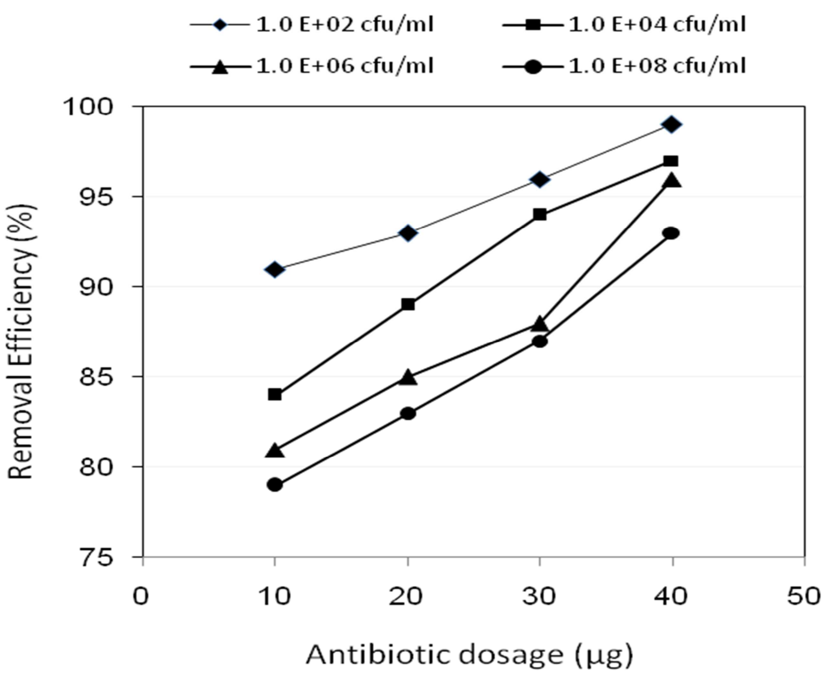


Figure 1. Removal efficiency of isolated P. aeruginosa from hospital under ultrasonic irradiation with ampicillin (t = 100 minutes)

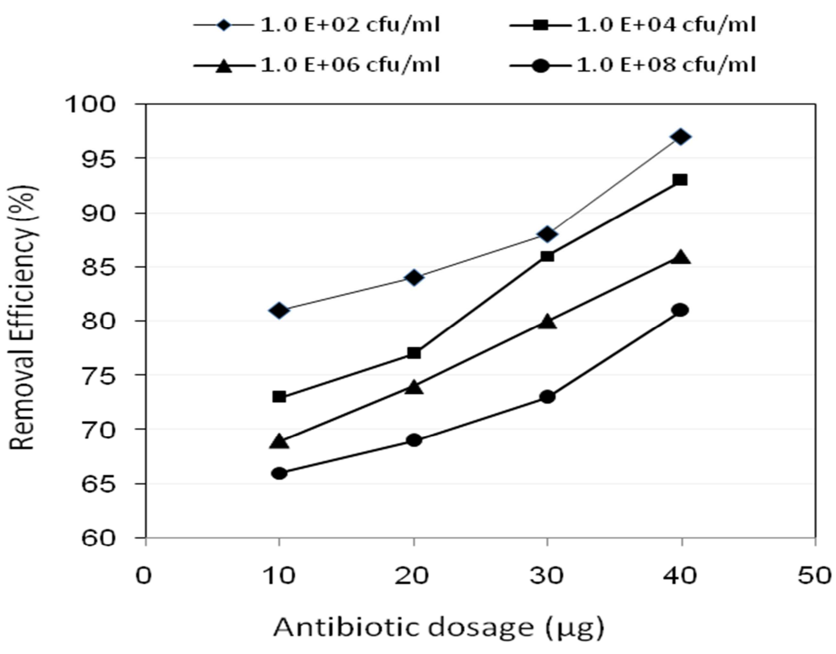


Figure 2. Removal efficiency of isolated S. aureus from hospital under ultrasonic irradiation with ampicillin (t = 100 minutes)

more resistant against US. It was also revealed that the studied bacteria are resistant to ampicillin. Therefore, we studied the effect of ampicillin in presence of US and it was noticed that simultaneous application of US together with antibiotic is more efficient in removing bacteria compared with applying US alone, which can be attributed to the synergistic effect.

The ultrasonolysis experiments on the standard strains of the abovementioned bacteria showed no significant difference in removal efficiency between standard and media strains. Thus, it was revealed that the bacteria resistant had no effect on the destruction efficiency of US.

Conflict of Interests

Authors have no conflict of interests.

Acknowledgments

This study was supported by School of Health, Kurdistan University of Medical Sciences. Therefore, the authors are thankful to all of the peoples facilitated the required conditions for conducting this project.

References

1. Kasper DL. Harrison's principles of internal medicine. Vol 1. 16th ed. New York, NY: McGraw-Hill, Medical Publishing Division; 2005.
2. Eriksen HM, Iversen BG, Aavitsland P. Prevalence of nosocomial infections in hospitals in Norway, 2002 and 2003. J Hosp Infect 2005; 60(1): 40-5.
3. Mason TJ, Joyce E, Phull SS, Lorimer JP. Potential uses of ultrasound in the biological decontamination of water. Ultrason Sonochem 2003; 10(6): 319-23.
4. Phull SS, Newman AP, Lorimer JP, Pollet B, Mason TJ. The development and evaluation of ultrasound in the biocidal treatment of water. Ultrason Sonochem 1997; 4(2): 157-64.
5. Delissalde F, Amabile-Cuevas CF. Comparison of antibiotic susceptibility and plasmid content, between biofilm producing and non-producing clinical isolates of Pseudomonas aeruginosa. Int J Antimicrob Agents 2004; 24(4): 405-8.
6. Kluytmans J, van Belkum A, Verbrugh H. Nasal carriage of Staphylococcus aureus: epidemiology, underlying mechanisms, and associated risks. Clin Microbiol Rev 1997; 10(3): 505-20.
7. Baron J, Finglod S. Methods for identification of ethiologic agents of infections diseases. In: Forbes BA, Sahm DF, Weissfeld AS, Bailey WR, editors. Baliy and Scottos diagnostic microbiology. 12th ed. New York, NY: Elsevier Mosby; 2007.
8. Eaton AD, Franson MAH, American Public Health Association. Standard methods for the examination of water and wastewater. 21th ed. Washington, DC: American Public Health Association; 2005.
9. Villamiel M, De Jong P. Inactivation of Pseudomonas fluorescens and Streptococcus thermophilus in Trypticase® Soy Broth and total bacteria in milk by continuous-flow ultrasonic treatment and conventional heating. Journal of Food Engineering 2000; 45(3): 171-9.
10. Alliger H. Ultrasonic disruption. American Laboratory 1975; 10: 75-85.
11. Piyasena P, Mohareb E, McKellar RC. Inactivation of microbes using ultrasound: a review. Int J Food Microbiol 2003; 87(3): 207-16.
12. Scherba G, Weigel RM, O'Brien WDJr. Quantitative assessment of the germicidal efficacy of ultrasonic energy. Appl Environ Microbiol 1991; 57(7): 2079-84.
13. Todar K. Bacterial resistance to antibiotics [Online]. [cited 2008]; Available from: URL: http://textbookofbacteriology.net/resantimicrobial.html
14. Johnson LL, Peterson RV, Pitt WG. Treatment of bacterial biofilms on polymeric biomaterials using antibiotics and ultrasound. J Biomater Sci Polym Ed 1998; 9(11): 1177-85.
15. Rediske AM, Rapoport N, Pitt WG. Reducing bacterial resistance to antibiotics with ultrasound. Lett Appl Microbiol 1999; 28(1): 81-4.
16. Mason TJ. Developments in ultrasound--non-medical. Prog Biophys Mol Biol 2007; 93(1-3): 166-75.

Journal of Advances in Environmental Health Research

Effluent quality of ammonia unit in Razi petrochemical complex

Nadali Alavi[1], Payam Amir-Heidari[2], Roza Azadi[3], Ali Akbar Babaei[1]

1 Environmental Technologies Research Center AND Department of Environmental Health Engineering, School of Public Health, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran
2 Department of Chemical Engineering, Amirkabir University of Technology, Tehran, Iran
3 Department of Environmental Health Engineering, School of Public Health, Ahvaz Jundishapur University of Medical Sciences, Ahvaz, Iran

Original Article

Abstract
Establishment of great industrial centers and ports along the Khur-Musa Estuary in Mahshahr Port (Khuzestan, Iran) have been discharged a high volume of industrial and non-industrial pollutants to this estuary. The most important pollutants in Khur-Musa include industrial wastes and effluents including ammonia and urea units. This research aimed to survey the qualitative parameters of effluent of ammonia unit No. 3 in Razi petrochemical complex, and comparing these parameters to the allowable effluent discharge standards in Iran. The main objective of this study was to investigate the performance of this unit, and providing proper solutions to solve the existing problems. Thus, at first, the process of production and sources of pollutants in the effluent were recognized and sampling points were determined. The data were collected by examinations on parameters chemical oxygen demand (COD), total suspended solids (TSS), nitrite ion (NO_2), nitrate ion (NO_3), pH, and (ammonia ion) NH_4, during a consecutive six-month period. The results of the measurements were recorded monthly, weekly, and daily. The results showed that the COD and the concentration of ammonia and nitrate ions in the effluent of studied unit were considerably higher than allowable values stated in the national standards of Iran. Comparison between stated parameters in the six-month period of sampling indicated a more desirable trend for the value of studied parameters in the last month of the study (September). In order to upgrading effluent treatment system, an effective action plan could be provided to optimize the current status of effluent from ammonia unit in Razi petrochemical complex.

KEYWORDS: Ammonia Unit, Petrochemical Complex, Effluent, Qualitative Parameters

Date of submission: 29 Oct 2012, ***Date of acceptance:*** 28 Jan 2013

Citation: Alavi N, Amir-Heidari P, Azadi R, Babaei AA. **Effluent quality of ammonia unit in Razi petrochemical complex.** J Adv Environ Health Res 2013; 1(1): 15-20.

Introduction

Environment is a great and complex set of diverse elements which has been formed as a result of gradual evolution of organisms and components of the earth's crust; therefore it affects the human activities and is affected by them. Human activities for development, in any way, will have different impacts on the environment. This impact is mostly caused by industrial development.[1] Through the two recent centuries, global nitrogen cycle has been changed substantially due to different human activities. Today nitrogen compounds enter into water bodies, in addition to natural sources, from man-made sources such as industrial wastes, untreated sewage, and effluent from waste treatment plants.[2] The main problem with the presence of nitrogen compounds in the effluents discharged to environment is consumption of dissolved oxygen in water, which may create great risks for aquatic ecosystem and marine life.[3] Razi

Corresponding Author:
Ali-Akbar Babaei
Email: babaei-a@ajums.ac.ir

petrochemical complex is one of the old petrochemical complexes in Iran, with 40 years of history in producing chemical fertilizers. This complex now is located in Mahshahr special economic zone (SEZ) and produces 675 tons of ammonia per year.

Establishment of great industrial centers and ports along the Khur-Musa Estuary has been discharged a high amount of industrial and non-industrial pollutants to this estuary. The most important pollutants in Khur-Musa include industrial wastes and effluents, overflow of produced ammonia and urea, sewages containing chemicals, and oil spill resulted from accidents in oil tankers and rigs. Khur-Musa with a wide grid of small estuaries has provided a favorable condition for the presence of aquatics; so that many commercial and non-commercial species permanently live in this area. In addition, many of these species use this estuary as a suitable place for spawning and as nursery.[4]

In addition to having valuable aquatics, Khur-Musa accepts a lot of rare migratory and native birds. In order to preserve this valuable ecosystem, it is essential to have more supervision on performance of petrochemical units in this area, particularly the ammonia unit.

The activity of Razi petrochemical complex, in addition to impacts on valuable ecosystem in Khur-Musa, will affect the neighboring cities such as Bandar Imam Khomeyni (BIK) and Bandar-e Mahshahr, and it may affect the health of residents in these cities. Therefore recognizing the negative impacts of this complex on environment is very important.[5] Since the petrochemical industries in Mahshahr port and Mahshahr SEZ are established close to the Khur-Musa Estuary and discharge their effluents to this water resource, and since the Khur-Musa is one of the special ecosystems located at the north of the Persian Gulf, this estuary is very important mainly due to its geographical position and biodiversity.

The objective of this research was surveying the qualitative parameters of effluent from ammonia unit No.3 in Razi petrochemical complex, in order to identify the current status of sources and values of pollutants emission, to decide on controlling strategies for minimizing pollutants in this industrial complex.

Materials and Methods

The ammonia unit is one of the most important production units in Razi petrochemical complex, whose main feed is sure natural gas, which is transmitted to this unit via a 174 km line from Masjed Soleyman gas wells. The unit produces 675 tons of ammonia per year. After mixing with steam and after reactions in the primary modifier, methane is converted to hydrogen (H_2), carbon monoxide (CO), and carbon dioxide (CO_2). CO_2 is the by-product of ammonia unit, which is transmitted to urea unit after separation.

The complementary reaction is completed in the secondary modifier by injecting air; and the required nitrogen for ammonia production simultaneously enters into the process by this air. The mixture of nitrogen and hydrogen, which is called synthesis gas, following the compression at special pressure and temperature, is converted to ammonia in catalytic reactor.

The main amount of produced ammonia is used for production of urea and diammonium phosphate (DAP) fertilizers in the Razi petrochemical complex, and the remainder is supplied to international markets. Optimization of ammonia unit started in 1995 and the modernization operation of this unit was finished in 2000.[6]

After determining the boundary of the system, the sampling points were determined using existing maps and by consulting with industrial managers. According to the type of study process, since the system was closed, two sampling stations were selected for sampling and measurement of pollution parameters of effluent. In the first station, the inlet flow to the pretreatment system, corrugated parallel interceptor (CPI), and in the second station, the outlet flow from ammonia unit were selected for sampling. In these two stations, the qualitative parameters of the effluent, including pH, total suspended solid (TSS) (Method 2540D), ammonia ion (NH_3) (Method 4500-NH_3 F), nitrate ion (NO_3) (Method 4500-NO_3 B), nitrite ion (NO_2) (Method 4500-NO_2 B), and chemical oxygen demand (COD) (Method 5220 B) were measured according to standard methods for water and wastewater sampling and analysis.[7,8]

Grab and composite samplings were done during a continuous 6-month period, as the following:

a) Monthly sampling (from April to September), which was done once per month for each of the effluent polluting indexes.

b) Weekly sampling, which was done during 4 consecutivet weeks in the fourth month of study (July) for the polluting parameters of the effluent.

c) Daily sampling, which was done in 6 days of the last week of fifth month (August).

d) Composite sampling (hourly); due to fluctuations in the quality of effluent in the case of COD measuring this type of sampling was done just for measuring this parameter.

It should be mentioned that each composite sample is a mixture of samples which were collected in 4-hour intervals in each day, and this experiments were repeated in 3 consecutive days. After collecting the required data and performing the experiments, the results were compared to the standard values issued by The Iranian Department of Environment.

Results and Discussion

pH

The minimum and maximum values of pH were 7.6 and 9.2, respectively. The minimum and maximum values of this parameter were measured in September and June, respectively. The standard deviation of this parameter was 0.428 (Table 1 and 2).

Ammonia (NH_4)

The average value of measured ammonia ion during the six-month sampling period (monthly, weekly, and daily) was 152.36 mg/l. The minimum value (25 mg/l) and maximum value (426 mg/l) of ammonia in the sampling period were related to weekly sampling (2nd week of July) and monthly sampling (August), respectively. The value of this parameter in the sampling period had many fluctuations; and the standard deviation of that was 63.26 (Table 1).

Table 1. Average values of effluent qualitative parameters

Time Period / Parameter	Monthly average (mg/l)	Weekly average (mg/l)	Daily average (mg/l)	Compound average (mg/l)	Allowable value (mg/l)
pH	8.2	8.67	8.98	-	6.5-8.5
NH_4	101	102.75	132.83	-	2.5
NO_2	9.5	11.37	11	-	10
NO_3	65.3	77.25	78	-	50
COD	240	426.5	282.66	105	100
TSS	179	59	58.16	-	-

COD: Chemical oxygen demand; TSS: Total suspended solid

Table 2. Concentration of effluent pollutants during the total period of sampling

Time Period / Parameter	Total average concentration (mg/l)	Maximum concentration (mg/l)	Minimum concentration (mg/l)	Standard deviation (SD)
pH	8.61	10.5	7.8	0.428
NH3	112.19	528	25	63.26
NO2	10.62	15	6	1.56
NO3	73.51	162	40	29.79
COD	316.38	850	124	24.63
TSS	98.72	64	32	45.92

COD: Chemical oxygen demand; TSS: Total suspended solid

Nitrate (NO_3)

The minimum and maximum nitrate concentrations in the sampling period were 162 and 40 mg/l, respectively. The average value observed was 73.51 mg/l. The standard deviation of nitrate concentration was 29.8 (Table 1).

Nitrite (NO_2)

The total average value of nitrite in the six-month period of sampling (monthly, weekly, and daily) was 10.62 mg/l. The minimum and maximum value of nitrite in the sampling period was related to monthly sampling (April) and weekly sampling (4th week of July), respectively. The standard deviation of this parameter was 1.56 (Table 1).

COD

COD is a criterion used for determination of power and level of pollution in domestic and industrial wastes. This parameter is also useful for analyzing industrial wastewaters and also for determination and control of organic matter content removal resulted in wastewater treatment plants. The average value of this factor in the sampling periods (monthly, weekly, and daily) was 100 mg/l. The average value of this factor in the composite sampling was 105 mg/l, which is nearly equal to the standard limit. It also should be mentioned that the value of this parameter had many fluctuations in the sampling periods. The minimum and maximum value of this parameter during the sampling periods was related to daily sampling and weekly sampling (the 1st week of July), respectively, and the standard deviation of this parameter in the six-month sampling period was 24.63 (Table 1).

Total Suspended Solid (TSS)

In this research, during the six-month sampling period, the average TSS was 98.72, and the maximum (179 mg/l) and minimum (59 mg/l) values of it were measured in September and April, respectively (Table 1).

Conclusion

pH

As shown in table 1, the total average value of pH is a bit higher than allowable range of discharge to surface waters (6.5-8.5). The six-month trend of changes in the pH of effluent in the studied unit indicates that in the 66% of the cases, this factor was higher than the allowable limits (Figure 1). pH of ammonia nitrate unit effluent in Shiraz petrochemical complex was high (average 10, and maximum 10.8), as well,[9,10] which indicated that the high volume of ammonia production in both of these two complexes increased the pH in their effluent.

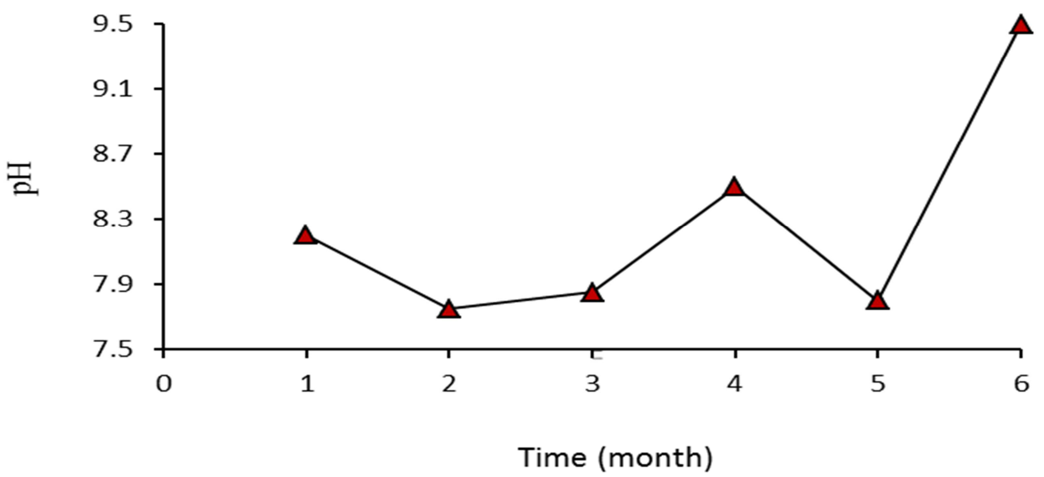


Figure 1. Monthly pH changes trend in effluent from ammonia unit in Razi petrochemical complex

Ammonia (NH_4)

The average value of the measured ammonia ion during the six-month sampling period (monthly, weekly, and daily) was much higher than the standard allowable value (2.5 mg/l) for discharge to surface waters. The results of sampling (monthly, weekly, and daily) indicated that in 100% of the cases, the value of this parameter in the effluent was higher than the standard allowable limit (Figure 2). Discharging this effluent without treatment is a threat to receiving waters. The results of similar researches on quality of effluent from ammonia nitrate unit in Shiraz petrochemical complex showed that the effluent of zone 2 in that complex had a high concentration of ammonia. The average concentration of ammonia of effluents discharging to water body was also 600 mg/l; and in the effluents discharging to lagoon this value was 910 mg/l, which can be returned to water treatment unit, if its ammonia is separated.[10] Therefore, since the outlet effluent from the under study unit and the other units of Razi petrochemical complex, after a primary treatment, are directly discharged to sea, this treatment is not enough ever, and the outlet effluent contains high value of NH_4 and COD.

Nitrate (NO_3)

According to figure 3, the total average value of nitrate in the sampling period (monthly, weekly, and daily) was also higher than allowable standard value (50 mg/l) for discharge to surface waters. According to the results of measuring nitrate parameter in the six-month sampling period (monthly, weekly, and daily), in the 62.57 % of the cases, the value of nitrate was higher than the standard allowable limit. According to a comparison between the value of nitrate in the studied unit and that in the ammonia nitrate unit of Shiraz petrochemical complex (average 1830 mg/l and maximum 3040 mg/l),[10] the discussed parameter in Razi petrochemical complex was much closer to standard allowable limit. Furthermore, the fluctuation of this parameter in the sampling period was not considerable.

Nitrite (NO_2)

As illustrated in figure 4, the total average value of nitrite in the six-month period of sampling (monthly, weekly, and daily) was almost equal to the standard allowable value (10 mg/l) for discharge to the surface waters.

According to the US Environmental Protection Agency (EPA) guidelines, the concentration of nitrite in drinking water should be less than 1 mg/l based on nitrogen. Moreover, its value in the effluent discharging to water sources must be less than 10 mg/l based on nitrogen. The average value of measured nitrite in the six-month sampling period was less than the standard allowable value (10 mg/l) for discharge to surface waters. One reason for the low value in effluents is its instability in the aqueous environments, and its conversion to nitrate.

COD

Chemical oxygen demand is a criterion used for determination of power and level of pollution in domestic and industrial wastes. This parameter is also useful for analyzing industrial wastewaters and also for determination and control of organic matter content removal resulted in wastewater treatment plants. The average value of this factor in the sampling periods (monthly, weekly, and daily) was higher than the standard allowable limit (100 mg/l) for discharger to surface waters; and the value of this parameter in all of the sampling periods was higher than the standards limit (Figure 5).

It should be mentioned that this parameter had many fluctuations in the sampling period, and this was probably due to process and equipment failure, operation errors, occasional or annual maintenance, etc. In the similar researches in the Bandar Imam petrochemical complex, the monthly average value of COD was reported 328 mg/l, which was higher than measured values in Razi petrochemical complex and the allowable standard limit.[5] In other researches in this complex, the annual average of COD was reported 220 mg/l.[11]

Total Suspended Solids (TSS)

The changing trend of this parameter in the sampling period had many fluctuations (Fig. 6). In a similar research in Bandar Imam petrochemical complex, in 2008 and 2009, the annual average value of this parameter in the outlet effluent from that complex was reported less than 100 mg/l, which is relatively less than that of Razi petrochemical complex.

Management Strategies

Following actions and management strategies are recommended for control of pollutants in the effluent of studied unit:

- Establishing and commissioning of waste treatment plant, considering the quality of outlet effluent from different units
- Performing actions to increase the performance of pollutants removal, including:

- Recovery of ammonia from effluent, through concentration and returning to ammonia production unit
- Diluting with hygienic waste to decrease the concentration of dissolved solids
- Establishing a treatment unit for ammonia removal at the beginning of the system
- Establishing a system to increase nitrification at the beginning, and then removing nitrate by de-nitrification processes at the end.

Decreasing the volume of effluent in the studied units.

Recommendations

Based on the results of experiments on qualitative parameters of the effluent during the six-month period of sampling (monthly, weekly, and daily), the results of measurement of ammonia, nitrate, and chemical oxygen demand were several times greater than the standard allowable limits obligated by Iranian Department of Environment for discharge to surface waters.

Conflict of Interests

Authors have no conflict of interests.

Acknowledgements

The authors would like to thank the Research and Technology Deputy of Ahvaz Jundishapur University of Medical Sciences for their financial support.

References

1. Chowdhury N, Nakhla G, Zhu J. Load maximization of a liquid-solid circulating fluidized bed bioreactor for nitrogen removal from synthetic municipal wastewater. Chemosphere 2008; 71(5): 807-15.
2. Rabalais NN. Nitrogen in aquatic ecosystems. Ambio 2002; 31(2): 102-12.
3. Waki M, Yokoyama H, Ogino A, Suzuki K, Tanaka Y. Nitrogen removal from purified swine wastewater using biogas by semi-partitioned reactor. Bioresour Technol 2008; 99(13): 5335-40.
4. Department of Planning and Budget of Khuzestan Province, (Department of Economic Affairs. Mahshahr city socio-economic report. Mahshahr, Iran: Department of Planning and Budget of Khuzestan Province; 2007. [In Persian].
5. Sabz Ali Pour S, Jafarzadeh Haghighifard N, Monavari M, Mojtahed Zadeh Z. Qualitative survey of the effluent from the olefin unit of bandar-e-imam petrochemical complex. Water and Wastewater 2007; 18(3): 39-49.
6. Razi Petrochemical Co. Razi Petrochemical Product Line Graph [Online]. [Accessed 2013 Oct 9]; Available from: URL: http://www.razip.com/aboutus-complex-fa.html#10 [In Persian].
7. American Society for Testing and Materials. Annual Book of Astm Standards 2002: Section Eleven, Water and Environmental Technology: Water (Ii). Conshohocken, PA: American Society for Testing & Materials; 2002.
8. Eaton AD, Franson MA, American Public Health Association. Standard Methods for the Examination of Water and Wastewater. Washington, DC: American Public Health Association; 2005.
9. Nasry Z. Investigations into the Quality of Wastewater in Iranian Industries. Journal of Water & Wastewater 2001; 16(40): 57-67.
10. Moula D. Survey of effluent quality and quantity of Shiraz petrochemical complex [Project]. Shiraz, Iran: Affairs Research and Development of Shiraz Petrochemical Complex; 2001. [In Persian].
11. Emami M. Corporate environmental responsibility in Bandar Emam Petrochemical Co. Proceedings of the International Conference on Environment; 2008 Dec 15-17; Penang, Malaysia.

Journal of Advances in Environmental Health Research

Investigation of potato peel-based bio-sorbent efficiency in reactive dye removal: Artificial neural network modeling and genetic algorithms optimization

Afshin Maleki[1], Hiua Daraei[1], Farzaneh Khodaei[1], Kolsum Bayazid-Aghdam[1], Reza Rezaee[1], Ali Naghizadeh[2]

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

Original Article

Abstract

Over the last few years, a number of investigations have been conducted to explore the low cost sorbents for the decontamination of toxic materials. Undoubtedly, agricultural waste mass is presently one of the most challenging topics, which has been gaining attention during the past several decades. Wastes are very cheap and easily available material in production of sorbent. Therefore, the Reactive Red 198 (RR198) removal efficiency from aqueous solutions by potato peel powder based sorbent (PP) was examined in this study. The Taguchi method was used in combination with full factorial methods to design the experiments. Based on the design of experiment outputs, 18 experimental sets were designed and the experiments were done in accordance with the experimental design. The sorption handmade batch reactor consists of a 200 ml beaker, 100 RPM magnetic stirrer, and a sampling port. Then, the experimental data were collected under desired conditions. In each sample sorbent was separated using a centrifuge (3000 rpm and 5 minutes). Then, dye concentrations were determined based on Beer's law and calibration plots using a UV-visible spectrophotometer. The wavelength resolution and the bandwidth were, respectively, 1 and 0.4 nm. The length of the optical path in glass cell was 1 cm. The maximum absorption wavelength was determined in each run to compensate the matrix effects. The results revealed that PP is effective for the sorption of RR198 from aqueous solutions. The maximum sorption of PP from RR198 solution was determined as 93 mg/g. Artificial neural network (ANN) model of dye removal efficiency (DR%) was developed based on the experimental data sets. The ANN model was strongly validated using statistical tests. The R^2 and RMSE of the test set were 0.98 and 4.3, respectively. The results demonstrate that PP can be successfully used as sorbent for RR198 removal from aqueous solutions. The results revealed that experimental parameters strongly influence the DR% and different experimental conditions cause different DR% (from 0 to 93).

KEYWORDS: Sorption, Potato Waste Powder, Design of Experiment, Artificial Neural Network, Genetic Algorithm, Dye Removal

Date of submission: 10 Mar 2013, ***Date of acceptance:*** 12 May 2013

Citation: Maleki A, Daraei H, Khodaei F, Bayazid-Aghdam K, Rezaee R, Naghizadeh A. **Investigation of potato peel-based bio-sorbent efficiency in reactive dye removal: Artificial neural network modeling and genetic algorithms optimization.** J Adv Environ Health Res 2013; 1(1): 21-8.

Introduction

Water and wastewater pollutions like toxic or colorful organic materials (such as dyes, pesticides, organic solvents, and etcetera), and toxic inorganic materials (especially heavy metals) have been a great concern in recent years. Conventional treatment techniques of water and wastewater include sorption, filtration, precipitation, flocculation, membrane technology, and advanced oxidation process. In

Corresponding Author:
Hiua Daraei
Email: hiua.daraei@muk.ac.ir

developing countries, like Iran, industries cannot afford to use conventional wastewater treatment, because they are not cost-effective. Therefore, the search for new efficient technologies capable of treating contaminated waste water in a cost effective manner is underway.[1]

Among the numerous treatment technologies developed for the removal of pollutions from water, sorption is receiving increasing attention. The sorbent used in the sorption processes are various materials, including activated carbon, obtained from agricultural byproducts and commercial activated carbons. However, the high cost of the activation process limits its use in wastewater treatment, particularly for developing countries.[2]

Over the last few years, a number of investigations have been conducted to explore low cost sorbents for the decontamination of toxic materials. Undoubtedly, agricultural waste mass is presently one of the most challenging topics, which has been gaining attention during the past several decades. Wastes are very cheap and easily available materials in the production of sorbent. Production of sorbent from different wastes not only achieves the removal of pollutants in harmless forms but also has environmental effects of reducing waste. In previous studies, different substances such as fruit and vegetable wastes, cone, leaves, and etcetera have been employed.[3]

Potato waste is disposed as a zero value waste in many countries as part of the production of French fries, crisps, puree, instant potatoes, and similar products. The management problem of potato wastes causes considerable concern for potato industries; thus, implying the need to identify an integrated and environmentally-friendly solution. However, potato waste can be used as sorbent to remove most pollutants in aqueous solutions. The produced waste ratio and composition depends on the procedure applied; steam, abrasion, or lye peeling. Potato waste is almost 15% to 40% of influent potatoes and it consists of 55% potato skins, 33% starch, and 12% inert material.[4]

A high quality model can be applied to the process control. Applications of artificial neural network (ANN) and genetic algorithm have been successfully employed in environmental engineering for process modeling and optimization because of reliable, robust, and salient characteristics in capturing the non-linear relationships of variables in complex systems.[5]

ANN are parallel computational procedures consisting of highly interconnected processing element groups named neurons.[6] Owing to their inherent nature to model and learn complexities, ANNs have found wide applications in various areas of wastewater treatment.[7-10] ANN has been recently used for CR% (color removal) and energy consumption (EnC) modeling in electrocoagulation (EC).[11, 12]

Genetic algorithms (GA) are adaptive heuristic search algorithms based on the evolutionary ideas of natural selection and genetic. They belong to the larger class of evolutionary algorithms, which generate solutions to optimize problems by carrying out stochastic transformations inspired by natural evolution, such as inheritance, mutation, selection, and crossover.[13-16]

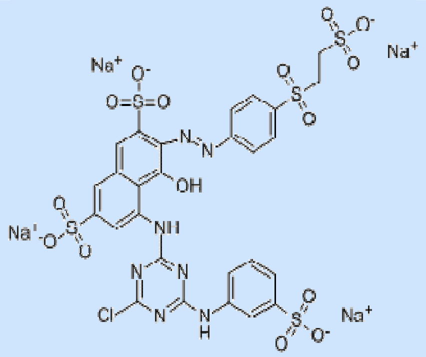
The present study had three objectives. First, to investigate the potential of PP as a sorbent in the removal of the model dye, Reactive Red 198 (RR198), from aqueous solutions. Second, DOE conducted studies to investigate the effects of five operational parameters: sorbent particle average size (S_z), initial pH (pH_0), dose of sorbent (D_s), initial dye concentration (C_0), and contact time (t_c) on sorption efficiency. The third objective was the application and assessment of ANN and GA for sorption system modeling and optimization.

Materials and Methods

RR198 was prepared from Alvan Sabet Co. (Iran). The chemical structure and some characteristics of this dye are shown in table 1. H_2SO_4 and NaOH were obtained from Merck. Distilled water was produced by a TKA Smart2Pure ultrapure water production system (Thermo Electron LED GmbH, Germany) for the preparation of dye solutions. UV-Vis spectrometer ($T90^+$ PG Instrument Ltd.)

was used for calibration curve and experimental measurements.

Table 1. The chemical properties of RR198

Molecular formula	C27H18ClN7Na4O15S5
Molecular structure	
Molecular weight	968.21
CAS number	145017-98-7

Potato wastes were collected from the garbage of local restaurants of Kurdistan University of Medical Sciences. Raw potato peal was washed with hot water to remove adhering dirt. Then, degradation was done by washing thoroughly with 1 M HCl solution and rinsing with distilled water several times. The degradation product was dried at 70ºC for 48 hours in order to gradually reduce the water content in the oven, crushed by a commercial mill, and sieved through two different sieve sizes with average size of 225 and 575 µm. The final product was stored in a sealed bottle for future application as sorbent.

The selected variables were S_z at two levels (225 and 575 µm), pH_0 at three levels (3, 7, and 11), C_0 at three levels (10, 50, and 100 mgl^{-1}), D_s at three levels (1, 5, and 10 gl^{-1}), and t_S at five levels (10, 30, 60, 90, and 150 min). A combined design of Taguchi for S_z, pH_0, C_0, D_s, and full factorial methods for t_c was used to design the experiments (DOE) using Minitab 14 (Minitab Inc., State College, PA, USA). The Taguchi was designed based on L_{18} orthogonal array with 4 factors. The order of experiments was made random in order to avoid noise sources, which could take place during an experiment. In these 18 experiments, the five levels of t_S were determined. All the selected experimental conditions can be seen in figure 1.[17]

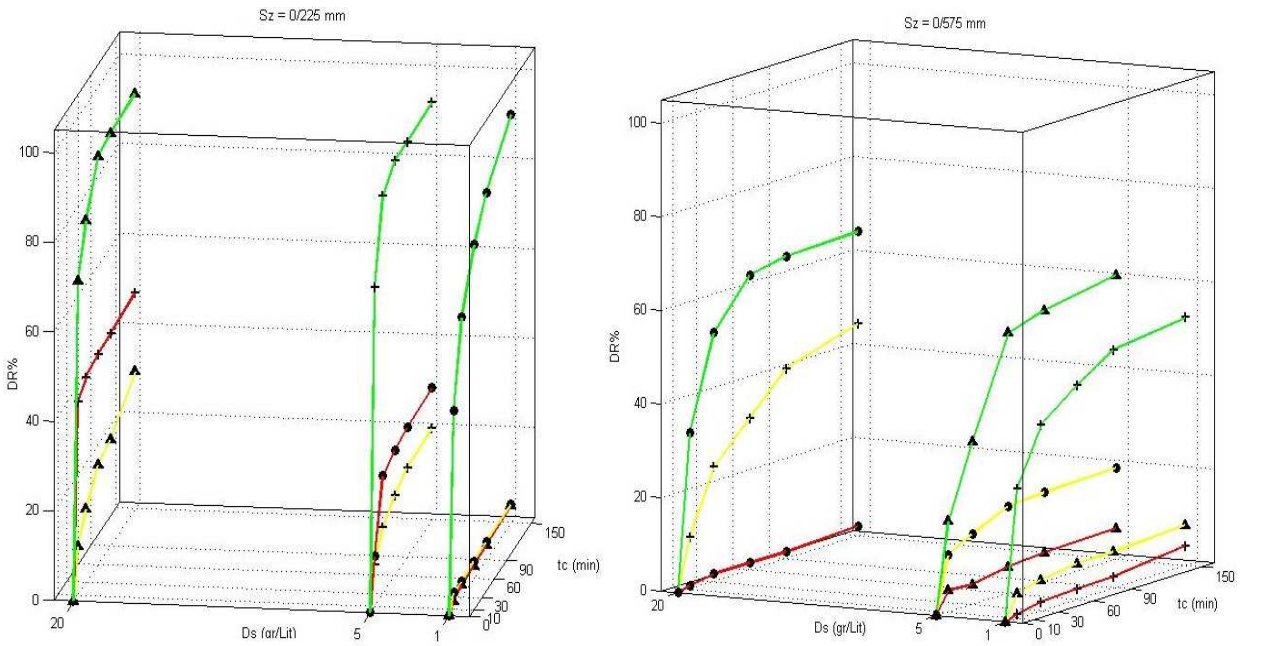


Figure 1. Ninety dye removal (DR%) of all 18 runs, green line (pH0 = 3), yellow line (pH0 = 7), red line (pH0 = 11), circle marker (C0 = 10 mg/l), plus sign marker (C0 = 50 mg/l), triangle marker (C0 = 100 mg/l)

To investigate the performance of synthetic wastewater containing DB41 using potato waste based sorbent in dye removal, DOE conducted sorption studies were carried out in batch experiments in a 200 ml beaker containing 100 ml DB41 and in room temperature as a function of S_z at two levels (225 and 575 µm), pH_0 at three levels (3, 7, and 11), C_0 at three levels (10, 50, and 100 mgl^{-1}), D_s at three levels (1, 5, and 10 gl^{-1}), and t_s at five levels (10, 30, 60, 90, and 150 min).

In each sample sorbent was separated using a centrifuge (3000 rpm and 5 minutes). Then, dye concentrations were determined based on Beer's law and calibration plots using a UV-visible spectrophotometer. The wavelength resolution and the bandwidth were, respectively, 1 and 0.4 nm. The length of the optical path in glass cell was 1 cm. The maximum absorption wavelength was determined in each run to compensate the matrix effects. The calibration plot was constructed in the range of each run concentration. The calibration plots usually provided a determination coefficient close to 99.9%. These data were used to calculate the sorption capacity of the sorbent. In most cases, an accurate dilution was necessary to obtain a measurable absorption. The percentage of dye uptake by the sorbent was computed using the equation:

$$\% \text{ Sorption} = (C_t - C_e)/C_t \times 100$$

where C_0 and C_t were the initial centrifuged sample and final concentration of RR198 in the solution, respectively.

The 90 data of dye removal (DR%) together with corresponding experimental conditions were used as a data set. The five operational parameters were considered as inputs of models whilst the DR% was considered as dependent variable. Data set was randomly divided into three parts; 60% as a training set, 20% as a validation set, and 20% as testing set. The ANN models were constructed based on the same datasets for both DR%. The multiple linear regression (MLR) and ANN models were constructed as two most popular linear and nonlinear models for comparison. For the ANN model, back propagation algorithm was used in this study, as it is very fast and can be employed quite easily. The number of hidden layers and nodes was determined via a trial and error procedure. GA toolbox in MATLAB (version 7) was used for generating the optimal solution for DR%. MATLAB functions using ANN model as the input were written for creating a fitness function for the optimization problem. The DR% component to be maximized was negated in the vector valued fitness function, since GA minimizes all the objectives. Experimental ranges were placed as bounds on the five inputs.[18-21]

Results and Discussion

Sorption process

Figure 2 shows all obtained data in 18 experiments. The effect of each operational parameter was illustrated in these figures, indicating that different levels of experimental parameters result in different DR%. In addition, it was found that PP is propitious for RR198 removal as sorbent.

SMLR models

The MLR models were developed for DR%. The model and related statistical characteristics are given in table 2.

Based on unbiased standardized coefficients presented in table 2, among linear parameters, D_s and t_S have a positive effect, but C_0, S_z, and pH_0 have negative effects on DR%. The most important parameters were pH_0 and D_s. Table 2 indicates that the MLR model does not have good predictability for DR% due to the complex mechanism of sorption process. It demonstrates new interest in using a more powerful modeling approach especially ANN model.

ANN modelling and GA Optimization

The ANN model was constructed for DR%. One hidden layer with 7 neurons was applied in the model. The tansig transfer function was selected for input and hidden layer, and purelin for output.[18,19] Once the networks were trained by experimental train data set, the weights and bias

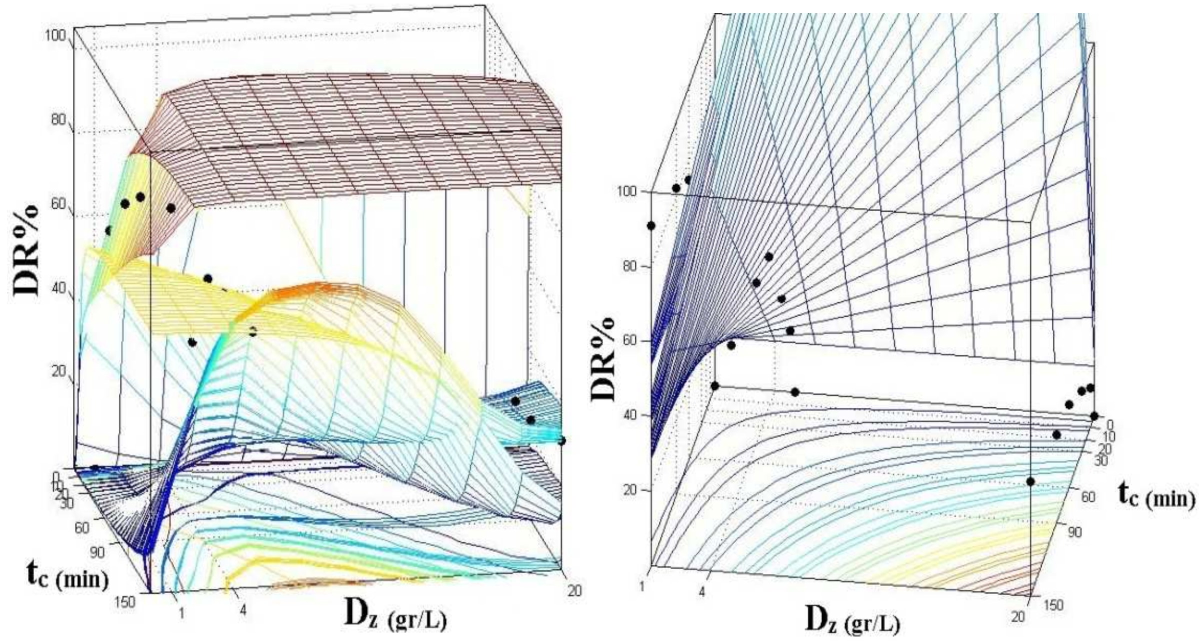


Figure 2. Sample plot of the artificial neural networks (ANN) (left) and multiple linear regression (MLR) (right) predicted values of dye removal (DR%) (colored surface) versus experimental data of DR% (black dot), for three sample conditions

Table 2. The MLR model and related statistical characteristics

	Coeff.	St. Coeff.	P
Constant	63.14	9.91	< 0.01
S_z	-0.04	0.01	0.02
pH_0	-5.52	0.76	< 0.01
C_0	-0.03	0.07	0.64
Ds	0.74	0.31	0.02
t_S	0.20	0.05	< 0.01
Data set	Train (64 data)		Test (44 data)
R^2	0.57		0.57
RMSE	19.3		18.6

Coeff.: Coefficients; St. Coeff.: Standardized coefficients; Sz: Sorbent particle average size; pH_0: Initial pH; Ds: Dose of sorbent; C_0: Initial dye concentration; RMSE: Root mean square error

of each neuron and layer were saved in the ANN model. Then, they were used to estimate the test set. The (5:7:1) ANN were trained using 64 data of the train set for DR% models by the back propagation algorithm. The parameters of ANN models are presented in table 3.

Moreover, figure 2 shows the samples of ANN and MLR model predictions and their corresponding experimental results together.

Figure 2 and comparison of table 2 with table 4 clearly show that ANN model outperformed the MLR model. Therefore, ANN model was used as optimization function in GA. GA optimization

Table 3. Network weights and biases of the artificial neural networks (ANN) model

Neuron	Input layer to hidden layer weights						Hidden layer to output layer weights	
	S_z	pH_0	C_0	D_s	t_S	Bias	Output	Bias
n_1	-1.445	1.395	1.167	-1.162	0.456	2.486	1.07	
n_2	-2.281	4.191	1.730	-0.976	-0.554	1.163	-0.84	
n_3	2.176	-0.673	1.859	-0.006	0.233	-0.323	1.84	
n_4	-1.644	-1.707	2.882	3.060	-2.604	-2.863	-0.5	1.07
n_5	0.684	1.240	2.427	-1.179	0.435	1.162	-1	
n_6	-3.698	-0.161	0.391	2.762	0.375	-1.135	2.23	
n_7	-0.124	-0.236	0.278	0.133	-9.259	-9.778	-4.77	

Sz: Sorbent particle average size; pH_0: Initial pH; Ds: Dose of sorbent; C_0: Initial dye concentration; n: neuron or processing elements

Table 4. Statistical characteristics of artificial neural networks (ANN) model of DR%

Data set	Train	Validation	Test
R^2	1	0.98	0.98
RMSE	0.8	3.8	4.3

RMSE: Root mean square error

process results in an optimal solution set with a set of decision variables. The input decision variables of the optimal solution (93.3% for DR%) were 396, 3.1, 66, 19.7, and 126 for S_z, pH_0, C_0, D_s, and t_S, respectively. Interpretation of table 2 and optimum values was used to interpret and to discriminate effect of each parameter.

Effect of experimental parameters

The influence of S_z on DR% was investigated at two levels of 225 and 575 µm. The results show that S_z clearly influences the DR% (Figure 1). Furthermore, as presented in optimal values of empirical parameters, the optimum value of S_z is 396 µm. On the one hand, DR% further decreased S_z from 575 to 396 µg, because of a more effective adsorption area for small sorbents. On the other hand, a decreasing in size from 396 µg to 225 µg of S_z caused the decreasing of DR%. DR% might increase due to a more effective volume of absorption in small particles.

The pH_0 of a suspension is an important factor that can affect the DR% of RR198 by PP. Sorption efficiency increases, as the pH_0 of the solution is decreased from 11 to 3.1. As the pH_0 of the solution decrease from 11 to 3.1, RR198 will get a natural or positive charge that might be more favorable as sorbent for PP. PP contains functional groups such as hydroxyl and carboxyl. These functional groups have a variety of structurally related pH dependent properties of generating appropriate atmosphere (positively and/or negatively charged sites) for attracting the cationic, natural, and anionic species of RR198.

The sorption behavior of RR198 on PP was investigated in the range of C_0 (10-100 mg/l) at three levels. As presented in optimal values of empirical parameters, the optimum value of C_0 was 66 mg/l. This means that sorption of RR198 on PP increased with the increasing of C_0 until C_0 reached an optimal level (66 mg/l). Later, an increase in concentration decreased the percentage binding. These observations can be explained by the fact that in medium concentrations, the ratio of sorptive surface area to the molecules available is high, thus, there is a greater chance of dye removal. When dye concentrations are increased, binding sites become more quickly saturated as the amount of mass concentration remains constant. However, it is important to see that the corresponding P-value of C_0 presented in table 2 statistically reveals that C_0 is not effective on DR%.

The D_s influence was investigated in the range of 1-20 mg/l at three levels. As presented in optimal values of empirical parameters, the optimum value of D_s was 19.7 g/l. DR% increased with the increasing of mass dosage from 1 to 19.7 g (near the maximum investigated range of D_s). This is due to the fact that more sorbent has more capacity and binding sites for sorption.

The effect of t_c on RR198 sorption on PP was studied in 0-150 minutes at five levels. DR% increases with increasing t_c then becomes stable (Figure 1). The optimum value obtained by GA algorithm was 126 minutes that is in accordance with figure 1. This level off is due to the attainment of equilibrium between sorbate and sorbent at optimum t_c or saturation of binding sites at that time.

Conclusion

The potential of PP for the sorption of RR198 from aqueous solution was investigated in the present study. Taguchi was used in combination with full factorial methods for the design of experiments, 18 experimental sets were designed, and the experiments were done in accordance with the experimental design. The handmade batch sorption was constructed as sorption reactor. The experimental data were collected under desired conditions. The effects of five experimental parameters on dye sorption were studied. The results demonstrate that PP can successfully be used as sorbent for RR198 removal from aqueous solutions. The results revealed that experimental parameters strongly influence the DR% and different experimental conditions cause different DR% (from 0 to 93). The ANN modeling technique was successfully applied to model the process, and a reliable model was constructed and tested. The optimization of the process over the ANN model was done by GA algorithm. The obtained optimum values and experimental parameters effects were in accordance with previous studies and famous reported scientific theories.

Conflict of Interests

Authors have no conflict of interests.

Acknowledgements

This work was financially supported by Kurdistan Environmental Health Research Center, Kurdistan University of Medical Sciences.

References

1. Robinson T, McMullan G, Marchant R, Nigam P. Remediation of dyes in textile effluent: a critical review on current treatment technologies with a proposed alternative. Bioresour Technol 2001; 77(3): 247-55.
2. Cheung C, Porter J, McKay G. Sorption kinetics for the removal of copper and zinc from effluents using bone char. Separation and purification technology 2000; 19(1): 55-64.
3. Bell JP, Tsezos M. Removal of hazardous organic pollutants by biomass adsorption. Water Pollution Control Federation 1987; 59(4): 191-8.
4. Aman T, Kazi AA, Sabri MU, Bano Q. Potato peels as solid waste for the removal of heavy metal copper(II) from waste water/industrial effluent. Colloids Surf B Biointerfaces 2008; 63(1): 116-21.
5. Turan NG, Mesci B, Ozgonenel O. The use of artificial neural networks (ANN) for modeling of adsorption of Cu (II) from industrial leachate by pumice. Chemical Engineering Journal 2011; 171(3): 1091-7.
6. Hagan MT, Demuth HB, Beale MH. Neural network design. Kolkata, India: Vikas Publishing House; 2003.
7. Himmelblau DM. Applications of artificial neural networks in chemical engineering. Korean Journal of Chemical Engineering 2000; 17(4): 373-92.
8. Ames A, Rogel-Hernandez E, Lin SW, Flores-López LZ, Castro JR, Wakida FT, et al. Prediction of metal ion rejection in electro-cross-flow ultrafiltration using an artificial neural network. Desalination and Water Treatment 2011; 36(1): 105-18.
9. Saien J, Soleymani AR, Bayat H. Modeling fentonic advanced oxidation process decolorization of direct red 16 using artificial neural network technique. Desalination & Water Treatment 2012; 40(1-3): 174-82.
10. Singh G, Kandasamy J, Shon H, Cho J. Measuring treatment effectiveness of urban wetland using hybrid water quality -- Artificial neural network (ANN) model. Desalination and Water Treatment 2011; 32(1-3): 284-90.
11. Körbahti BK, Artut K, Geçgel C, Qzer A. Electrochemical decolorization of textile dyes and removal of metal ions from textile dye and metal ion binary mixtures. Chemical Engineering Journal 2011; 173(3): 677-88.
12. Olmez-Hanci T, Kartal Z, Arslan-Alaton I. Electrocoagulation of commercial naphthalene sulfonates: process optimization and assessment of implementation potential. J Environ Manage 2012; 99: 44-51.
13. Tsutsui S, Goldberg DE. Search space boundary extension method in real-coded genetic algorithms. Information Sciences 2001; 133(1-4): 229-47.
14. Hasseine A, Kabouche A, Meniai AH, Korchi M. Salting effect of NaCl and KCl on the liquid—liquid equilibria of water+ ethyl acetate+ ethanol system and interaction parameters estimation using the genetic algorithm. Desalination and Water Treatment 2011; 29(1-3): 47-55.
15. Sashi Kumar GN, Mahendra AK, Sanyal A, Gouthaman G. Genetic algorithm-based optimization of a multi-stage flash desalination plant. Desalination and Water Treatment 2009; 1(1-3): 88-106.
16. Tabesh M, Hoomehr S. Consumption management in water distribution systems by optimizing pressure reducing valves' settings using genetic algorithm. Desalination and Water Treatment 2009; 2(1-3): 95-100.
17. Ebrahimi R, Maleki A, Shahmoradi B, Daraei H, Mahvi AH, Barati AH, et al. Elimination of arsenic contamination from water using chemically modified wheat straw. Desalination and Water Treatment 2013; 51(10-12): 2306-16.
18. Daraei H, Irandoust M, Ghasemi JB, Kurdian AR. QSPR probing of Na+ complexation with 15-crown-5 ethers derivatives using artificial neural network and multiple linear regression. Journal of Inclusion Phenomena and Macrocyclic Chemistry 2012; 72(3-4): 423-35.
19. Hatami T, Rahimi M, Daraei H, Heidaryan E, Alsairafi AA. PRSV equation of state parameter modeling through artificial neural network and adaptive network-based fuzzy inference system. Korean Journal of Chemical Engineering 2012; 29(5): 657-67.

20. Maleki A, Daraei H, Alaei L, Abasi L, Izadi A. Dye Removal Probing by Electrocoagulation Process: Modeling by MLR and ANN Methods. J Chem Soc Pak 2012; 34(15): 1056-69.
21. Nasri F, Daraei H, Hatami T, Maleki A. Phase equilibrium of binary system carbon dioxide-methanol at high pressure using artificial neural network. J Chem Soc Pak 2012; 34(1): 1070-8.

Journal of Advances in Environmental Health Research

Heavy metal contamination in soil and some medicinal plant species in Ahangaran lead-zinc mine, Iran

Mehrdad Cheraghi[1], Seyed-Meysam Mosavinia[1], Bahareh Lorestani[1]

1 Department of the Environment, School of Basic Sciences, Hamadan Branch, Islamic Azad University, Hamadan, Iran

Original Article

Abstract

Ahangaran lead-zinc mining area located in the west part of Iran is a mountainous region. In this study, medical plants and soils from 3 different sites in this area were collected in spring 2012. Soil and medical plants were analyzed for heavy metals [lead (Pb), zinc (Zn), cadmium (Cd) and copper (Cu)] concentrations using inductively coupled plasma (ICP) optical emission spectrometer (Varian 710-Es) and the physical properties of soils [(pH) and electrical conductivity (EC)] were measured. Soil and medical plants of the mineralized zone and surrounding areas have higher heavy metal contamination ($P < 0.05$) as compared to the reference site, which can be attributed to the dispersion of metals due to mining. This high heavy metal contamination may pose potential threats to local medical plants and soil of Ahangaran region. Furthermore, the concentrations of Pb and Cd in soil surrounding the mine were higher than the US environmental protection agency (USEPA) standard, and the concentration of Pb in medical plant species surrounding the mine was higher than the world health organization (WHO) standard for edible plants ($P < 0.05$).

KEYWORDS: Mine, Medical Plant, Heavy Metals, Contamination

Date of submission: 18 Mar 2013, ***Date of acceptance:*** 22 May 2013

Citation: Cheraghi M, Mosavinia SM, Lorestani B. **Heavy metal contamination in soil and some medicinal plant species in Ahangaran lead-zinc mine.** J Adv Environ Health Res 2013; 1(1): 29-34.

Introduction

The pollution of soil ecosystem with lead (Pb), zinc (Zn), cadmium (Cd) and copper (Cu), are considered as global environmental problem. These metals have both natural resources such as weathering/erosion of parent rocks and ores deposits, and anthropogenic resources such as mining, smelting, industrial emission, waste water irrigation and application of fertilizers have all contributed to elevated concentrations of heavy metals in the environment.[1-4]

Mining activities have a serious environmental impact on soils and plants. Moreover, there are may be safety risks for people working in mines or for those living close by the risk of habitat destruction.[5] The negative impact of these mining activities on the surroundings is mainly due to the presence of high volumes of tailings that usually have adverse conditions to natural plants growing on it.[6] Some plant species can grow in these severe conditions. High concentration of heavy metals in medical plants can cause oxidative stress and stomata resistance.[7,8] It can also affect photosynthesis and chlorophyll florescence processes.[9] Pb, Zn, Cd and Cu are potentially poisonous for medical plants i.e. phytotoxicity results in chlorosis, weak plants growth, and may even be accompanied by decrease nutrient uptake, disorders in plant metabolism, and a reduced ability to fixate molecular nitrogen.[10]

Moreover, Cu can inhibit photosynthesis and

Corresponding Author:
Seyed-Meysam Mosavinia
Email: meysam.mosavinia@yahoo.com

reproductive processes; Pb can reduce chlorophyll production, while Zn stimulates the growth of leaves and shoots.[11-13]

The use of plants for medicinal purposes extends long before recorded history. Mankind has had no choice but to use medicinal plants in all ages. Although chemical medications have developed in the past half century, their harmful side effects have revitalized inclination toward herbal medicine. Iran is one of the countries with the most diversity of medicinal plants due to its climate diversity. There are more than 1200 herbal species, of which 315 species belong to 71 families and 209 genera. This study aimed to investigate the contamination of soil and three medicinal plants growing (Table 1) in Ahangaran Mine site to Pb, Zn, Cu and Cd. and calculation of one sample t-test (BCF).

Materials and Methods

The medical plants and soil samples used in this study were collected from a known metal-contaminated site located in an urban area, called Ahangaran lead-zinc mine of Malayer city, west of Iran (Figure 1). It lies in 34° 11′ 08″ N latitude and 48° 59′ 25″ E longitude. The site has been vacant, with an area of approximately 1,600,000 m^2, and is covered mainly by grasses. Human activities such as mining have contributed to metal concentrations in this site. Selected characteristics of the soil samples collected from this study are shown in table 2.

Samples of soil and plants were collected in spring 2012. In the study area, three native medical plant species were randomly collected from the area surrounding the iron mine. Soil

Table 1. Selected plant species along with their family and local names in the study area

No.	Species scientific name	Abbreviations	Family name	Local name
1	Echinophora platyloba	E. platyloba	Apiaceae	Tighedoragh
2	Achillea millefolium	A.millefolium	Asteraceae	Bomadaran
3	Centaurea cyanus	A. cyanus	Asteraceae	Golegandom

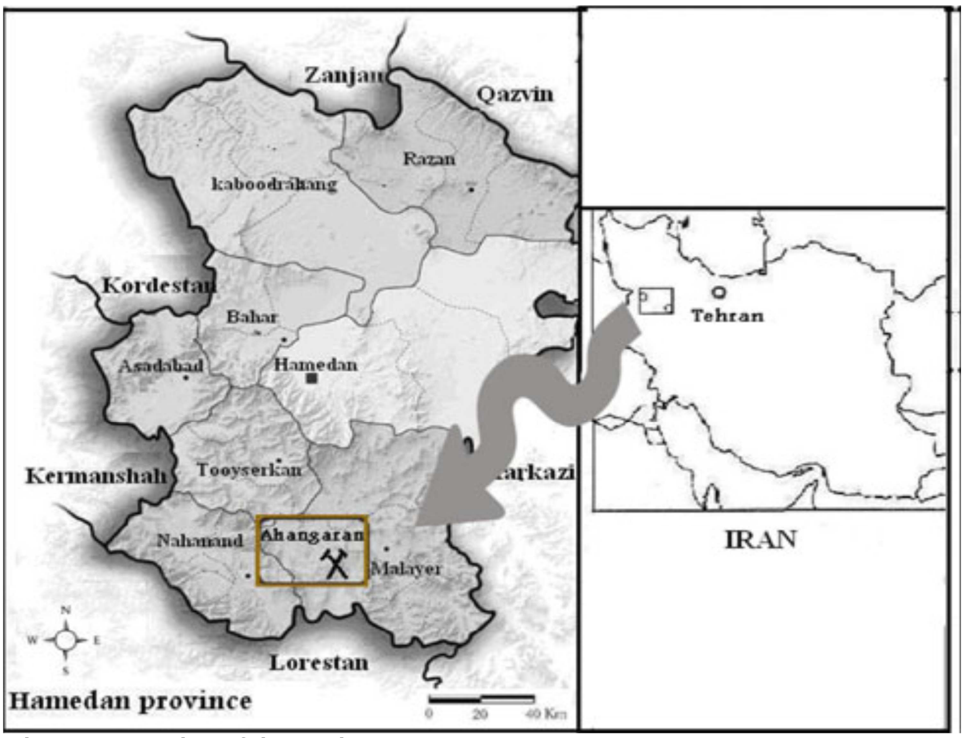


Figure 1. Location of the study area7

Table 2. Soil characteristics of the surrounding area in Ahangaran mine

Site	EC (ds/mm)	pH	TDS (mg/l)	Salinity	Soil texture
Site 1	182.8	7.67	109.5	0.4	loam-sandy
Site 2	328.0	7.85	197.6	0.4	loam-sandy
Site 3	143.2	7.50	168.2	0.4	loam-clay-sand

EC: Electrical conductivity; TDS: Total dissolved solids

sample was collected up to a depth of 30 cm from the base of each uprooted plant. Samples were cleaned from soil and packed in polyethylene bags and properly marked. Unmineralized zone (reference site) soil and plant samples were also collected about 10 km away from the mineralized sites. Herbarium sheet of all different plant species was prepared, identified and taxonomically classified with help of taxonomist in the University of Bu Ali Sina, Hamadan, Iran.

Soil samples were air-dried and passed through a 2 mm sieve before the analysis. Parameters such as pH and electrical conductivity (EC) were determined in a soil i.e. solution ratio 1:5, using a pH meter and an EC meter, respectively, according to the procedure adopted form Das and Maiti.[14] Particle size was determined by the hydrometer method.[15]

For heavy metals determination, soil samples were ground in ball mill to finer than 200 mesh size. 0.5 g of the finely ground soil sample was accurately weighed into Teflon® beaker with cover, 40 ml HF (hydrofluoric acid) and 10 ml conc. Hydrochloric acid (HCl) was added, the covered beaker was heated to 130-140° C; to complete attack, the acid was evaporated then 1:1 HCl was added and the solution was diluted to 100 ml with double-distilled water.[16] Digested soil samples were analyzed for Pb, Zn, Cu, Cd using ICP optical emission spectrometer (Varian 710-Es).

Plant samples were washed with double-distilled water (DDW), oven dried at 70° C and powdered with electric grinder. Accurately, 2.0 g of plant samples were taken in the pyrex beaker and digested with mixture of acids [HNO_3 (nitric acid), $HClO_4$ (perchloric acid)] and aqua regia); and dilute the extract to 50 ml with DDW, according to the digestion method adopted from Ryan.[17] Digested medical plants samples were analyzed for Pb, Zn, Cu, Cd using ICP optical emission spectrometer (Varian 710-Es).

Statistical analyses of experimental data were performed using SPSS for Windows (version 18.0, SPSS Inc., Chicago, IL, USA). Data were tested for goodness of fit to a normal distribution, using a Kolmogorov-Smirnov one-sample test. One sample t-test was used for the comparison of the heavy metals in the soil of the contaminated site to those of the uncontaminated (reference site) and the US environmental protection agency (USEPA) standard for heavy metals in soil.[18] Independent t-test and one sample t-test were used for the comparison of the heavy metals in the medical plants of the contaminated site to those of the uncontaminated (reference site) and the world health organization (WHO) standard for edible plants,[18] respectively.

The ability of plants to tolerate and accumulate heavy metals is useful for phytoextraction and phytostabilization purpose and was measured using bioconcentration factor (BCF) defined as the ratio of metal concentration in plant roots to soils [(metal) root/(metal)] soil.[19]

BCF = metal in whole plant DW (distilled water)/metal in soil DW.

Results and Discussion

Physical and Chemical Properties of the Soil

As shown in table 2, soils in the surrounding area of mine were slightly alkaline, with an average pH of approximately 7.67. The pH conditions were suitable for plant growth. The average of EC, were 218 [deci Siemens (dS/mm)]. Besides, texture of soil was loam-sandy in the site 1 and 2 and loam-clay-sand in the site 3.

Heavy Metals Concentrations in Soil Samples

Table 3 summarizes the heavy metals concentrations in soil samples collected from the contaminated site 1, site 2, site 3 and reference sites and standards. According to table 3, the order of heavy metals concentrations in all the three contaminated sites were Pb > Zn > Cu > Cd.

According to results presented in table 3 and one sample t-test results in table 4, the Pb, Zn, Cu and Cd contents in the soil of the surrounding area of the mine were significantly higher than these metals concentration in the reference site ($P < 0.05$).

As shown in table 3, the concentrations of the studied metals in the soil of the contaminated sites were higher than USEPA standards for heavy metals concentration in soil. Table 4 shows that it was only the Pb and Cd concentrations in the soil of the surrounding area of the mine that was significantly higher than the EPA standards. Rodrigez observed that concentrations of heavy metals in agricultural and ranges soils surrounding the mine were very high[20] and also Ghaderian reported that concentrations of heavy metals in the soils of Sarcheshmeh copper mining area (Iran) were significantly higher than those of non-contaminated soils.[1]

Heavy Metals Concentrations in Medical Plant Samples

Table 5 summarizes the heavy metals concentrations in the medical plants samples, collected from the contaminated site 1, site 2, site 3 and the reference site. According to table 4, the order of heavy metals concentrations in all three medical plants samples was Zn > Pb> Cu > Cd. The metal (Pb, Zn, Cu and Cd) contents in the medical plants samples were higher than metals concentration in the reference site and WHO standards for edible plants.

As shown in table 6, all the studied metals in the contaminated sites were significantly higher than the reference site ($P < 0.05$). Table 6 also illustrated it was only the Pb concentration in the medical plants that was significantly higher than

Table 3. Heavy metals concentrations in soil (mg/kg)

Metals	Soil samples					EPA standard
	Contaminated site				Reference site	
	Site 1	Site 2	Site 3	Average		
Cu	228.4	212.8	208.5	216.4	18.0	200
Zn	691.0	688.4	504.2	628.0	134.0	600
Pb	1754.0	1648.2	2028.0	1810.0	47.0	500
Cd	12.1	12.7	14.4	13.0	0.2	5

EPA: Environmental Protection Agency

Table 4. One sample t-test results for the comparison of the heavy metals in the soil of the contaminated site with those of the uncontaminated (reference) site and Environmental Protection Agency (EPA) standard

Metals	Comparison with the reference		Comparison with EPA standard	
	t	P	t	P
Cu	32.845	0.001	2.740	0.111
Zn	7.986	0.015	0.451	0.696
Pb	15.579	0.004	11.577	0.007
Cd	18.680	0.003	11.711	0.007

EPA: Environmental Protection Agency

Table 5. Heavy metals concentrations in medical plants (mg/kg)

Metals	Echinophora platyloba		Achillea millefolium		Centaurea cyanus		Average for contaminated site	Average for reference site	WHO standard
	Contaminated Site 1	Reference	Contaminated Site 2	Reference	Contaminated Site 3	Reference			
Cu	52.0	25.0	74.8	30.0	50.2	24.0	59.	26.0	40.0
Zn	392.2	38.0	480.0	50.0	403.0	45.0	425.0	44.0	60.0
Pb	102.0	12.0	158.6	16.0	152.6	17.0	138.0	15.0	2.0
Cd	4.6	0.2	4.4	0.3	4.5	0.2	4.4	0.7	0.5

WHO: World Health Organization

Table 6. Independent t-test and one sample t-test results for the comparison of the heavy metals in the medical plants of the contaminated site with those of the reference site and world health organization (WHO) standards for edible plants, respectively

Metals	Comparison with reference		Comparison with WHO standard	
	t	P	t	P
Cu	4.017	0.048	0.327	0.757
Zn	13.665	0.005	2.030	0.098
Pb	6.813	0.020	2.600	0.048
Cd	64.000	< 0.001	1.965	0.108

WHO: World Health Organization

Table 7. Accumulation of Cu, Zn, Pb and Cd in the selected medical plants

Metals	Bioconcentration factor (BCF)		
	Echinophora platyloba	Achillea millefolium	Centaurea cyanus
Cu	0.26	0.36	0.24
Zn	0.65	0.69	0.80
Pb	0.06	0.08	0.07
Cd	0.31	0.29	0.26

Pb concentration in the WHO standard. Del Rio et al. indicated that plants grown around Aznalcollar mine in Spain had so much contain heavy metals such as Pb, Zn, Cu[21] and also increased heavy metals concentrations in soils and plants affected by mining activities have been frequently reported.[22]

Accumulation of Metals in Medical Plants

Bioconcentration factor (BCF) can be used to estimate a plant's potential for phytoremediation purpose. A plant's ability to accumulate metals from soils can be estimated using the BCF, which is defined as the ratio of metal concentration in roots to that in soil. Among the 3 screened plants Achillea millefolium growing at site 2 had the highest BCF for Cu (BCF = 0.36; Table 5), though its total Cu concentration in the plant was < 1000 mg/kg. Among the 3 screened plant, Echinophora platyloba growing at site 1 had the highest BCF for Zn (BCF = 0.65; Table 5), though its total Cd concentration in the plant was < 1000 mg/kg. Moreover, among the 3 screened plants Centaurea cyanus growing at site 3 had the highest BCF for Zn (BCF = 0.8; Table 7).

Conclusion

This paper aimed to investigate the impact of Ahangaran lead-zinc mine on the heavy metal pollution of soils and medical plants species. The obtained results have clearly revealed that the order of Cu, Zn, Pb and Cd concentrations in soil and medical plants in all the three contaminated sites was Pb > Zn > Cu > Cd. The concentrations of Cu, Zn, Pb and Cd in soil samples and medical plants species surrounding the mine were significantly higher than reference site ($P < 0.05$). The Pb and Cd concentrations in the soil samples were significantly higher ($P < 0.05$) as compared to the USEPA standard for soils. In addition, the Pb concentration in the medical plants was higher ($P < 0.05$) as compared to the WHO standard for edible plants.

Conflict of Interests

Authors have no conflict of interests.

References

1. Ghaderian SM, Ghotbi Ravandi AA. Accumulation of copper and other heavy metals by plants growing on Sarcheshmeh copper mining area, Iran. Journal of Geochemical Exploration 2012; 123(0): 25-32.
2. Shah MT, Begum S, Khan S. Pedo and biogeochemical studies of mafic and ultramfic rocks in the Mingora and Kabal areas, Swat, Pakistan. Environmental Earth Sciences 2010; 60(5): 1091-102.
3. 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.
4. Muhammad S, Shah MT, Khan S. Health risk assessment of heavy metals and their source apportionment in drinking water of Kohistan region, northern Pakistan. Microchemical Journal 2011; 98(2): 334-43.
5. Jung MC. Heavy Metal Concentrations in Soils and Factors Affecting Metal Uptake by Plants in the Vicinity of a Korean Cu-W Mine. Sensors 2008; 8(4): 2413-23.
6. Nouri J, Lorestani B, Yousefi N, Khorasani N, Hasani AH, Seif F, et al. Phytoremediation potential of native plants grown in the vicinity of Ahangaran lead-zinc mine (Hamadan, Iran). Environmental Earth Sciences 2011; 62(3): 639-44.
7. Fayiga AO, Ma LQ, Cao X, Rathinasabapathi B. Effects of heavy metals on growth and arsenic accumulation in the arsenic hyperaccumulator Pteris vittata L. Environ Pollut 2004; 132(2): 289-96.
8. Shah BA, Shah AV, Singh RR. Sorption isotherms and kinetics of chromium uptake from wastewater using natural sorbent material. Int J Environ Sci Tech 2009; 6(1): 77-90.
9. Monni S, Uhlig C, Hansen E, Magel E. Ecophysiological responses of Empetrum nigrum to heavy metal pollution. Environ Pollut 2001; 112(2): 121-9.
10. Gardea-Torresdey JL, Peralta-Videa JR, de la Rosa G, Parsons JG. Phytoremediation of heavy metals and study of the metal coordination by X-ray absorption spectroscopy. Coordination Chemistry Reviews 2005; 249(17-18): 1797-810.
11. Guala SD, Vega FA, Covelo EF. The dynamics of heavy metals in plantGÇôsoil interactions. Ecological Modelling 2010; 221(8): 1148-52.
12. Ling T, Guanghua Z, Jun R. Effects of chromium on seed germination, root elongation and coleoptile growth in six pulses. Int J Environ Sci Tech 2009; 6(4): 571-8.
13. Ayari F, Hamdi H, Jedidi N, Gharbi N, Kossai R. Heavy metal distribution in soil and plant in municipal solid waste compost amended plots. Int J Environ Sci Tech 2010; 7(3): 465-72.
14. Das M, Maiti SK. Comparison between availability of heavy metals in dry and wetland tailing of an abandoned copper tailing pond. Environ Monit Assess 2008; 137(1-3): 343-50.
15. Rowell DL. Soil science: methods and applications. New York, NY: Longman Scientific & Technical; 1994.
16. Rashed MN. Monitoring of contaminated toxic and heavy metals, from mine tailings through age accumulation, in soil and some wild plants at Southeast Egypt. J Hazard Mater 2010; 178(1-3): 739-46.
17. Ryan J, Estefan G, Rashid A. Soil and Plant Analysis Laboratory Manual. Aleppo, Syria: ICARDA p. 172; 2001.
18. Mardukh Rohani N. Evolution of heavy metal concentration in compost, soil cover and button mashroom (case study: green house in Kurdistan Province) [MSc Thesis]. Hamadan, Iran: Islamic Azad University, Hamadan Branch; 2012.
19. Yoon J, Cao X, Zhou Q, Ma LQ. Accumulation of Pb, Cu, and Zn in native plants growing on a contaminated Florida site. Sci Total Environ 2006; 368(2-3): 456-64.
20. Rodriguez L, Ruiz E, Alonso-Azcarate J, Rincon J. Heavy metal distribution and chemical speciation in tailings and soils around a Pb-Zn mine in Spain. J Environ Manage 2009; 90(2): 1106-16.
21. Del RioM, Font R, Almela C, Velez D, Montoro R, De Haro BA. Heavy metals and arsenic uptake by wild vegetation in the Guadiamar river area after the toxic spill of the Aznalcollar mine. J Biotechnol 2002; 98(1): 125-37.
22. De Koe T. Agrostis castellana and agrostis delicatula on heavy metal and arsenic enriched sites in NE Portugal. Sci Total Environ 1994; 145(1-2): 103-9.

Journal of Advances in Environmental Health Research

Mobility of zinc and copper in contaminated clay soil influenced by *Actinidia deliciosa* and incubation times

Bahareh Lorestani[1], Hajar Merrikhpour[1], Sanaz Ashoorloo[1], Mehrdad Cheraghi[1]

1 Department of Environment, Islamic Azad University, Hamedan Branch, Hamedan, Iran

Original Article

Abstract

As a low cost byproduct, *Actinidia deliciosa* shell can be made into sorbent materials which are used in heavy metals immobilization. It has been investigated as a replacement for currently expensive methods of heavy metal immobilization from soil. In this study, soil samples were contaminated with copper (Cu) and zinc (Zn) at the rate of 600 ppm in separate dishes. The 5% *Actinidia deliciosa* shell was added into the samples. The samples were incubated for 3 hours, and 1, 3, 7, 14, 21, and 28 days at 28° C with constant moisture. After incubation, metals in contaminated soil with *Actinidia deliciosa* shell and control soils were fractionated by the sequential extraction procedure. The results of this study indicated that addition of *Actinidia deliciosa* shell led to increased organic matter fraction and stabilized Cu and Zn in contaminated soil. In the control soils, the dominating chemical form for Zn and Cu were Fe-Mn oxides and residual, respectively. Sequential extraction also revealed that the addition of *Actinidia deliciosa* decreased the easily accessible fraction of Zn through the transformation into less accessible fractions. The experiment was performed in three replicates and two treatments.

KEYWORDS: *Actinidia Delicious*, Stabilization, Incubation, Sequential Extraction

Date of submission: 20 Mar 2013, ***Date of acceptance:*** 23 May 2013

Citation: Lorestani B, Merrikhpour H, Ashoorloo S, Cheraghi M. **Mobility of zinc and copper in contaminated clay soil influenced by *Actinidia deliciosa* and incubation times.** J Adv Environ Health Res 2013; 1(1): 35-43.

Introduction

Contamination of heavy metals represents one of the most pressing threats to soil sources.[1] The pollution of the soil ecosystem with heavy metals is considered as a global environmental issue. Some of these elements such as copper (Cu) and zinc (Zn) are essential micronutrients for living organisms but at elevated concentrations, they can be toxic to higher plants and other organisms.[2] Cu and Zn have both natural resources such as weathering/erosion of parent rocks and ores deposits and anthropogenic resources such as mining, smelting, energy, electroplating, fuel production, intensive agriculture, waste water irrigation, sludge dumping and dust.[3-7] In soil ecosystems, the toxicity of heavy metals depends upon various factors including total concentration of metals, specific chemical form, metal binding state and properties.[8] High levels of heavy metals may pose an important hazard to human health and the environment not only because of their direct toxic effects on organisms, but also due to their further potential for increasing exposure along the food chain through bioaccumulation.[2] As chemical hazards, heavy metals are non-biodegradable and remain almost indefinitely in the soil environment.[9]

To overcome the high costs and limits remediation technology sources, new technologies

Corresponding Author:
Sanaz Ashoorloo
Email: sanaz.ashoorloo@yahoo.com

should be investigated which can be implemented at lower costs and without the possibility of adverse environmental consequences.[10,11]

The immobilization, which transforms heavy metals into less bio available forms, is considered as one of the most effective ways to remediate the heavy metals contaminated soils.[12,13]

Agricultural wastes or by-products have been investigated for their uses as sorbent materials for heavy metals due to the tendency of heavy metals to form stable complexes with organic ligands.[14,15] Many studies have been conducted to investigate the stabilization of heavy metals using conventional stabilizing agents such as Portland cement, quicklime, and fly ash.[16,17] Few studies have involved immobilizing heavy metals using natural wastes such as oyster shells.[18,19] The immobilization of heavy metal by calcined egg shell in contaminated soil performed by Kim et al.[20]

Actinidia deliciosa shell as a low cost byproduct can be made into sorbent materials which are used in heavy metals immobilization. It has been investigated as a replacement for expensive methods of heavy metals immobilization from soil currently.

Therefore, the present study aimed to evaluate the effect of Actinidia deliciosa and time on distribution and mobility of Zn and Cu in soil using the sequential method.

Materials and Methods

Soil sample was collected from 0-30 cm soil horizon, in Hamadan, Iran. Samples were air-dried and passed through a 2 mm sieve before analyzing. Particle size was determined by the hydrometer method. Sample was then analyzed for metals (Zn and Cu).The pH and electrical conductivity (EC) values (solid: distilled water = 1:5) of the soil sample was measured by a pH meter and an EC meter, respectively.

The soluble ions of the soil sample were analyzed such as sodium (Na^+), calcium (Ca^{2+}), magnesium (Mg^{2+}), potassium (K^+), chloride (Cl^-), sulfate (SO_4^{2-}), nitrate (NO_3^-) and phosphate (PO_4^{3-}). Calcium, Mg^{2+}, and Cl^- were determined by titration. Sodium and K^+ were measured by flame photometry. Sulfate and PO_4^{3-} were determined by spectrophotometric turbidimetry. Nitrate was measured by colorimetry with an UV-visible spectrophotometer.[21]

Kiwi fruit with scientific name of Actinidia deliciosa, belongs to Actinidia class, Ericales order and Actinidiaceae family, and grows in temperate climate.

In this study, Actinidia deliciosa shell was washed with double-distilled water (DDW), oven dried at 70° C and powdered with electric grinder, then mixed with soil samples.

In addition, the total Cu and Zn concentrations were determined in the Actinidia deliciosa shell.[22]

Soil was placed in plastic cups and heavy metals were added at the rate of 600 ppm for Zn and Cu in separate dishes, and then each soil sample were mixed thoroughly. The soil was amended with Zn and Cu using $ZnCl_2$ and $CuCl_2$, respectively.[23]

The samples were incubated for 3 hours, and 1, 3, 7, 14, 21, and 28 days at 28° C. The appropriate amount of water was added to cause the soil to the estimated field capacity. The samples were kept moisture By adding distilled water as needed, all the incubation experiments were carried out in duplicate. Soil samples without Actinidia deliciosa shell and amended with heavy metals were prepared as the control soils.[23,24]

Prior to incubation, a sequential extraction of Salbu[25] method was used to extract metals in contaminated soil with Actinidia deliciosa shell and control soils (Table 1).[26] The metal concentrations for Zn and Cu were analyzed by ICP (inductively coupled plasma) and optical emission spectrometry (Varian 710-Es).

Graphs were plotted using Microsoft Excel 2010 and statistical analysis was performed using SPSS for Windows (version 18.0, SPSS Inc., Chicago, IL, USA).

Table 1. Sequential extraction procedure and the corresponding forms by the method of Salbu

Form/ association	Fraction	Operational definition
EXCH	F1	20 ml of 1 M NH4OAc* at pH 7 for 2 hours at room temperature.
CARB	F2	20 ml of 1 M NH4OAc at pH 5 for 2 hours at room temperature.
Fe–Mn	F3	20 ml of 0.04 M NH2OH-HCl† in 25% HOAc‡ for 6 h in a water bath at 60°C.
OM	F4	15 ml of 30% H2O2§ at pH 2 for 5.5 h in a water bath at 80°C.
RES	F5	5 ml of 3.2 M NH4OAc in 20% HNO3‖ was added to the residue of F4. Sample was shaken for 0.5 hours, and finally diluted to 20 mL with distilled water.

*Ammonium acetate, †Hydroxylamine hydrochloride, ‡Acetic acid, §Hydrogen peroxide, ‖Nitric acid; EXCH: Exchangeable; CARB: Carbonate-bound; Fe–Mn: Fe-Mn oxides; OM: Organic matter; RES: Residual

Results and Discussion

Characterization of soils

Selected chemical and physical properties of the soils are given in table 2. Results showed that texture of soil was clay-loam. The pH and electrical conductivity (EC) values were 7.22 and 0.1215 (ds/m), respectively. Thus, the soil sample was neutralized and non-saline. Moreover, the results showed that no element was detected in the primary soil and Actinidia deliciosa shell.

Concentration of Cu in contaminated soil with Actinidia deliciosa shell and control soil

Tables 3 and 4 represent the Cu concentration in the samples in each fraction, and figure 1 shows the change of Cu (%) in different fractions as well.

Furthermore, tables 3 and 4 illustrate the concentration of Cu in five fractions in the control soil and contaminated soil with Actinidia deliciosa shell, incubated for 3 hours, 1, 3, 7, 14, 21, and 28 days. There were some differences between the control soil and the contaminated soil with Actinidia deliciosa shell in Cu distributions.

Table 2. Some physical and chemical properties of the studied soils

Solution cations and anions (mg/l)								%			Soil texture	EC (ds/m)	pH
Ca^{2+}	K^+	Mg^{2+}	Na^+	PO_4^{3-}	Cl^-	$SO4^{2-}$	NO_3^-	Sand	Silt	Clay	Clay-loam	0.1512	7.22
32	45.2	9.6	26.2	0.6	81.6	13.3	69.4	26	43	31			

EC: Electrical conductivity

Table 3. Concentration (mg/kg) of Cu in each fraction in the contaminated soil with Actinidia deliciosa shell

Time	Exchangeable	Carbonate	Fe-Mn oxides occluded	Organic matter	Residual
3 hours	17.5	48.4	71.5	30.6	70.6
1 day	16.2	42.1	334.9	143.3	55.0
3 days	414.1	31.5	629.7	269.8	47.0
7 days	34.6	61.2	87.2	37.3	2.3
14 days	36.7	70.7	88.9	38.1	2.3
21 days	38.1	48.5	102.2	43.8	32.3
28 days	34.2	40.0	84.6	37.1	5.0

Table 4. Concentration (mg/kg) of the Cu in each fraction in the control soil

Time	Exchangeable	Carbonate	Fe-Mn oxides occluded	Organic matter	Residual
3 hours	8.5	36.2	13.0	2.6000	35.7
1 day	6.6	28.3	0.01	0.0075	67.3
3 days	16.0	20.7	27.6	0.0075	71.4
7 days	0.01	14.7	189.1	0.0075	22.0
14 days	0.01	26.4	175.1	0.0075	17.8
21 days	0.01	14.2	216.3	0.0075	25.9
28 days	0.01	28.6	141.0	0.0075	21.3

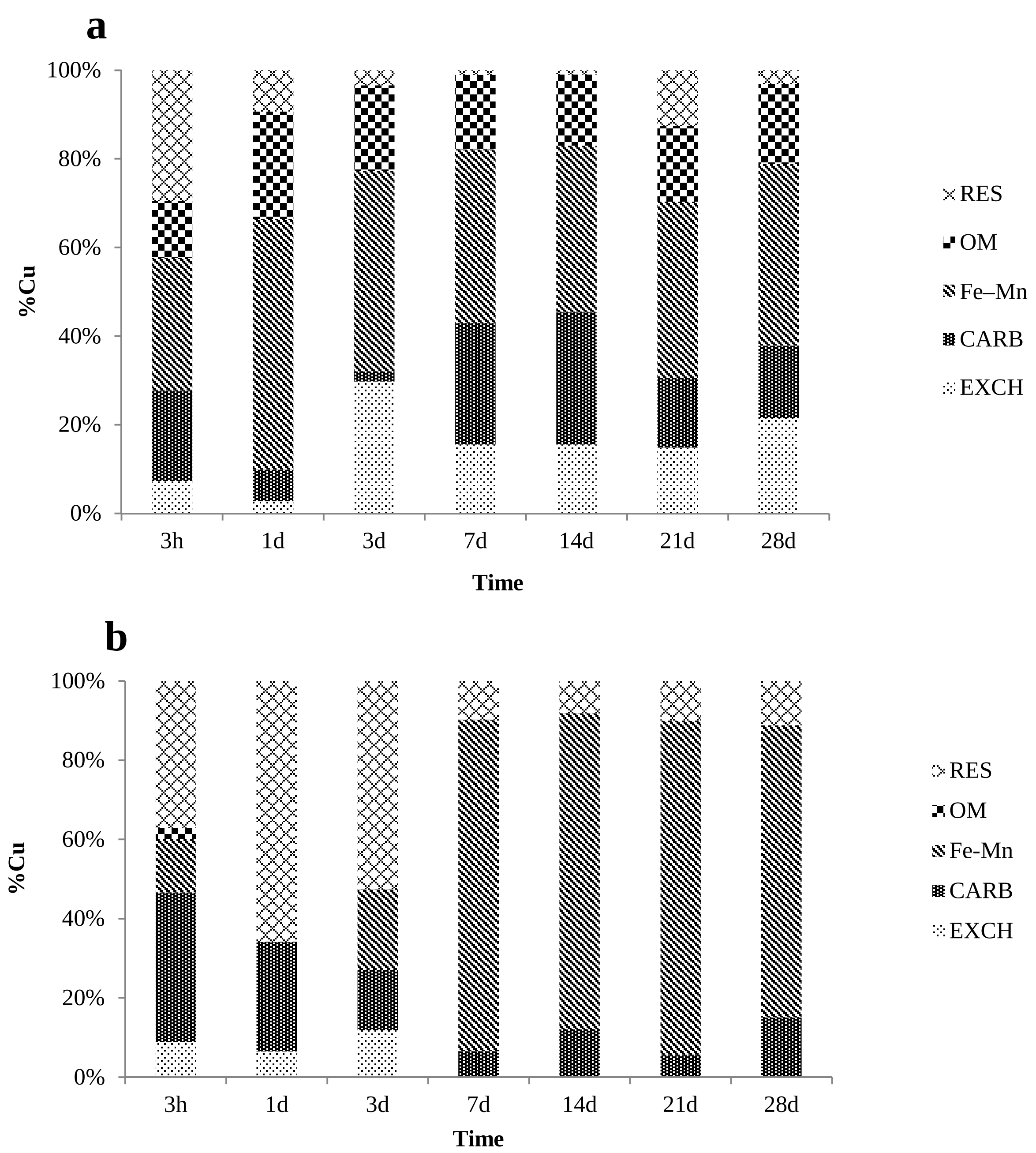


Figure 1. The change of Cu (%) in different fractions with time in contaminated soil with (a) Actinidia deliciosa shell (b) in the control soil

RES: Residual; OM: Organic matter; Fe–Mn: Fe-Mn oxides; CARB: Carbonate-bound; EXCH: Exchangeable

According to the statistical comparisons, performed by the 95% level using the independent t-test, there was a statistically significant difference between the amount of absorbed Cu in the organic matter (OM) fraction in the contaminated soil with Actinidia delicious and the control soil, about the carbonate fraction; there was also a statistically significant difference between the two cases. Regarding the other soil fractions, there was not a statistically significant difference between the contaminated soil with Actinidia deliciosa shell and the control soil (Table 5).

Table 5. Statistical test results for Cu in each fraction between the contaminated soil with Actinidia deliciosa and the control soil

Fractions	Sig	df	t
Exchangeable	0.160	6.02	1.57
Carbonate-bound	0.002	9.89	4.21
Fe-Mn oxides	0.310	8.21	1.04
Organic matter	0.040	6.00	2.50
Residual	0.630	11.48	-0.04

Sig: Significant; Df: Degree of freedom

The addition of Actinidia deliciosa shell had resulted in increased Cu concentrations in OM fraction and thus Cu stabilized. Cu has high affinity for organic matter.[23] Ok et al. indicated that waste oyster shells (WOS) amendments improved the soil quality and stabilized heavy metal in contaminated soil.[11] In the contaminated soil with Actinidia deliciosa shell, the highest contents of Cu are associated with Fe-Mn fraction, with the following order:

Fe-Mn > OM > CABN > EXCH > RES

The results also showed that in the contaminated soil with Actinidia deliciosa shell, the highest contents of Zn in OM fraction are associated at 1 day (24.2%) (Figure 1). On the other hand, although Cu has absorbed in the organic phase, the exchangeable amount has increased. A major part of the residual fraction in the contaminated soil with Actinidia deliciosa shell decreased as compared to the control soil, which showed that part of the Cu from the residual fraction has moved to the organic and exchangeable fractions. Moreover, at 7-14-21-28 days Fe-Mn fractions has decreased and at 1-3 days and 3 hours carbonate the fraction has decreased, which represented the Cu movement from these fractions to the organic and exchangeable fractions. Results of the Cu classification in the control soil showed that Fe and Mn fraction had maximum percentage of Cu absorption at 7, 14, 21, and 28 days, and the remaining fraction had the maximum percentage of the Cu absorption at 3 hours and 1-3 days.

In the control sample, the dominating chemical form for Cu was the RES, with the Fe-Mn of the secondary importance, with the following order:

RES > Fe-Mn > CABN > EXCH > OM

Cu absorption in the OM fraction at all times was lower than the other soil fractions, so that, in 3 hours, it was 2.79% and in the other times i.e. 1, 3, 7, 14, 21, and 28 days, it was negligible (Figure 1).

Besides, after the OM fraction, the RES fraction had the lowest amount of the Cu absorption in all the time periods.

Concentration of Zn in contaminated soil with Actinidia deliciosa shell and the control soil

Tables 6 and 7 illustrate the Zn concentration in the samples in each fraction and figure 2 shows the change of Zn (%) in different fractions.

Moreover, the tables 6 and 7 suggest the concentration of Zn in five fractions in the control and contaminated soil with Actinidia deliciosa shell, incubated for 3 hours, 1, 3, 7, 14, 21, and 28 days. There were some major differences between the control and contaminated soil in the Cu distributions.

According to the statistical comparisons, using the independent t-test, at 95% level, there was a statistically significant difference in the organic and exchangeable fractions in the Zn absorption in the contaminated soil with Actinidia deliciosa shell and the control soil. There was no statistically significant difference in comparison to the other soil fractions (Table 8).

The addition of Actinidia deliciosa shell had resulted in increased Zn concentrations in OM fraction and stabilized Zn. Yoon et al. indicated that treatment with WOS was effective for the adsorption and stabilization of the heavy metals in soil.[27]

Figure 2 shows that OM fraction increased markedly following Actinidia deliciosa shell addition in soil in all the times periods.

The results also showed that in the contaminated soil with Actinidia deliciosa shell, the highest contents of Zn in OM fraction are associated at 3 hours (28.7%) (Figure 2). Besides, there was no high difference between the 3

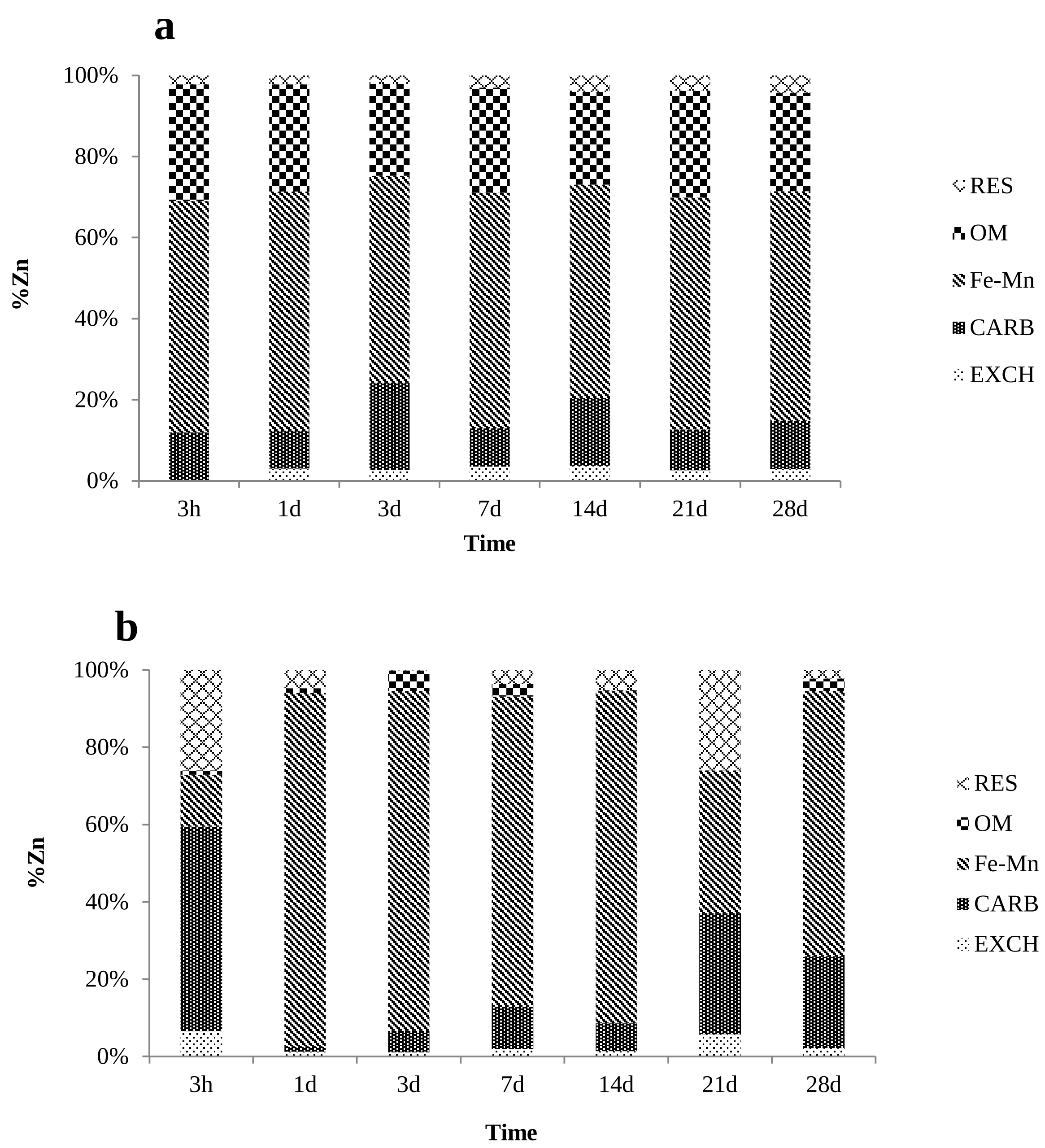


Figure 2. The change of Zn (%) in different fractions with time in contaminated soil with (a) Actinidia deliciosa shell (b) in control soil
RES: Residual; OM: Organic matter; Fe–Mn: Fe-Mn oxides; CARB: Carbonate-bound; EXCH: Exchangeable

Table 6. Concentration (mg/ kg) of Zn in each fraction in the contaminated soil with Actinidia deliciosa shell

Time	Exchangeable	Carbonate	Fe-Mn oxides occluded	Organic matter	Residual
3 hours	0.51	48.1	232.0	116.8	9.1
1 day	12.4	38.2	242.4	108.6	9.1
3 days	15.2	124.5	296.6	131.4	11.9
7 days	15.7	41.7	263.9	117.6	13.3
14 days	15.3	68.5	220.5	95.8	16.5
21 days	10.4	41.0	234.5	107.7	15.5
28 days	10.6	42.0	203.2	87.1	15.3

Table 7. Concentration (mg/ kg) of Zn in each fraction in the control soil

Time	Exchangeable	Carbonate	Fe-Mn oxides occluded	Organic matter	Residual
3 hours	6.4	50.9	12.9	1.1	24.9
1 day	5.2	5.9	422.2	5.3	21.5
3 days	5.5	27.8	439.6	26.6	0.2
7 days	7.2	39.1	289.2	11.9	12.7
14 days	6.4	31.8	380.8	1.2	22.8
21 days	5.9	32.1	37.8	0.0075	26.6
28 days	7.6	81.2	234.2	10.9	7.3

Table 8. Statistical test results for Zn in each fraction between the contaminated soil with Actinidia deliciosa and the control soil

Fractions	sig	df	t
Exchangeable	0.04	6.24	2.47
Carbonate-bound	0.21	11.09	1.31
Fe-Mn oxides	0.8	6.36	-0.2
Organic matter	0.000	10.24	15.33
Residual	0.4	7.12	-0.9

Sig: Significant; Df: Degree of freedom

hours and 28 days after the 28 days. These results demonstrated that the main effect of Actinidia deliciosa shell as adsorbent has occurred in 3 hours.

Therefore, the Zn amount in the exchangeable fraction -which is the available fraction for the plant-, has decreased from 6.65% in the control soil to 0.12% to the contaminated soil with Actinidia deliciosa shell (Figure 2). Almas et al. found that the heavy metal in the mobile fractions decreased significantly in the soil treated with organic matter.[28]

In the contaminated soil with Actinidia deliciosa shell at all the times except from 3 hours and 21 days, the Fe and Mn fractions decreased as compared to the control soil, which showed a small amount of Zn from this fraction has moved to the organic fraction. Furthermore, after 3 hours and 21 days, carbonate and exchangeable fractions in the contaminated soil with Actinidia deliciosa shell have decreased and transferred to the organic fraction. Kim et al. found that the application of calcined eggshell particularly decreased the mobile fraction of the heavy metals.[20] Ok et al. reported that sequential extraction revealed that the addition of rapeseed residue decreased the easily accessible fraction of cadmium by 5-14% and lead (Pb) by 30-39% through the transformation into less accessible fraction.[29]

In the contaminated soil with Actinidia deliciosa shell, the highest contents of Zn were associated with Fe-Mn fraction, with the following order:

Fe-Mn > OM > CABN > RES > EXCH

In the control soil, the dominating chemical form for Zn was Fe-Mn oxides, suggesting that Zn had a preference for oxides at the expense of other fractions.

After 28 incubation days, the Fe-Mn oxides fraction remained the most dominant fraction in all the times, except 3 hours, with the following order:

Fe-Mn > CABN > RES > EXCH > OM

Conclusion

In this study, Actinidia deliciosa shell was used to immobilize Cu and Zn in contaminated soil. The addition of Actinidia deliciosa shell led to increased OM fraction. Besides, according to the statistical comparisons, performed to the 95% level using the independent t-test, there was a statistical significant difference between the amount of absorbed Cu and Zn in the OM fraction in the contaminated soils with Actinidia delicious and the control soils. In the contaminated soils with Actinidia deliciosa shell, most of the added Cu and Zn were found in the Fe-Mn fraction. In the control samples, most of the Cu and Zn were found in the residual and Fe-Mn oxides fractions.

Conflict of Interests

Authors have no conflict of interests.

Acknowledgements

This paper was issued from MSc thesis by Sanaz Ashoorloo under dissertation number 17130607902002. Special thanks go to Hamedan Branch, Islamic Azad University.

References

1. Nouri J, Khorasani N, Lorestani B, Karami M, Hassani AH, Yousefi N. Accumulation of heavy metals in soil and uptake by plant species with phytoremediation potential. Environmental Earth Sciences 2009; 59(2): 315-23.
2. Ghaderian SM, Ghotbi Ravandi AA. Accumulation of copper and other heavy metals by plants growing on Sarcheshmeh copper mining area, Iran. Journal of Geochemical Exploration 2012; 123(0): 25-32.
3. Igwe JC., Abia AA. A bioseparation process for removing heavy metals from waste water using biosorbents. Afr J Biotechnol 2006; 5(12): 1167-79.
4. Chanpiwat P, Sthiannopkao S, Kim KW. Metal content variation in wastewater and biosludge from Bangkok's central wastewater treatment plants. Microchemical Journal 2010; 95(2): 326-32.
5. Shah MT, Begum S, Kha S. Pedo and biogeochemical studies of mafic and ultramfic rocks in the Mingora and Kabal areas, Swat, Pakistan. Environmental Earth Sciences 2010; 60(5): 1091-102.
6. 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.
7. Kong S, Lu B, Ji Y, Zhao X, Chen L, Li Z, et al. Levels, risk assessment and sources of PM10 fraction heavy metals in four types dust from a coal-based city. Microchemical Journal 2011; 98(2): 280-90.
8. Muhammad S, Shah MT, Khan S. Heavy metal concentrations in soil and wild plants growing around Pb-Zn sulfide terrain in the Kohistan region, northern Pakistan. Microchemical Journal 2011; 99(1): 67-75.
9. Wuana RA, Okieimen FE, Imborvungu JA. Removal of heavy metals from a contaminated soil using organic chelating acids. Environ Sci Tech 2010; 7(3): 485-96.
10. Ok YS, Kim JG. Enhancement of Cadmium Phytoextraction from Contaminated Soils with Artemisia princeps var. orientalis. SOURCEJournal of Applied Sciences 2007; 7(2): 263-8.
11. Ok YS, Lim JE, Moon DH. Stabilization of Pb and Cd contaminated soils and soil quality improvements using waste oyster shells. Environ Geochem Health 2011; 33(1): 83-91.
12. Gadepalle VP, Ouki SK, Van-Herwijnen R, Hutchings T. Immobilization of heavy metals in soil using natural and waste materials for vegetation establishment on contaminated sites. Soil and Sediment Contamination 2007; 16(2): 233-51.
13. Hashimoto Y, Matsufuru H, Takaoka M, Tanida H, Sato T. Impacts of chemical amendment and plant growth on lead speciation and enzyme activities in a shooting range soil: an x-ray absorption fine structure investigation. J Environ Qual 2009; 38(4): 1420-8.
14. Shen J, Duvnjak Z. Adsorption Isotherms for Cupric and Cadmium Ions on Corncob Particles. Separation Science and Technology 2005; 40: 1461-81.
15. Cui YS, Du X, Weng LP, Zhu YG. Effects of rice straw on the speciation of cadmium (Cd) and copper (Cu) in soils. Geoderma 2008; 146(1-2): 370-7.
16. Moon DH, Grubb DG, Reilly TL. Stabilization/solidification of selenium-impacted soils using Portland cement and cement kiln dust. J Hazard Mater 2009; 168(2-3): 944-51.
17. Ok YS, Yang JE, Zhang YS, Kim SJ, Chung DY. Heavy metal adsorption by a formulated zeolite-Portland cement mixture. J Hazard Mater 2007; 147 (1-2): 91-6.
18. Kumpiene J, Lagerkvist A, Maurice C. Stabilization of As, Cr, Cu, Pb and Zn in soil using amendments--a review. Waste Manag 2008; 28(1): 215-25.
19. Moon DH, Cheong KH, Choi SB, Kham J, Kim KW, Koi I, et al. Assessment of waste oyster shells for the stabilization of Pb- contaminated mine tailing in The Republic of Korea. Proceedings of the 10th International Geotechnology and Sustainable Development; 2009a Sep 7-11; September Bochum Germany; 2009.
20. Kim RY, Sung JK, Kim SC, Jang BC, Ok YS. Effect of calcined eggshell on fractional distribution and plant uptake of Cd, Pb and Zn in contaminated soils near mine. Proceedings of the 19th World Congress of Soil Science: Soil solutions for a changing world; 2010 Aug 1-6; Brisbane, Australia; 2010.
21. Rowell DL. Soil science: methods and applications. London, UK: Longman Scientific & Technical p. 345; 1994.
22. Ward NI, Reeves RD, Brooks RR. Lead in soil and vegetation along a New Zealand State Highway with low traffic volume. Environmental Pollution (1970) 1975; 9(4): 243-51.
23. Jalali M, Khanlari ZV. Effect of aging process on the fractionation of heavy metals in some calcareous soils of Iran. Geoderma 2008; 143(1-2): 26-40.
24. Terzano R, Spagnuolo M, Medici L, Dorriné W, Janssens K, Ruggiero P. Microscopic single particle characterization of zeolites synthesized in a soil polluted by copper or cadmium and treated with coal fly ash. Applied clay science 2007; 35(1-2): 128-38.
25. Salbu B, Krekling T. Characterisation of radioactive

particles in the environment. Analyst 1998; 123(5): 843-50.
26. Nguyen Ngoc M, Dultz S, Kasbohm J. Simulation of retention and transport of copper, lead and zinc in a paddy soil of the Red River Delta, Vietnam. Agriculture, Ecosystems & Environment 2009; 129 (1-3): 8-16.
27. Yoon GL, Kim BT, Kim BO, Han SH. Chemical-mechanical characteristics of crushed oyster-shell. Waste Manag 2003; 23(9): 825-34.
28. Almas A, Singh BR, Salbu B. Mobility of cadmium-109 and zinc-65 in soil influenced by equilibration time, temperature, and organic matter. Journal of environmental quality 1999; 28(6): 1742-50.
29. Ok YS, Usman AR, Lee SS, Abd El-Azeem SA, Choi B, Hashimoto Y, et al. Effects of rapeseed residue on lead and cadmium availability and uptake by rice plants in heavy metal contaminated paddy soil. Chemosphere 2011; 85(4): 677-82.

Journal of Advances in Environmental Health Research

Effect of Azolla filiculoides on removal of reactive red 198 in aqueous solution

Mohammad-Ali Zazouli[1], Davoud Balarak[2], Yusef Mahdavi[2]

1 Department of Environmental Health Engineering, School of Health and Health Sciences Research Center, Mazandaran University of Medical Sciences, Sari, Iran
2 Student Research Committee, Department of Environmental Health, School of Health, Mazandaran University of Medical Sciences, Sari, Iran

Original Article

Abstract

The textile dyes are considered as major environmental problems. The dyes can be removed by various methods. Therefore, this study aimed to evaluate the adsorption rate of Reactive Red 198 (RR198) from aqueous solution by activated Azolla filiculoides. This was an empirical-lab study. The Azolla was used as an adsorbent to remove Reactive Red 198 dye. The effect of various parameters was investigated on adsorbent performance and the adsorption isotherms were determined. The dye concentration was measured by spectrophotometer (DR4000) in λ_{max} = 518 nm. The results indicated that A. filiculoides biosorbent had a large specific surface area (36 m^2/g). Using the Langmuir equation, the biosorption capacity (q_m) for RR198 was 12.2 mg/g. The results showed that the removal ratio of RR198 reached to 97.3% from wastewater containing 10 mg/l RR198. The biomass could be used as a potential biosorbent for the removal of RR198 from industrial wastewater.

KEYWORDS: Biosorption, Azolla Filiculoides, Reactive Red 198 Dye

Date of submission: 21 Mar 2013, ***Date of acceptance:*** 23 May 2013

Citation: Zazouli MA, Balarak D, Mahdavi Y. **Effect of Azolla filiculoides on removal of reactive red 198 in aqueous solution.** J Adv Environ Health Res 2013; 1(1): 44-50.

Introduction

Textile dyes are considered as one of the major environmental problems because the dyes can be toxic by decomposition.[1-3] The dye production amount[4-8] is estimated between 7 × 10^5-10^6 which is used in various industries such as production of cosmetic, leather, paper and textile.[9,10] Among this industries, the textile have high dye consumption and can generate high volume wastewater with dye concentration in range of 10-200 mg/l.[7,11] The dyes have carcinogenic and mutagenic properties and can cause to allergy and dermatitis.[12,13] Mainly, the dyes have one or more benzene molecular structure which due to toxicity and slow degradation, can affect the environment seriously. Therefore, these wastewaters must be treated by suitable methods. Various methods such as biological processes, membrane processes, advanced oxidation processes (AOPs) and etc. were used to treat textile effluents.[14,15] Most studies which conducted on dye removal were based on AOPs that despite high efficiency in dye removal, the formation of by-products and their cost were consider as a major problem.[11] Adsorption process is performed on activated carbon which the carbon has high capacity and adsorption surface; however it is expensive and utilizing it requires to expertise.[16,17] Therefore, using natural and low cost adsorbents instead of commercial carbon has been considered by researchers.

Corresponding Author:
Davoud Balarak
Email: dbalarak2@gmail.com

Today, many researchers use the various natural adsorbents including Chitosan, fly ash, peach kernel, olive, charcoal, barley and wheat straw, sawdust to remove organic and inorganic pollutants.[9,10] Other methods such as biosorption, bioaccumulation, and biodegradation were suggested to textile effluent treatment.[18,19] Azolla filiculoides is a floating aquatic fern which is growing rapidly in stagnant wetlands and cover the surface of water. Therefore, it is a risk for aquatic life [20,21] especially in Anzali wetlands in north of Iran. The researchers were seeking a method to eliminate this plant from water and reuse.[21] In many countries of world, it is used as high efficiency and inexpensive adsorbent to remove organics such as dyes and heavy metals with regarding to its adsorbing properties. [18,20,22-25] Because there was no study on reactive red 198 (RR198) removal by Azolla filiculoides; Therefore, this research aimed to investigate the removal of a textile dye RR198 from aqueous solutions by dried Azolla filiculoides as an effective and low cost biosorbent. The effects of various operating parameters were studied including pH, biosorbent dosage and contact time.

Materials and Methods

The RR198 dye was supplied from Alvan Sabet Co. The stock solution (1000 mg/l) was prepared and desired concentration of dye solution was prepared by dilution of stock solution. General characteristics and chemical structures of RR198 are presented in table 1 and figure 1, respectively. All the chemicals used were analytical grade.

Table 1. The characteristics of Reactive Red 198 dye[17]

Name	Molecular weight	λmax (nm)	Molecular formula
Reactive Red198	967.5	518	$C_{27}H_{18}ClN_7Na_4O_{15}S_5$

Azolla filiculoides was obtained from paddies surrounding Sari, Iran. It was dried in the sun. They were then powdered and sieved to select 1-2 mm particle sizes for using as a biosorbent. The biomass was treated with 0.1M HCL for 5 hours followed by washing with distilled water and then dried.[18]

The literature review indicated that the most important effective variables on adsorption were including pH, adsorbent dose, contact time and dye concentration. Because the dye concentration in textile effluent was 10-200, therefore the initial dye concentration was selected 10, 25, 50, 100, and 200. Absorbent dosage (0.2-1.4 g), contact time (10, 20, 30, 45, 60, 90, 120, 180 and 240 minutes) and pH (3, 5, 7, 9 and 11) were investigated. The experiments in batch system were carried out in a 250 ml erlenmeyer flask. In each adsorption experiment, the specific concentrations of dye solution were added into the flask. The desired condition was adjusted and then the specific dosage of adsorbent was added. The samples were mixed by a magnetic stirrer with 180 rpm for 60 min. After the requirement time, the samples were centrifuged at 3,600 rpm for 10 min. Finally, the residual concentrations were measured using spectrophotometer (DR4000) in λmax = 518 nm.[13,18]

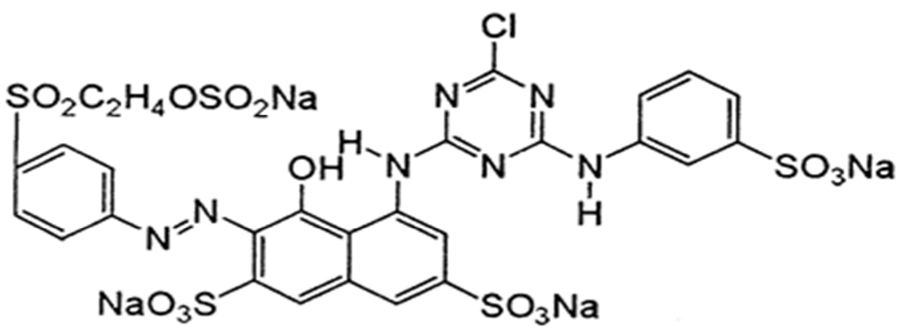


Figure 1. The chemical structure of Reactive Red 198[17]

Results and Discussion

The specific surface area of adsorbent was one of the most important parameters on adsorption ability. The more surface area of material was, the greater the porosity of the material could be. Therefore, it will have higher contact surface with the adsorption. The surface area of dried Azolla was 36 m^2/g.

Effect of Contact Time and Initial Dye Concentration

The adsorption percentage increases by increasing of contact time; however adsorption ratio reached to equilibrium after 90 minutes. With regarding to present study, the dye removal efficiency increased by increasing contact time which was due to more contact between pollutants and adsorbent. In the initial minutes of process, the dye adsorption was rapidly done. Adsorption rate decreased with time which was due to declining of dye concentration and decreasing active points on adsorbent surface area. There were a lot of empty spaces in the early stages of absorption and they were occupied by dye molecules with time. It was in accordance with several studies that conducted on dye removal by Azolla.[3,20]

The dye removal efficiency decreased by increasing initial concentration, so that adsorption rate in concentration of 10 mg/l was double than 200 mg/l. When the initial RR198 concentration increased, the adsorbent sites was filled earlier and the dye removal efficiency decreased. The results of this study were agreed with previous studies. The results of this study were in accordance with previous studies.[3,26] Figure 2 illustrates the effect of contact time and initial dye concentration on removal efficiency.

Effect of pH and Adsorbent Dosage

Figures 3 and 4 suggest the effect of pH and adsorbent dosage on adsorption ratio. Many researchers expressed that the pH plays an essential role in the electrostatic attraction between the adsorbent and the dye. In this study, the maximum dye removal was observed in neutral pH. The efficiency was decreased in acidic or alkaline pH, which it was inconsistent with the Mahvi study on dye removal by activated carbon and the study of Wang on dye removal by Red mud.[3,27]

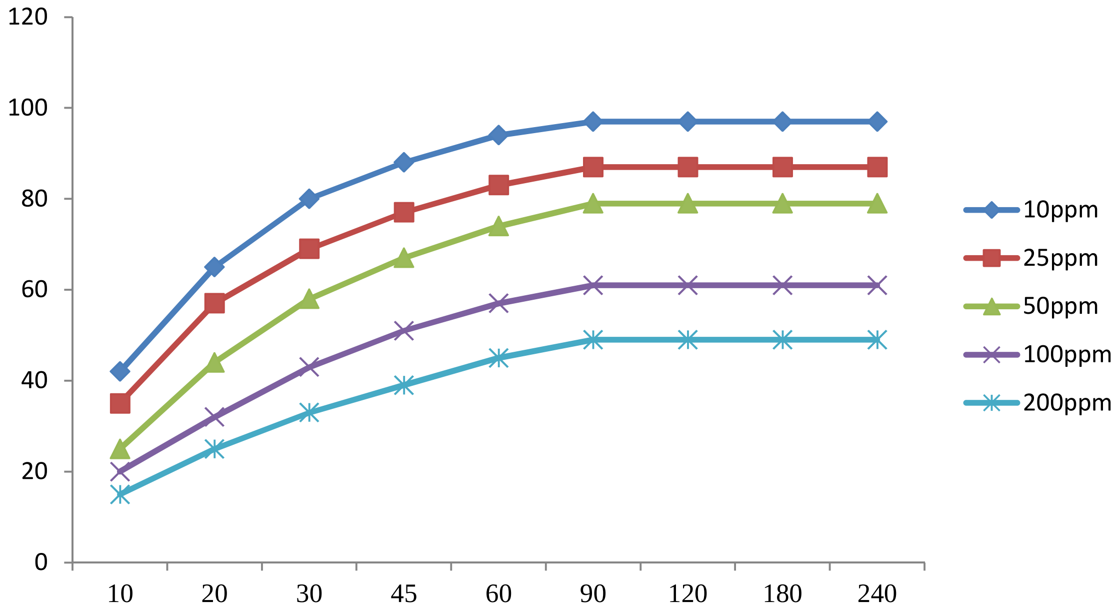


Figure 2. Effect of contact time and initial dye concentration on removal efficiency
(pH = 3, adsorbent dosage 1 gr/100 cc)

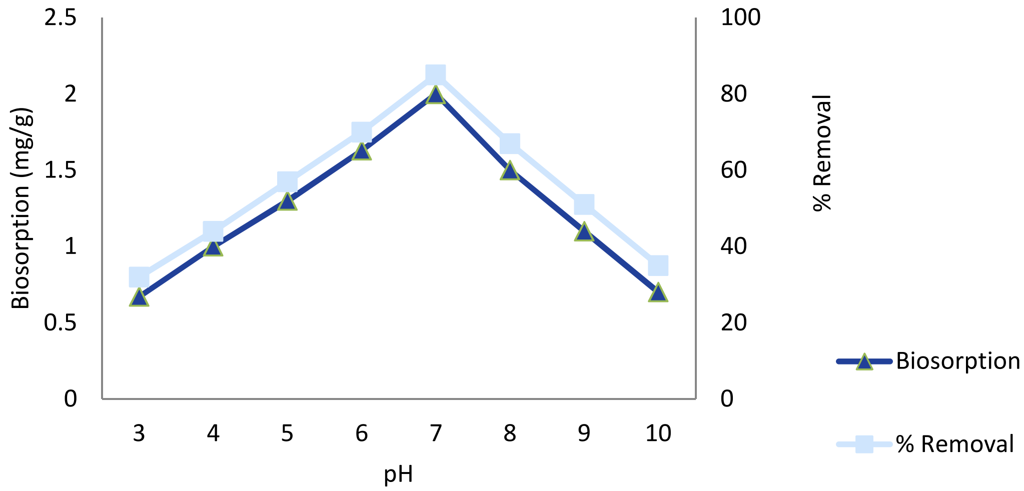


Figure 3. Effect of pH on adsorption
(Initial dye concentration of 25mg/l, contact time = 90 minutes, adsorbent dosage 1 gr/100 cc)

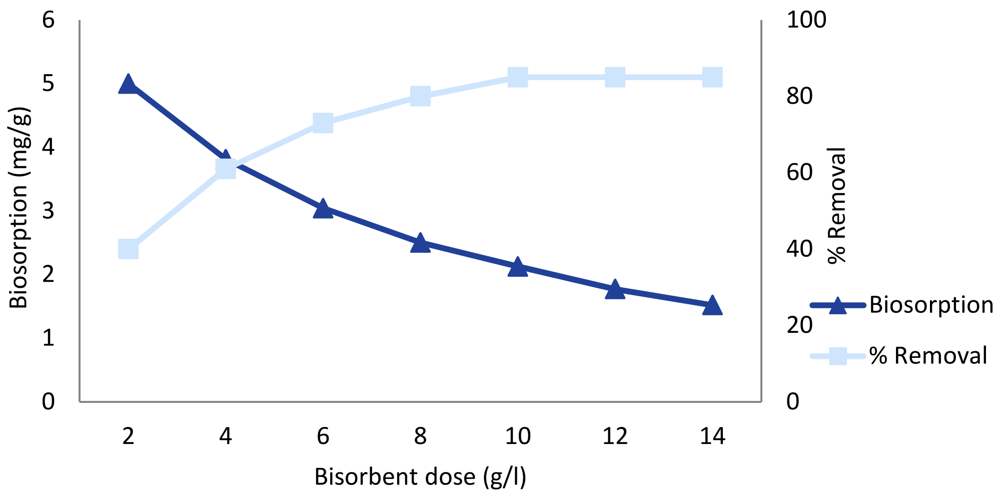


Figure 4. Effect of adsorbent dose on adsorption
(Dye initial concentration 25mg/l, contact time = 90 min, pH = 3)

The dye removal efficiency increased by increasing adsorbent dosage up to concentration of 10 g/l; however thereafter, it reached to equilibrium. The adsorption rate increased by adsorbent dosage increasing which was due to increasing the active surface of adsorbent. The results showed that although efficiency increased with increasing adsorbent dose, the dye adsorbed per gram of adsorbent decreases and it was because the active sites of adsorbent were not saturated. So that, when the adsorbent dose was increasing, the total capacity of the adsorbent surface points were not used completely and this reduced the absorption rate per unit mass of the adsorbent.[20,28]

Adsorption Isotherms

The adsorption of adsorbate (RR198) onto the adsorbent (A. filiculoides) was modeled using the Langmuir and Freundlich equations. The Langmuir isotherm assumed monolayer coverage of an adsorbate onto the solid surface of adsorbent, uniform energy of sorption, and no transmigration of adsorption in the plane of the surface.[29] At equilibrium, the Langmuir isotherm can be expressed as equation 1:

$$\frac{1}{q_e} = \frac{1}{K_L q_m}\frac{1}{C_e} + \frac{1}{q_m}$$

where q_e is the amount of adsorbate adsorbed at equilibrium (mg/g); C_e is the equilibrium concentration of the adsorbate or the adsorbate unadsorbed in the solution (mg/L); q_m (mg/g) is the maximum theoretical biosorption capacity and K_L is a measure of biosorption energy, indicating the affinity between adsorbent and adsorbate.[30]

The Freundlich equation is also often used as an empirical relationship between the concentration of an adsorbate on the surface of an adsorbent and the concentration of the adsorbate in the solution at equilibrium.[30] The Freundlich equation is based on the hypothesis of multi-layer adsorption and the linear form is given by the equation 2:

$$\log q_e = \log k + \frac{1}{n}\log c_e$$

where q_e is the adsorbate adsorbed at the equilibrium (mg/g); C_e is the equilibrium concentration of the adsorbate or the unadsorbed adsorbate in the solution (mg/L); and K is a constant, indicative of adsorption capacity.[29] Figure 5 shows the Freundlich and Langmuir equation obtained by the adsorption of RR198 onto dried A. filiculoides.

With regarding to obtained equilibrium, data of using this plant to RR198 adsorption indicated that the data were better fitted on Langmuir isotherm (R^2 = 0.999) than Freundlich isotherm (R^2 = 0.932) which was in agreement with the studies that were performed by this plant to dye removal.[18,20,31]

Conclusion

Based on the results, the dried Azolla can be used as an effective and low cost adsorbent to treat effluent containing dye. The removal efficiency depends upon parameters such as initial dye concentration, adsorbent dose, pH, and contact time. The data were best fitted on Langmuir isotherm.

Conflict of Interests

Authors have no conflict of interests.

Acknowledgements

Hereby, authors are grateful from Student Research Committee of Mazandaran University of Medical Sciences, Iran due to supporting this research.

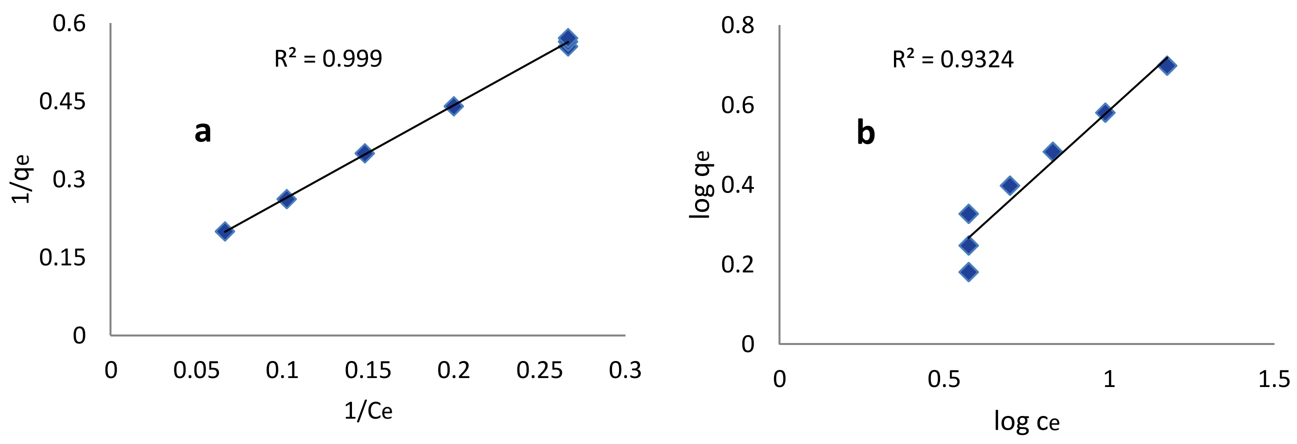


Figure 5. Isotherm models: (a) Langmuir (b) Freundlich

References

1. Zazouli M, Yazdani J, Balarak D, Ebrahimi M, Mahdavi Y. Investigating the Removal Rate of Acid Blue 113 from Aqueous Solution by Canola. J Mazandaran Univ Med Sci 2013; 22(2): 71-8. [In Persian].
2. Crini G, Badot PM. Application of chitosan, a natural aminopolysaccharide, for dye removal from aqueous solutions by adsorption processes using batch studies: A review of recent literature. Progress in Polymer Science 2008; 33(4): 399-447.
3. Mahvi AH, Heibati B. Removal Efficiency of Azo Dyes from Textile Effluent Using Activated Carbon Made from Walnut Wood and Determination of Isotherms of Acid Red18. Journal of Ardabil health 2011; 1(3): 7-15.
4. Nateghi R, Bonyadinejad GR, Amin MM, Assadi A. Nickel oxide nanoparticles application as an efficient adsorbent for dye removal from synthetic wastewater treatment. J Health Syst Res 2010; 6(Supplement): 1015-21. [In Persian].
5. Ghanizadeh G, Asgari G. Removal of Methylene Blue Dye from Synthetic Wastewater with Bone Char. Iran J Health Environ 2009; 2(2): 104-13.
6. Yazdanbakhsh AR, Mohammadi AS, Sardar M, Mohammadi H, Zarabi M. Investigation of Iron Powder, Hydrogen Peroxide and Iron Hydrogen Peroxide for Removal of Acid Yellow Powder 36 Dye from Aqueous Solutions. Iran J Health Environ 2010; 2(4): 296-303. [In Persian].
7. Asilian H, Moussavi GR, Mahmoudi M. Adsorption of Reactive Red 198 Azo Dye from Aqueous Solution onto the Waste Coagulation Sludge of the Water Treatment Plants. Iran J Health Environ 2010; 3(1): 93-102. [In Persian].
8. Ghaneian MT, Ehrampoush MH, Ganizadeh Gh, Shahi M, Momtaz M. Application of Ozonation on the removal of Reactive Red 198 dye at alkaline Condition. Toloo e Behdasht 2010; 9(2-3): 11-21. [In Persian].
9. Samarghandi M, Noori Sepehr M, Zarrabi M, Norouzi M, Amraie F. Mechanism and Removal Efficiency of C.I. Acid Blake 1 by Pumice Stone Adsorbent. Iran J Health Environ 2011; 3(4): 399-410. [In Persian].
10. Shen D, Fan J, Zhou W, Gao B, Yue Q, Kang Q. Adsorption kinetics and isotherm of anionic dyes onto organo-bentonite from single and multisolute systems. J Hazard Mater 2009; 172(1): 99-107.
11. Naddafi K, Nabizadeh Nodehi R, Jahangiri Rad M. Removal of Reactive Blue 29 Dye from Water by Single-Wall Carbon Nanotubes. Iran J Health Environ 2011; 3(4): 359-68. [In Persian].
12. Ghaneian M, Ehrampoush M, Ghanizadeh G, Dehvary M, Abootoraby M, Jasemizad T. Application of Solar Irradiation/K2S2O8 Photochemical Oxidation Process for the Removal of Reactive Blue 19 Dye from Aqueous Solutions. Iran J Health Environ 2010; 3(2): 165-76. [In Persian].
13. Hadi M, Samarghandi MR, Azizian S, Samadi MT, Shokoohi R, Rahmani A. Using Thomas Model to Evaluate Dye Removal from Aqueous Solutions in Fixed-bed Columns of Activated Carbon. Journal of Water and Wastewater 2011; 22(77): 23-34. [In Persian].
14. Rahmani AR, Samarghandi MR. Electrocoagulation Treatment of Color Solution Containing Colored Index Eriochrome Black T. Journal of Water and Wastewater 2009; 20(69): 52-8. [In Persian].
15. Toor M, Jin B. Adsorption characteristics, isotherm, kinetics, and diffusion of modified natural bentonite for removing diazo dye. Chemical Engineering Journal 2012; 187(0): 79-88.
16. Hosseinzadeh E, Zare M, Torabi E, Rahimi S, Shokouhi R. Sodium Alginate Magnetic Beads for Removal of Acid Cyanine 5R from aqueous solution. Hormozgan Med J 2012; 16(2): 101-11. [In Persian].
17. Ghaneian MT, Ehrampoush MH, Ghanizadeh GH, Momtaz M. Study of eggshell performance as a natural sorbent for the removal of reactive red 198 dye from aqueous solution. Toloo e Behdasht 2011; 10(1): 70-81. [In Persian].
18. Padmesh TV, Vijayaraghavan K, Sekaran G, Velan M. Batch and column studies on biosorption of acid dyes on fresh water macro alga Azolla filiculoides. J Hazard Mater 2005; 125(1-3): 121-9.
19. Vijayaraghavan K, Yun YS. Bacterial biosorbents and biosorption. Biotechnol Adv 2008; 26(3): 266-91.
20. Tan Cy, Li G, Lu XQ, Chen Zl. Biosorption of Basic Orange using dried A. filiculoides. Ecological Engineering 2010; 36(10): 1333-40.
21. Filizadeh Y. Survey Ecology Excessive Growth of Azolla in Anzali Wetland and Quality Control. Iran Journal of Natural Resources 2002; 55(1): 65-82.
22. Vafaei F, Khataee AR, Movafeghi A, Salehi Lisar SY, Zarei M. Bioremoval of an azo dye by Azolla filiculoides: Study of growth, photosynthetic pigments and antioxidant enzymes status. International Biodeterioration & Biodegradation 2012; 75(0): 194-200.
23. Pandey VC. Phytoremediation of heavy metals from fly ash pond by Azolla caroliniana. Ecotoxicol Environ Saf 2012; 82: 8-12.
24. Bennicelli R, Stepniewska Z, Banach A, Szajnocha K, Ostrowski J. The ability of Azolla caroliniana to remove heavy metals (Hg(II), Cr(III), Cr(VI)) from municipal waste water. Chemosphere 2004; 55(1): 141-6.
25. Jain SK, Gujral GS, Jha NK, Vasudevan P. Production of biogas from Azolla pinnata R.Br and Lemna minor L.: Effect of heavy metal contamination. Bioresource Technology 1992; 41(3): 273-7.

26. Shokohi R, Jafari S, Siboni M, Gamar N, Saidi S. Removal of Acid Blue 113(AB113) dye from aqueous solution by adsorption onto activated red mud: a kinetic and equilibrium study. Sci J Kurdistan Univ Med Sci 2011; 16(2): 55-65. [In Persian].
27. Wang S, Boyjoo Y, Choueib A, Zhu ZH. Removal of dyes from aqueous solution using fly ash and red mud. Water Res 2005; 39(1): 129-38.
28. Colak F, Atar N, Olgun A. Biosorption of acidic dyes from aqueous solution by Paenibacillus macerans: Kinetic, thermodynamic and equilibrium studies. Chemical Engineering Journal 2009; 150(1): 122-30.
29. Dogan M, Abak H, Alkan M. Biosorption of Methylene Blue from Aqueous Solutions by Hazelnut Shells: Equilibrium, Parameters and Isotherms. Water, Air, and Soil Pollution 2008; 192(1-4): 141-53.
30. Low KS, Lee CK, Tan BF. Quaternized wood as sorbent for reactive dyes. Appl Biochem Biotechnol 2000; 87(3): 233-45.
31. Zazouli M, Balarak D, Mahdavi Y, Ebrahimi M. Adsorption rate of 198 reactive red dye from aqueous solutions by using activated red mud. Iranian Journal of Health Sciences 2013; 1(1): 36-43. [In Persian].

Journal of Advances in Environmental Health Research

Site selection for wastewater treatment plant using integrated fuzzy logic and multicriteria decision model: A case study in Kahak, Iran

Behzad Shahmoradi[1], **Ali-Asghar Isalou**[2]

1 Kurdistan Environmental Health Research Center, Kurdistan University of Medical Sciences, Sanandaj, Iran
2 Department of Urban Planning, School of Technology, University of Kurdistan, Sanandaj, Iran

Original Article

Abstract

One of the environmental issues in urban planning is finding a suitable site for constructing infrastructures such as water and wastewater treatment plants. There are numerous factors to be considered for this purpose, which make decision-making a complex task. We used an integrated fuzzy logic and multicriteria decision model to select a suitable site for establishing wastewater treatment plant in Kahak, Iran. We used super decision software and a geographic information system (GIS) for scoring the parameters. The western part of Kahak was found to be a suitable place for constructing municipal wastewater treatment plant. Our findings indicated that decision makers and policy makers would be able to achieve better results concerning the most suitable location for wastewater treatment plant easily through combining these two models.

KEYWORDS: Fuzzy Logic, Multicriteria Decision Making, Wastewater Treatment Plant, Site Location

Date of submission: 16 Mar 2013, ***Date of acceptance:*** 17 May 2013

Citation: Shahmoradi B, Isalou AA. **Site selection for wastewater treatment plant using integrated fuzzy logic and multicriteria decision model: A case study in Kahak, Iran.** J Adv Environ Health Res 2013; 1(1): 51-61.

Introduction

Rapid growth of urban settlements together with a change in their usage pattern during recent half century has led not only to increase in urban systems input rate but also it has had great impact on their output rate. One of the important outputs is municipal wastewater, which severely threats natural ecosystems. Hence, it is necessary to take effective steps toward achievement of environmental goals of sustainability through developing treatment plants in suitable sites, but finding a suitable site for this purpose involves considering wide range of criteria that makes decision making complicated. These complexities justify the necessity of a systematic method for analyzing the decision in a framework that processes spatial data; a method which could justify awareness, expert and judgment.[1] Anagnostopoulos and Vavatsikos[2] extended fuzzy-analytic hierarchy process (FAHP) model for determining wastewater treatment plant site. The factors used in this investigation include slope, topography, geology, land use, distance from road, railroad, river, settlements, faults, coastline, etc. They categorized suitable sites for constructing wastewater treatment plant in Rodopi City and identified fuzzy model and network analysis process as a combined suitable model for decision makers in determining a suitable site for wastewater treatment plant. Anagnostopoulos et al.[3] in another study tried to find the most suitable location for wastewater treatment plant of a region using FAHP method. They found out that the combination of multi-criteria decision making model and geographic information system (GIS) is a valuable tool for determining the treatment

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

plant site. In their study, they used 4 indices (12 criteria) to achieve their goal.

Deepa and Krishnaveni[4] using analytic hierarchy process (AHP) method and GIS tried to determine a suitable site for decentralized wastewater treatment plant in Shollinganallur region. In their study, they used 5 criteria: Topography, slope, land use, population, and soil.

In these studies, we can find that multicriteria decision making methods such as AHP and also fuzzy model have been identified as common applied models during recent years. Furthermore, they insisted that GIS is the most suitable spatial analysis tool and a combination of different information layers. The most significant point in these studies is that the role of combined models in determining suitable sites for wastewater treatment plant construction is highly significant. Hence, in present study, we used fuzzy and analytic network process (ANP) combined model which has higher capability compared to other decision making models in order to obtain better results. On the other hand, more criteria were considered in present study than previous ones. Based on the criteria and mentioned model, we tried to determine a suitable place for constructing a wastewater treatment plant in Kahak, Iran.

Materials and Methods

In order to facilitate computations and enhance the accuracy in scoring, in present study we used Super Decision Software. The mentioned software is designed based on network analysis process model and it is able to perform paired comparison among elements and clusters, bounded, harmonic and inharmonious matrices and compute the weight of each criterion with highest accuracy.

Due to its various capabilities in the field of spatial analysis, GIS is the other software which is used in these studies; such that Spatial Analyst Extension provides the opportunity to define fuzzy model and develop related maps. On the other hand, this extension with the ability to superimpose raster layers makes development of final map possible. It must be mentioned that some plans from related organizations were prepared with Shp format; but other maps were adopted from main maps. For example, we can refer to topography layer which was obtained from DEM raster layer.

The present study tries to find the most suitable site for constructing wastewater treatment plant in Kahak city using combined model of network analysis and fuzzy process. Increasing the accuracy in final results, matching two mentioned model with data nature (discrete and continuous) and commonality of combined models are of important reasons for selecting fuzzy-ANP combined model.[5] Hence, firstly we introduced and collected the criteria and then we identified the methods of network analysis process separately. Then, using Super Decision software, we performed related computations for the structure of ANP model. In the next step, we determined the thresholds (minimum and maximum) of optimal site for wastewater treatment plant through reviewing the literatures and then we implemented all final data of network analysis process model in database of basic maps related to discrete data (in GIS environment) and with reliance on fuzzy formula we prepared fuzzy maps. Finally, by superimposing all layers, we determined the final area for constructing the wastewater treatment plant (Figure 1).

By reviewing the literatures, we found that each of researchers has used a certain set of criteria for determining suitable site for wastewater treatment plant referred in introduction of present study. Based on these studies, 12 criteria were categorized in the form of two general groups of discrete and continuous indices, such that discrete indices included 6 criteria (soil, slope, topography, geology, land use, and wind) and continuous indices included 6 criteria (distance from main city, underground water, surface water, roads, and settlements).

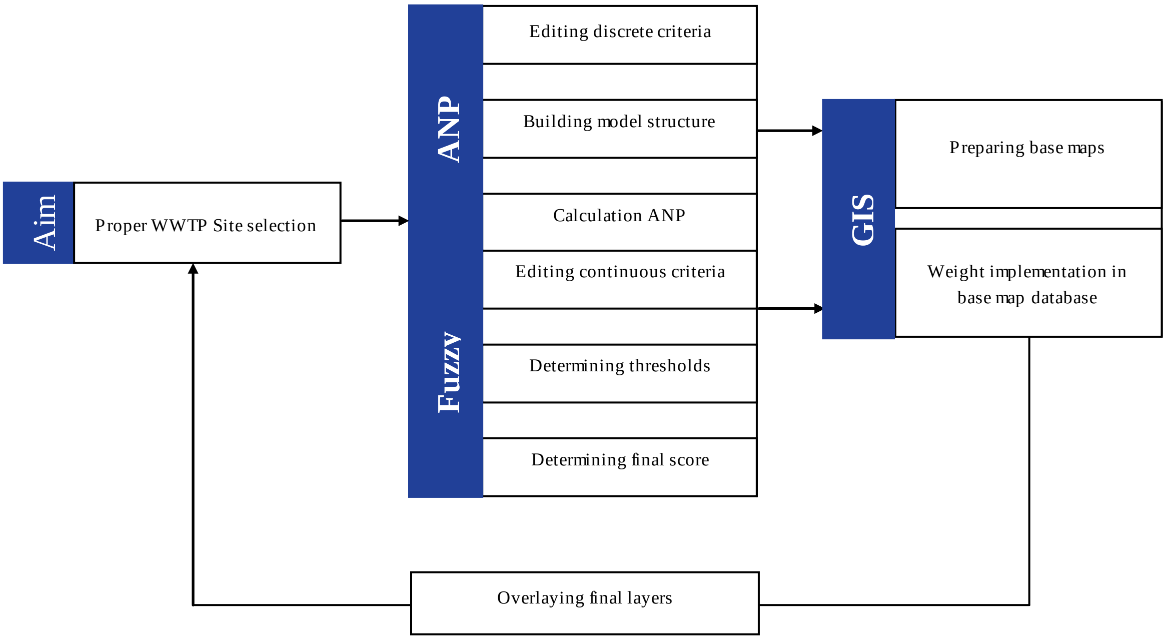


Figure 1. Procedure framework
WWTP: wastewater treatment plant; ANP: Analytic network process; GIS: Geographical Information System

ANP is one of multi-criteria decision making techniques and is a set-up model. This model is designed based on AHP and "Network" to replace "hierarchy".[6]

Some of the fundamental ideas in support of ANP are : (1) ANP is built on the widely used AHP; (2) by allowing for dependence, the ANP goes beyond the AHP by including independence and hence also the AHP as a special case; (3) the ANP deals with dependence within a set of elements (inner dependence), and among different sets of elements (outer dependence); (4) the looser network structure of the ANP makes possible the representation of any decision problem without concern for what comes first and what comes next as in a hierarchy; (5) ANP is a non-linear structure that deals with sources, cycles, and sinks having a hierarchy of linear form with goals in the top level and the alternatives in the bottom level; (6) ANP portrays a real-world representation of the problem under consideration by prioritizing not only just the elements but also groups or clusters of elements as is often necessary; and (7) the ANP utilizes the idea of a control hierarchy or a control network to deal with different criteria, eventually leading to the analysis of benefits, opportunities, costs, and risks. By relying on the control's elements, the ANP parallels what the human brain does in combining different sense data as for example does the thalamus.[7] The main stages of the model can be classified in four categories:

Step I (model construction and problem structuring): The problem should be clearly stated and decomposed into a rational system such as a network. The framework can be determined based on decision-maker opinion via brainstorming or other appropriate methods.[8]

Step II (pairwise comparisons and local priority vectors): The elements are compared pairwisely with respect to their impacts on other elements. The way of conducting pairwise comparisons and obtaining priority vectors is the same as in the AHP. The relative importance values are determined on a scale of 1-9, where a score of 1 indicates equal importance between the two elements and 9 represents the extreme importance of one element compared with the other one. A reciprocal value is assigned to the inverse comparison; that is, $a_{ji}=1/a_{ij}$ where a_{ij}

denotes the importance of the i^th^ element compared with the j^th^ element. Also, a_{ii} =1 is preserved in the pairwise comparison matrix. Then, the eigenvector method is employed to obtain the local priority vectors for each pairwise comparison matrix. To test consistency of a pairwise comparison, a consistency ratio (CR) can be introduced with consistency index (CI) and random index (RI). Table 1 shows the average RI for corresponding matrix size. If the CR is less than 0.1, the pairwise comparison is considered acceptable.[7,9-11] By formulas 1 and 2 it can be calculated from the index weights consistency rate:

(1) $CI=\frac{\lambda_{max}-n}{n-1}$ Eq.

(2) CR = CI/RI Eq.

Step III (supermatrix formation): A supermatrix, known as partition matrix, is formed by setting the local priority vectors on suitable columns. Local priority vectors are classified and occupied in suitable places based on effect flow from one component to another. Supermatrix may consist of zero value. In general, there exists interdependence between clusters, the sum of one column in the supermatrix is mostly bigger than 1. In case the supermatrix is not stochastic, the cluster is weighted and column is normalized to transform into a stochastic matrix where the sum of columns are 1. This matrix can be called as a weighted supermatrix.[12]

Step IV (calculation of global priority vectors and weights): In the final step, the weighted supermatrix is raised to limiting power to get the global priority vectors as in Eq. (3):

(3) $\lim =_{K\to\infty} W^K$ Eq.

If the supermatrix has the effect of cyclicity, there may be two or more N limiting supermatrices. In this case, the Cesaro sum is calculated as in Eq. (4) to get the average priority weights as follows:[13]

(4) $\lim_{K\to\infty}(1/N)\sum W_i^k$ Eq.

Where W is the weighted supermatrix, N indicates the sequence, and k is the exponent determined by iteration.[5]

Zadeh[14] introduced the fuzzy set theory to deal with the uncertainty due to imprecision and vagueness. A major contribution of fuzzy set theory is its capability of representing vague data. The theory also allows mathematical operators and programming apply to the fuzzy domain. A fuzzy set is a class of objects with a continuum of grades of membership.[15]

The fuzzy set theory is a logic that the degree of the membership of each element can be calculated based on it, such that the membership degree of each element in the fuzzy set is defined spectrally among the data between [0,1]. In addition, in this logic in order to make fuzzy data, there are various functions of fuzzy logic.[16]

Among the most important functions, triangular functions, linear function, trapezoidal function, linear function J, etc. could be mentioned. Here, it was tried to determine membership degree of each pixels in the fuzzy logic set by triangular fuzzy logic. This set is defined by three values a ≤ b ≤ c for any number of which a membership function is defined. This membership function has the following formula and diagram (Figure 2).

Kahak is located 30 km from Qom, at longitude of 50° 30°- 51° 00 and latitude of 34°- 34° 30° (Figure 3). This town is the center of Kahak district having a population of 2789 based on 2006 census.

In recent decades, rapid growth of the city has caused environmental issues that are increasingly important. Unfortunately, the lack of wastewater treatment is one of the most important environmental problems in the region (Kahak) so that the release of domestic, industrial, commercial, and other types of wastewater in open spaces or disposed of by absorption wells

Table 1. Average ratio of inconsistency for corresponding matrix size10

(n)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Random index (RI)	0	0	0.58	0.90	1.12	1.24	1.32	1.41	1.45	1.49	1.51	1.48	1.56	1.57	1.59

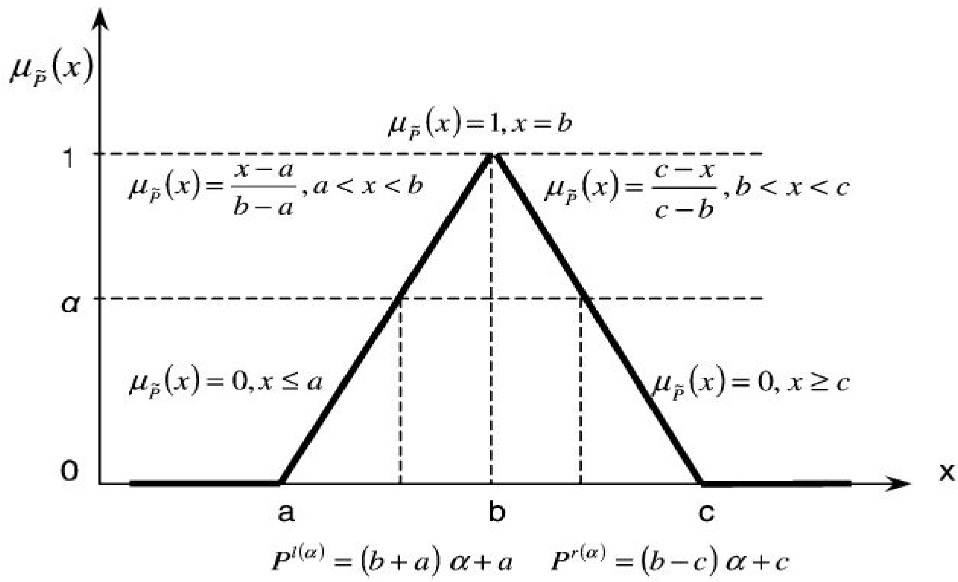


Figure 2. Left and right representation of a TFN, $\tilde{p}'$ adopted from Kahraman et al.[17] In this kind of fuzzy numbers, $\mu_{\tilde{P}}(x)$ is fuzzy function, (b) is the central value with the highest probability, (a) and (c) represent the fuzziness[18]

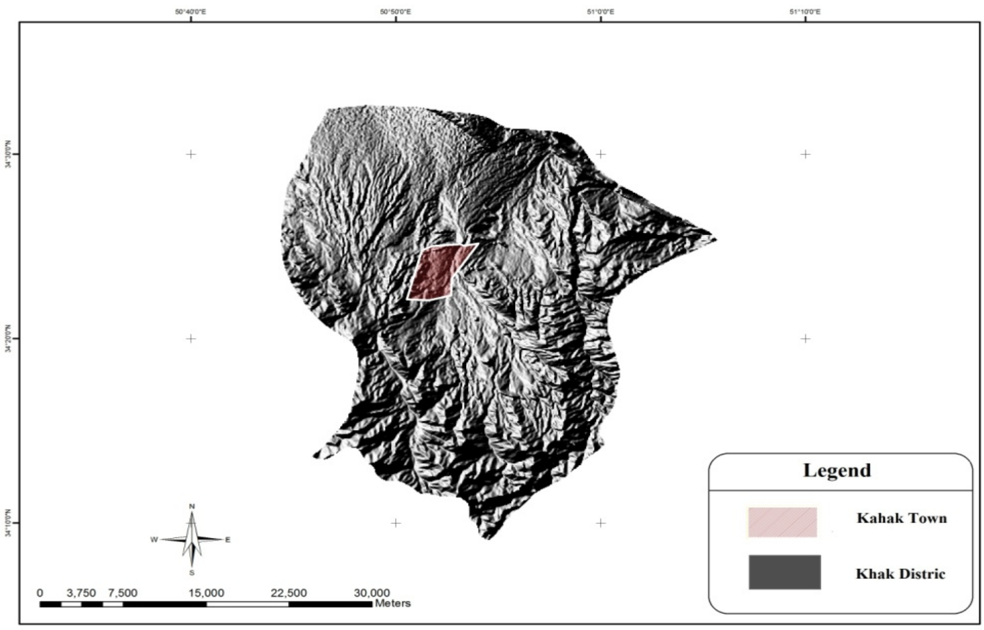


Figure 3. Position of the Kahak Town

has caused both of these methods present a serious threat to ecosystem region. On the other hand, locating infrastructures in the region requires supplying water and construction of municipal wastewater treatment plant that is essential to supply water for irrigation.

Results and Discussion

Making continuous criteria fuzzy

In this part of study, 6 criteria (distance from main city, distance from settlements, distance from faults, distance from roads, distance from main rivers, and penetrating waters) were selected as continuous criteria (Figure 4). The main reason for selecting these criteria and including them in continuous macro-criteria group was that based on long or small distance of wastewater treatment plant site from 6 mentioned criteria, it could have negative or positive consequences from social, economic and environmental aspects for Kahak Town. Hence, the spectral feature of each of these criteria induces the authors to put them in continuous criteria group. But it is necessary to determine maximum and minimum thresholds of each criterion based on performed studies and or available rules in order to achieve better results.

Distance from roads

Anagnostopoulos and Vavatsikos[2] in their study identified 300 meters distance from the main roads for constructing wastewater refinery. We similarly supposed at least 300 meters distance as suitable distance and for which we considered 3000 meters maximum threshold.

Distance from settlements and main city

Meinzinger[19] believes that constructing wastewater treatment plant in 1500 meters distance from main settlements is a suitable distance. In present study, we supposed 550-5000 meters as suitable distance because we believe that small distance of these installations from main settlements would lead to transmission of odor and pollution to city. On the other hand, long distance involves huge costs for constructing infrastructures. For other mall settlements which have more density around the cities, 150-1500 meters seems suitable.

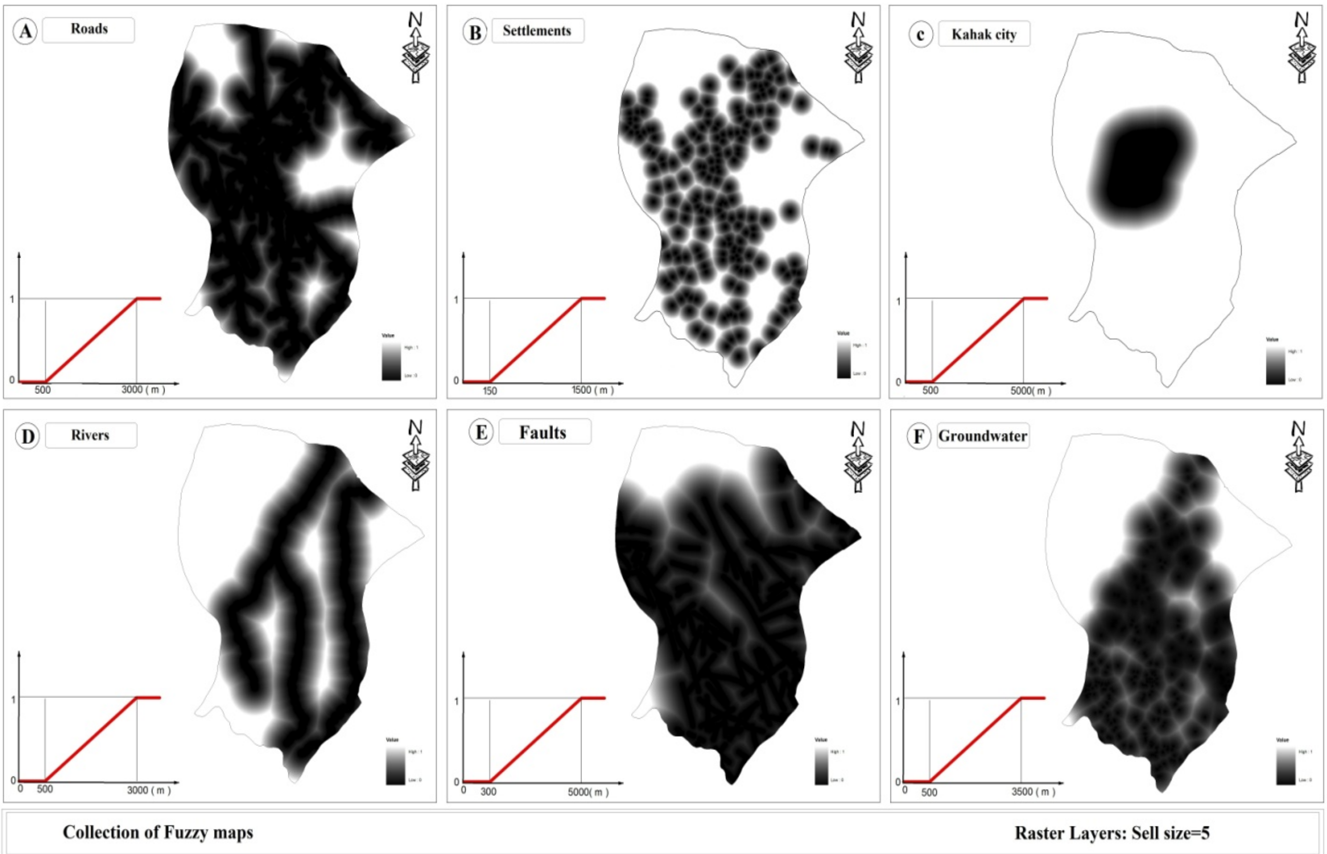


Figure 4. Collection of fuzzy maps

Distance from rivers and faults

In order to protect natural resources, Anagnostopoulos and Vavatsikos[2] identified minimum 500 meters and maximum 3 kilometers from main rivers as a suitable area for constructing wastewater refinery. They also considered minimum 300 meters and maximum 5 kilometers distance from faults for the purpose of their study.

Distance from penetrating waters (well and spring)

Protecting the resources and preventing them from being polluted are of important points emphasized in many studies in terms of finding a suitable site for refinery. Therefore, we considered minimum 500 meters and maximum 3500 meters distance from wells and springs as a suitable area for preventing them from being polluted (Table 2).

Table 2. Minimum and maximum distance for wastewater treatment plant site for defining fuzzy membership functions

	Index	Minimum Distance	Maximum Distance
A	Roads	500	3000
B	Settlements	150	1500
C	Kahak	500	5000
D	Main rivers	500	3000
E	Faults	300	5000
F	Groundwater	500	3500

When all minimum and maximum values for each criterion is determined, we can make all data layers relating to continuous data fuzzy through following steps in GIS environment:

In first step, we computed and determined direct distances from regarded terrains through Spatial Analyst-Distance instruction (ΔX).

In the second step, we used Spatial Analyst-Raster calculation instruction:

$\Delta X / X_{MAX}$ B) $\Delta X / X_{MAX}$ A)

ANP calculations for discrete criteria

According to conducted studies concerning locating urban wastewater refinery, the authors selected 6 criteria for this part of research and then based on their similarities they grouped them into two clusters: Physical and ground conditions. Each of these clusters is consisted of 3 criteria: For physical cluster, topography, slope and wind direction' for ground condition cluster, geology, soil and land use were considered. Then, using Super Decision software, we designed and developed ANP model. In this model, each arrow represents the influence of a cluster on other clusters. For example, physical cluster impacts natural cluster and it mutually takes effect. Of course, there is interdependence among internal elements of each cluster that is indicated by an arrow on top of them (in the form of a returning ring to the cluster itself) (Figure 5). From the arrows we can find that 4 main matrices should be formed for ANP calculations because in network analysis process each arrow represents a matrix.

After developing the matrices, paired comparisons among clusters and each element (criteria) must be conducted. In this regard, we asked 5 experts to present their ideas concerning the relative importance of each element relating the location of municipal wastewater refinery. After integrating the ideas of professionals, the related data were entered in Super Decision software through which paired comparisons were conducted. After completing the paired comparisons among the clusters and their elements, we obtained compatibility rate equal to zero and this rate was accepted. By incorporating the results of each matrix into one matrix, we obtained primary super-matrix in which the sum of each line is more than one. Therefore, Super Decision software forms harmonious super-matrix in line with normalizing the primary super-matrix (Figure 6). The final results of superiority of priorities are indicated in 6 subgroups in numerical and graphical forms in figure 7. As one can see, the criterion of region's slope with normalized score of 0.76 is more important than others and then we have land use of region with 0.68 score in determining the place of municipal wastewater treatment plant of Kahak city compared to other parameters.

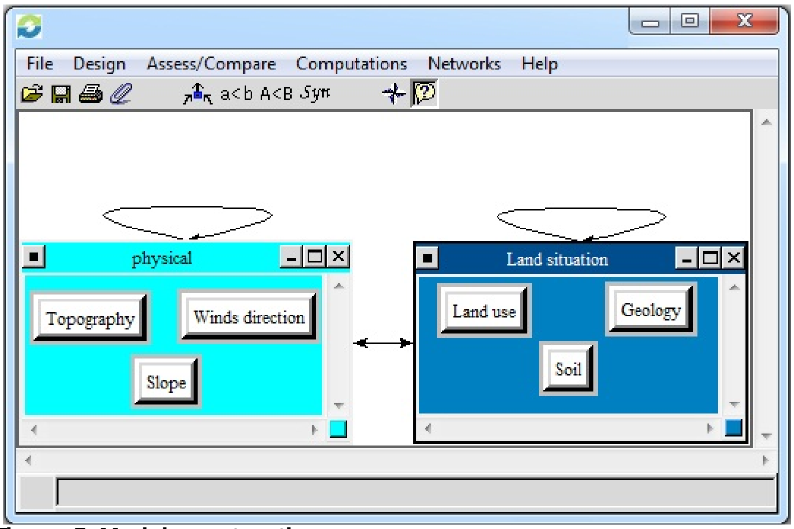


Figure 5. Model construction

Cluster	Node Labels	Land situation: Geology	Land situation: Land use	Land situation: Soil	physical: Slope	physical: Topography	physical: Winds direction
Land situation	Geology	0.125033	0.000000	0.000000	0.067475	0.375702	0.056988
Land situation	Land use	0.000000	0.125033	0.000000	0.391872	0.089089	0.407110
Land situation	Soil	0.000000	0.000000	0.125033	0.040652	0.035209	0.035901
physical	Slope	0.687192	0.657454	0.641687	0.500000	0.000000	0.000000
physical	Topography	0.130208	0.155900	0.174181	0.000000	0.500000	0.000000
physical	Winds direction	0.057567	0.061613	0.059100	0.000000	0.000000	0.500000

Done

Figure 6. Weighted supermatrix

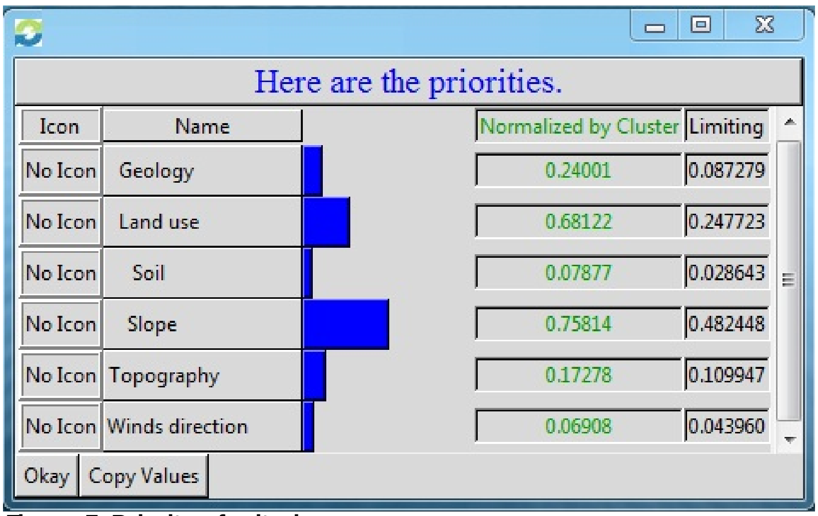


Figure 7. Priority of criteria

All normalized scores were reevaluated by 1-9 time scale in order to determine the relative importance of each sub-criterion (variables). Using GIS, all scores of each of sub-criteria were incorporated in related 6 layers. In last step, using Spatial Analyst Extension, all 6 layers were converted to raster format with Sell Size 5 to be prepared for final computations (Figure 8).

Combination of Fuzzy-ANP models

In order to implement the model through Kahak region, all layers were prepared in Shp format. Based on triangular fuzzy function, data layers of continuous criteria were converted to fuzzy form. All layers were fuzzified in GIS environment through Spatial Analyst extension. On the other hand, for weighting the discrete layers, a new column was developed in database of basic maps and obtained final scores were assigned to corresponding layers using Super Decision software. Then, all discrete layers which were in vector form were converted to raster layers with Sell Size 5 using Extension (Spatial Analyst).

In the final step, it was required to combine data layers. There are different methods for combining data layers but in present study we used Raster layers superimposition with sell size 5 using Extension (Spatial Analyst- Raster Calculator). After integrating the layers, the value of each pixel was determined and it was found that based on figure 9, western part of Kahak city is the most suitable location for constructing wastewater treatment plant.

Conclusion

In present study, application of two decision making tools, i.e. fuzzy multi criteria and ANP models in combined manner for determination of a suitable location for constructing wastewater treatment plant was identified. Precisely, by the help of studies performed up to now concerning determination of a suitable location for constructing wastewater treatment plant, we could determine main indices and criteria and moreover we divided the criteria to two groups called discrete and continuous ones so that they

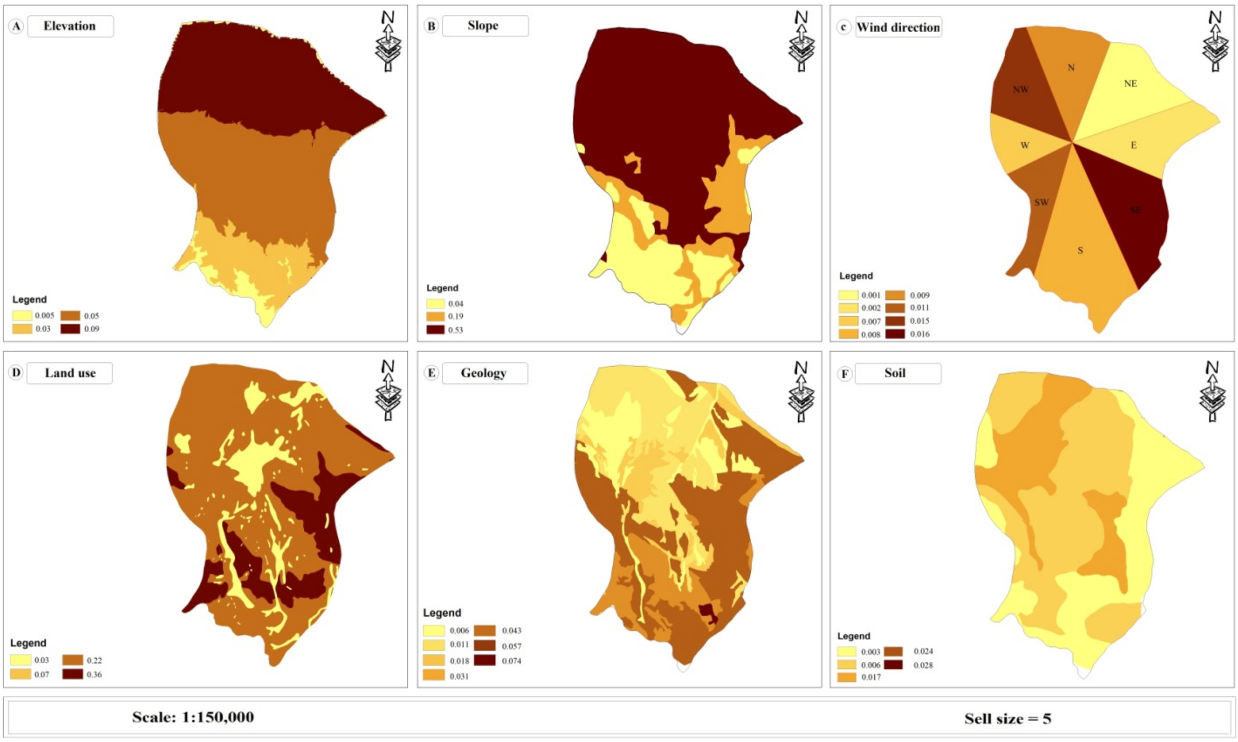


Figure 8. The raster maps calculated by ANP model

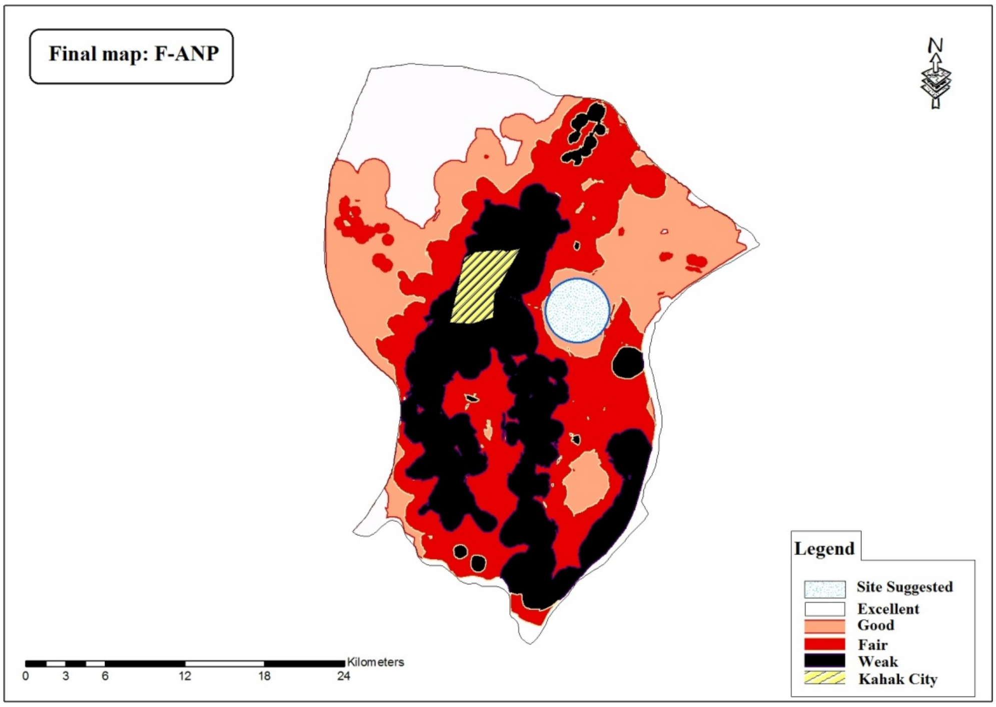


Figure 9. Final fuzzy logic and analytic network process map indicating the most suitable site for wastewater treatment plant

matched the combined model. After conducting the computations, incorporating and combining the data in GIS software environment, the western part of Kahak was found to be a suitable place for constructing municipal wastewater refinery. These findings indicated that through combining these two models, decision makers and policy makers would be able to achieve better results concerning the most suitable location for wastewater treatment plant easily. In previous studies, the authors had used this model for finding a suitable location for landfill, but the difference is that in the present study, computational software such as Super Decision for decision making was used and the results indicated that this software makes the computations easier and it reduces the possibility of error. Application of newer models and more criteria is another difference in this study compared to previous studies.

Conflict of Interests

Authors have no conflict of interests.

References

1. Neshastehgar M. Application of the integrated Multi-Criteria Multi-Decision in site selection of non-concentrated wastewater treatment plants in metropolitans. [MSc Thesis]. Tehran, Iran: Sanati Sharif University; 2009.
2. Anagnostopoulos KP, Vavatsikos AP. Using GIS and fuzzy logic for wastewater treatment processes site selection: the case of rodopi prefecture. AIP Conference Proceedings 2007; 963(2): 851-5.
3. Anagnostopoulos KP, Gratziou M, Vavatsikos AP. Natural systems for wastewater treatment site selection using GIS and fuzzy AHP [Online]. [cited 2008]; Available from: URL: http://www.srcosmos.gr/srcosmos/showpub.aspx?aa=8234
4. Deepa K, Krishnaveni M. Suitable site selection of decentralised treatment plants using multicriteria approach in GIS. Journal of Geographic Information System 2012; 4(3): 245-60.
5. Wolfslehner B, Vacik H, Lexer MJ. Application of the analytic network process in multi-criteria analysis of sustainable forest management. Forest Ecology and Management 2005; 207(1-2): 157-70.
6. Faraji Sabokbar HA, Rezaali M. Comparison of discrete and continuous spatial models case study: site selection for rural industry in district of torghabeh.

Human Geography Research 2009; 41(67): 69-83. [In Persian].
7. Chang C, Wu CR, Chen HC. Analytic network process decision-making to assess slicing machine in terms of precision and control wafer quality. Robotics and Computer-Integrated Manufacturing 2009; 25(3): 641-50.
8. Chang CW, Wu CR, Lin CT, Lin HL. Evaluating digital video recorder systems using analytic hierarchy and analytic network processes. Information Sciences 2007; 177(16): 3383-96.
9. Yüksel I, Dagdeviren M. Using the analytic network process (ANP) in a SWOT analysis- A case study for a textile firm. Information Sciences 2007; 177(16): 3364-82.
10. Lee H, Lee S, Park Y. Selection of technology acquisition mode using the analytic network process. Mathematical and Computer Modelling 2009; 49(5-6): 1247-82.
11. Saaty TL. The Analytic hierarchy process: planning, priority setting, resource allocation. 2nd ed. New York, NY: McGraw-Hill; 1980.
12. Yazgan HR, Boran S, Goztepe K. An ERP software selection process with using artificial neural network based on analytic network process approach. Expert Systems with Applications 2009; 36(5): 9214-22.
13. Neaupane KM, Piantanakulchai M. Analytic network process model for landslide hazard zonation. Engineering Geology 2006; 85(3-4): 281-94.
14. Zadeh LA. Fuzzy sets. Information and Control 1965; 8: 338–53.
15. Dagdeviren M, Yüksel I. A fuzzy analytic network process (ANP) model for measurement of the sectoral competititon level (SCL). Expert Systems with Applications 2010; 37(2): 1005-14.
16. Isalou AA, Zamani V, Shahmoradi B, Alizadeh H. Landfill site selection using integrated fuzzy logic and analytic network process (F-ANP). Environmental Earth Sciences 2013; 68(6): 1745-55.
17. Kahraman C, Ertayb T, Büyüko"zkanc TG. A fuzzy optimization model for QFD planning process using analytic network approach. European Journal of Operational Research 2006; 171(2): 390-411.
18. Razmi J, Rafiei H, Hashemi M. Designing a decision support system to evaluate and select suppliers using fuzzy analytic network process. Computers & Industrial Engineering 2009; 57(4): 1282-90.
19. Meinzinger F. GIS-based site identification for the land application of wastewater: Christchurch City, New Zealand. [MSc Thesis]. Lincoln, UK: Lincoln University; 2003.