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The kinetics of the removal of copper ions from aqueous solutions using magnetic nanoparticles supported on activated carbon

Mohammad Javad Ebrahimi Zarandi[1,✉], Azita Khosravan[2], Mahmoud Reza Sohrabi[1], Morteza Khosravi[1], Mehran Davallo[1]

1. Department of Chemistry, North Tehran Branch, Islamic Azad University, Tehran, Iran
2. Department of New Materials, Institute of Science and High Technology and Environmental Science, Graduate University of Advanced Technology, Kerman, Iran

ABSTRACT

Removal of Cu(II) from aqueous solution supplies is possible through the process of adsorption. One of these processes involves the preparation of magnetic nanoparticles on activated carbon (AC). Adsorbed coppre ions on the surface of Fe_3O_4-AC are separated from aqueous solutions using external magnetic fields. In the present study, magnetic nanoparticles were synthesized using the co-precipitation method. Fe_3O_4-supported AC was also used for the removal of copper ions from an aqueous solution. In additon, the effects of parameters such as pH, adsorbent dosage, and initial Cu(II) concentration on the removal process were investigated. The optimal conditions for the removal of Cu(II) ions from aqueous solutions were at the pH of 7, adsorbent dosage of 0.1 gram, and initial Cu(II) concentration of 10 mg/l. Removal percentage was estimated at 96.37% for Fe_3O_4-AC, while it was 61.52% for AC. Langmuir, Freundlich, and Temkin isotherm models were also used in equilibrium studies. According to the findings, Temkin isotherm was well-fitted with the experimental data. In the kinetic studies, pseudo-first-order and pseudo-second-order models were assessed, and the pseudo-first-order equation provided the optimal correlation with the obtained data.

Keywords: Kinetics, Copper Ions, Magnetic Nanoparticles, Activated Carbon

Introduction

Heavy metals in subterranean water and industrial wastewater are a major concern for the ecology of today's world, and even the smallest portions of these elements in water could cause toxicity. Exposure to heavy metals, even at the trace level, is a confirmed health risk factor for humans.[1] The presence of copper, cadmium, nickel, and others metals in the aqueous environment has a potentially damaging effect on human physiology and other biological systems when the acceptable levels are exceeded.[2]

Copper is a heavy metal with wide applications in industries such as painting, electroplating, fertilizers, pulp and packaging,[3] textile, and batteries.[4] These industries hasten the accumulation of copper in the environment.[1] Unlike organic pollutants, copper ions are not biodegradable. At high concentrations, copper is significantly toxic and could lead to crucial ecological and general health problems, as well as complications such as anemia,[4] high cholesterols, greenish hair,[5] stomach and intestine discomfort,[5] muscle cramps, convulsion, and even death.[6, 7] Among various copper ions, Cu(II) has been shown to have debilitative effects on aqueous solutions.[8]

Heavy metals cannot be degraded or destroyed. The growing demand for clean and safe water with extremely low levels of heavy metal ions has urged researchers to develop advanced technologies for the removal of heavy metal ions. The technologies developed for the elimination of Cu(II) from industrial wastewater include chemical synthetics, ion exchange, coagulation, electrolysis, reverse osmosis, and adsorption.[9] The conventional methods that are often used for the removal of heavy metals from liquid effluents (e.g., precipitation and

flocculation) are associated with numerous limitations, such as costly equipment, continuous replenishment of chemicals, time-consuming procedures, and production of secondary pollution.

In this regard, alternative methods (e.g., adsorption) have been reported to have several advantages over the other techniques for water reuse in terms of the initial costs, simplicity of design, ease of operation, low quantity of the generated residues, easy recovery of heavy metals, and the possibility of adsorbent reuse.[2] However, the fundamental problem regarding the use of various absorbents is the separation of these absorbents after the absorption process of pollutants.

In recent years, the magnetic absorption technology has become an innovation for resolving ecological problems considering its high efficiency and easy elimination following a refining process.[10] This technology has been frequently used for the refining of wastewater. After using magnetic absorbents, it can be easily separated by a magnetic force. As a composite with other absorbents, iron oxide is effectively applied in the production of magnetic absorbents.[10, 12] Recent advances suggest that many of the issues involving water quality could be resolved or greatly ameliorated using nanoparticles (NPs), nanofiltration or the other products resulting from the development of nanotechnology.[13]

In a study in this regard, Adeli *et al*. used sodium dodecyl sulfate covered in magnetic nanoparticles in order to remove copper, nickel, and zinc from a wastewater sample obtained from Iran Khodro, which is an automotive industry in Iran. The synthesis for metal ion elimination proved to be satisfactory in the elimination of Cu(II).[14] In another research, Ozmen *et al*. used the reclaimed nanomagnetic particles of Fe_3O_4.[15] Moreover, Hao *et al*. employed amino agent nanomagnetic particles for the effective elimination of Cu(II) from aqueous solutions.[1]

With this background in mind, the present study aimed to investigate the role of magnetic NPs immobilized on activated carbon composites in the removal of Cu(II) from

aqueous solutions using the batch adsorption method, as well as its synthetic and isotherm properties. The experimental equilibrium adsorption data were analyzed using various kinetic and isotherm models.

Materials and Methods
Experimental Materials

All the chemicals in the present study were of an analytical grade, supplied by Merck (Germany). The chemicals included copper nitrate (Cu $[NO_3]_2.3H_2O$), ferric sulfate ($FeSO_4.7H_2O$), ferric chloride ($FeCl_3.6H_2O$), ammonium hydroxide solution (NH_4OH 25%), hydrochloric acid (HCl), sodium hydroxide (NaOH), and activated carbon.

Preparation of Fe₃O₄-AC

The chemical precipitation method was applied to prepare particles with homogeneous composition and narrow size distribution.[7] Chemical precipitation is probably the most common and efficient method to obtain magnetic particles. In addition, a complete precipitation of Fe_3O_4 was achieved under alkaline conditions.

In the next stage, $FeSO_4·7H_2O$ (1.39 g), $FeCl_3·6H_2O$ (2.7 g), and activated carbon (10 g) were dissolved in double distilled water (80 ml) with vigorous stirring in an inert atmosphere. While the solution was being heated at the temperature of 80 ºC, 10 milliliters of 25% ammonium hydroxide solution was added. The reaction was carried out for 30 minutes at the temperature of 80 ºC with constant stirring. The resulting suspension was cooled down to room temperature and repeatedly washed with double distilled water afterwards.[16]

Adsorbent Analysis Methods

The supported magnetic NPs (Fe_3O_4-AC) and AC were characterized using scanning electron microscopy (SEM) (model: MV 2300) at 25 Kv. The Cu(II) concentration remaining in the solution was measured using a flame atomic absorption spectrophotometer (model: Perkin Elmer 2380). The pH of the solutions was continuously measured using a pH meter (model: Metrohm 744).

Adsorption Studies

Adsorption of the Cu(II) ions by Fe$_3$O$_4$-AC was evaluated using the batch method, and the effects of various parameters were also investigated, including pH (5, 7, 8, and 9), adsorbent dosage (0.1, 0.2, and 0.5 g/L), and concentration (10, 15, and 20 mg/l).

In each run, 100 milliliters of the Cu(II) solution with different pH values, initial concentrations, and adsorbent dosages were shaken. Additionally, a Cu(II) solution was prepared by dissolving 3.78 grams of Cu(NO$_3$)$_2$.3H$_2$O in 1,000 milliliters of distilled water. The pH of the solution was adjusted by adding diluted HCl and NaOH (0.1 M). All the adsorption experiments were conducted at room temperature with an agitation rate and constant speed of 100 rpm. After the equilibrium, the sample was centrifuged at 3000 rpm for 10 minutes, and the filtrates were analyzed by atomic absorption. The removal of Cu(II) capacities (q) was calculated based on the following equation:

$$q_e = (C_o - C_e)\ V/W \qquad (1)$$

where C_o and C_e represent the initial and equilibrium concentrations of Cu(II) (mg/l), respectively, V is the volume of the solution (L), and W denotes the weight of the adsorbent (g).

Results and Discussion
Morphological Analysis

The particle size and morphology of Fe$_3$O$_4$-AC and AC representative of the SEM images are shown in Figures 1 and 2, respectively. As is depicted, Fe$_3$O$_4$ NPs with the diameter of 20-50 nm were observed on the surface of AC. Clearly, Fe$_3$O$_4$-AC was essentially mono-dispersed and had a similar mean diameter of 34 nm (Figure 1). Furthermore, no aggregation was observed in the Fe$_3$O$_4$ particles, which indicated that the aggregation of Fe$_3$O$_4$ NPs was properly controlled by the presence of AC. According to the findings, AC had higher size distribution compared to Fe$_3$O$_4$-AC, which demonstrated that the coating process could not result in the significant aggregation of the prepared materials in the solution, and it is only effective in

maintaining the morphological uniformity of Fe$_3$O$_4$-AC.

As is illustrated in Figure 2, AC was mainly monodispersed and had a rough surface, with the size within the range of 90-220 nm. According to the SEM analysis, the surface of AC was not uniform, and numerous pores were observed on its surface. Co-precipitation in aqueous solutions is probably the most common and efficient method to obtain magnetic particles, which was used in the present study to prepare Fe$_3$O$_4$-AC.[16] The synthesized magnetic NPs (Fe$_3$O$_4$) using this method, which were supported on AC, were observed to have higher narrow size distribution.[17]
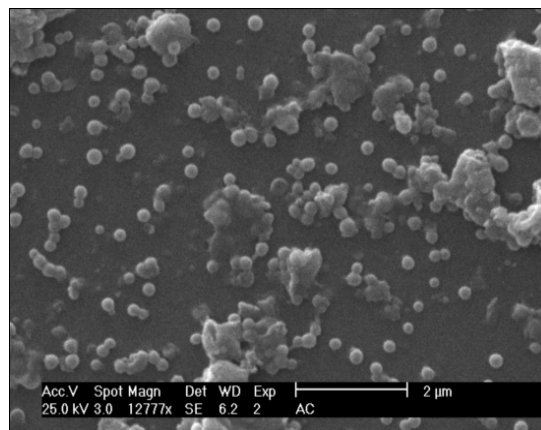

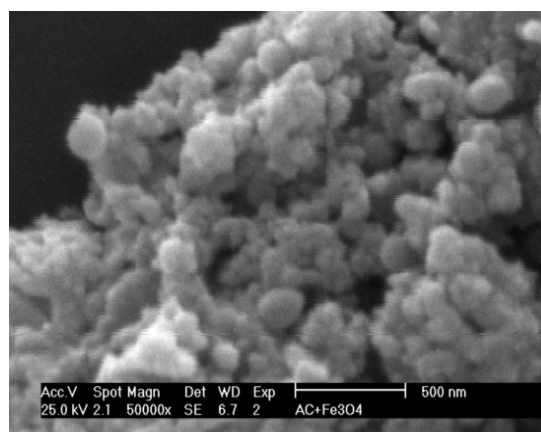Fig. 1. SEM image of Fe$_3$O$_4$-activated carbon (AC)

Fig. 2. SEM image of AC

Effects of pH

The pH of the solution plays a key role on the adsorption of metal ions. In order to determine the effects of pH on the removal of the Cu(II) ion by Fe$_3$O$_4$-AC, some experiments

were carried out with various pH values, while the other parameters remained constant. Furthermore, the effects of pH were investigated using the initial concentration of copper ions (10 mg/l) and Fe_3O_4-AC (0.1 and 0.2 g). The initial pH values were adjusted with HCl (0.1 M) and NaOH (0.1 M) in order to form a series of pH (5, 7, 8, and 9). The adsorption capacity of pH indicated that neutral pH was optimal (Figure 3).

Copper ions in aqueous solutions may be present in several forms, such as Cu(II), Cu(OH)$^+$, and Cu(OH)$_2$. Cu(II) is the predominant species at the pH of <6.[18] In this study, negatively charged repulsion forces on the nanocomposite surface at the pH of >7 were observed to reduce the metal ion removal and adsorption by the Fe_3O_4 nanocomposite site.[19]
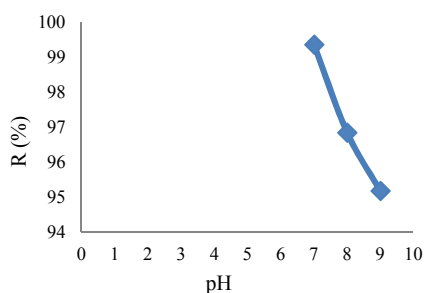

Fig. 3. Removal rate of Cu^{+2} at variable pH

Effects of Adsorbent Dosage

Effects of the adsorbent dosage were evaluated at room temperature using various Fe_3O_4-AC values (0.1, 0.2, and 0.5 g). In all the runs, the initial concentration of the copper ions was fixed (10 mg/L). The results indicated that the adsorbent dosage of 0.1 gram had the highest adsorption capacity. Evidently, the removal rate of copper ions decreased at higher adsorbent dosages (Figure 4).
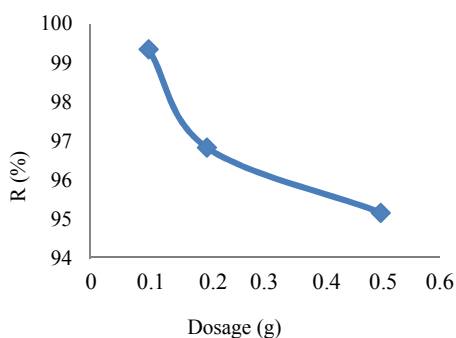

Fig. 4. Removal rate of Cu^{+2} at variable dosages

Effects of Initial Concentration

The removal uptake mechanism is particularly dependent on the initial concentration of copper ions. After identifying the optimal pH and adsorbent dosage, an experiment was performed at various concentrations of the copper ions (10, 15, and 20 mg/L). The highest removal rate was observed at the concentration of 10 mg/L (Figure 5).

After identifying the optimal pH, adsorbent dosage, and initial concentration, the removal of copper ions was performed in a batch reactor at different times. The experimental results indicated the copper removal rate to be 96.37% for Fe_3O_4-AC after 25 minutes and 97.67% at the equilibrium time (one hour), while it was 61.52% for AC after 25 minutes and 62.50% at the equilibrium time (one hour).
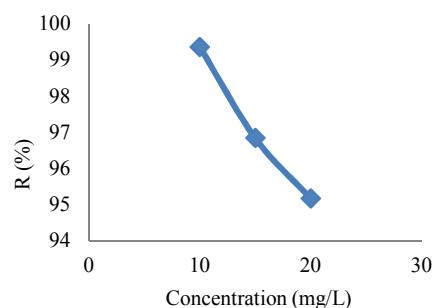

Fig. 5. Removal rate of Cu^{+2} at variable concentrations

Adsorption Isotherms

The equilibrium adsorption isotherm is essential to realizing the mechanism of adsorption systems. In the current research, we used the Langmuir, Freundlich, and Temkin isotherm equations to interpret the experimental data.

Langmuir Isotherm

The Langmuir isotherm[20, 21] theory is based on the assumption that adsorption on a homogeneous surface (i.e., surface consisting of identical sites) is equally available for adsorption and with equal adsorption energies. In addition, the adsorbent was observed to saturate after one layer of the adsorbate molecules were

formed onto the surface.[21] The linearized form of the Langmuir adsorption isotherm equation is as follows:

$$C_e/q_e = 1/K_l \, q_m + C_e/q_e \qquad (2)$$

The Langmuir constants (q_m and k_m) could be calculated from the plot C_e/q_e versus C_e. Figure 6 shows the Langmuir adsorption isotherm of the copper ions by the supported magnetic NPs on AC. The inherent features of the Langmuir isotherm could be expressed in terms of a dimensionless constant separation factor or equilibrium parameter (R_L), which is defined based on the following equation:

$$R_L = 1/kC_o \qquad (3)$$

The R_L value indicated the type of the isotherm, which could be irreversible ($R_L=0$), favorable ($0<R_L<1$), linear ($R_L=1$) or unfavorable ($R_L>1$). The isotherm model parameters for the copper ions by the supported magnetic NPs on AC are presented in Table 1.

Freundlich Isotherm

The linearized Freundlich isotherm equation that corresponded to adsorption on the heterogeneous surface was as follows:

$$\text{Log } q_e = \log K_f + 1/n \log C_e \qquad (4)$$

where C_e is the equilibrium concentration of the solute (mg/L), and q_e denotes the equilibrium adsorption capacity (mg/g). The Freundlich isotherm constants k_f and $1/n$

were calculated based on the plot of $Ln \, q_e$ versus $Ln \, C_e$ (Figure 7). The slope ($1/n$) measures surface heterogeneity, and heterogeneity becomes more frequent as $1/n$ approaches zero.[24]

In the present study, the R^2 values of the Freundlich isotherm were higher than 0.969, while lower than 0.999, indicating that the model was unable to adequately describe the correlation between the amount of the adsorbed copper ions by the magnetic NPs and its equilibrium concentration in the solution.
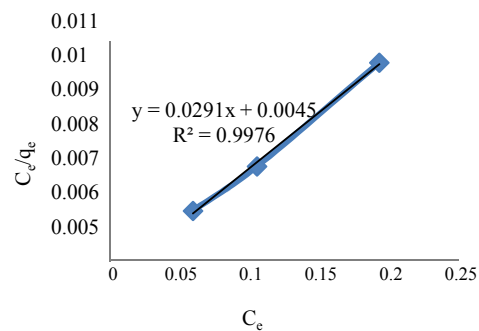
y = 0.0291x + 0.0045
R^2 = 0.9976

Fig. 6. Langmuir isotherm
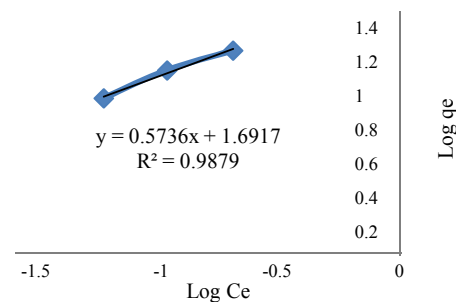
y = 0.5736x + 1.6917
R^2 = 0.9879

Fig. 7. Freundlich isotherm

Table 1. Isotherm constants for copper ion removal by magnetic nanoparticles

Langmuir isotherm				Freundlich isotherm			Temkin isotherm		
q_m (mg/g)	K_L (mg/L)	R_L	R^2	n	K_f (mg/g)	R^2	B	K_T (mg/L)	R^2
0.0291	-223.43	-4.47×10^{-4}	0.9976	0.581	1.19	0.9875	18.935	5.58	0.9998

Temkin Isotherm

The Temkin isotherm equation assumes that the adsorption heat of all the molecules in the layer decreases linearly with coverage due to adsorbent interactions, and adsorption is characterized by the uniform distribution of the binding energies up to the maximum binding energy. The linearized equation is as follows:

$$q_e = B \, Ln \, K_T + B \, Ln \, C_e \qquad (5)$$

where $B=RT/b$ and K_T are the equilibrium binding constant (mg/l) corresponding to the maximum binding energy, and constant B denotes the adsorption heat (B and K_T as the constants). A plot of q_e versus $log \, c_e$ (Figure 8) enabled the determination of the isotherm constants and B. The obtained K_T and B

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values, along with the values of the correlation-coefficients and average relative error, are presented in Table 1.

The Temkin isotherm model is characterized by the linear reduction of the adsorption heat of all the molecules in the layer due to the interactions between the sorbent and adsorbate.
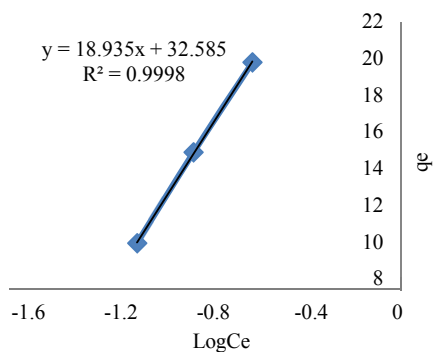
y = 18.935x + 32.585
R² = 0.9998

Fig. 8. Temkin isotherm

Table 2 shows the comparison of the adsorption capacity (mg/g) of the magnetic NPs-AC from the adsorption isotherm for the copper ions, as well as the different adsorbents reported in the literature.[22-25]

Table 2. Comparison of adsorption capacity of various adsorbents for copper ions

Sorbents	Capacity (mg/g)	Refs.
Fe_3O_4 magnetic NPs coated with humic acid	46.3	22
Chitosan-bound Fe_3O_4 magnetic NPs	21.5	23
Activated carbon modified by poly (N,N-dimethylaminoethyl methacrylate)	31.46	24
Magnetic nano-adsorbent modified by gum Arabic	38.5	25
Fe_3O_4-Activated carbon	9.208	This work

Adsorption Kinetics

In order to analyze the adsorption kinetics of the copper ions, the pseudo-first and pseudo-second orders were applied to the data, and the rate controlling step was determined using the intra-particle diffusion model.

Pseudo-First-Order Model

The first-order rate Lagergren equation is widely used for the sorption of a solute from a liquid solution,[26] as follows:

$$Log (q_e-q_t)=logq_e-k_t/2.303 \qquad (6)$$

where k is the pseudo-first-order reaction rate constant (1/min), q_e and q_t (mg/g) represent the amounts of the metal ions adsorbed at the equilibrium, and t denotes times (minute). The k value was calculated from the slope of the linear plot of $log\ q_e$-q_t versus t, indicating the application of the first-order kinetic model (Figure 9). Moreover, the pseudo-first order showed the occupation rate of the adsorption sites to be proportional to the number of the unoccupied sites.

Pseudo-Second-Order Model

The adsorption kinetics may also be described by a pseudo-second-order equation.[25, 26] The differential equation is as follows:

$$t/q_t=1/kq_e^2+t/q_e \qquad (7)$$

where q_e and q are defined as in the pseudo-first-order model, and k denotes the rate of the constant of the pseudo-second-order model for adsorption (mg/g min). The k and q_e values were calculated from the plot of t/q_t versus t,[25, 26] indicating the application of the second-order kinetic model (Fig. 10).

The results of the kinetic parameters are shown in Table 3. The validity of each model could be verified by the fitness of the straight lines (R^2 values). Furthermore, the correlation-coefficient values (R^2) of the pseudo-second-order model were observed to be lower than those of the pseudo-first-order model, demonstrating that the pseudo-first-order model was better followed than the pseudo-second-order model.
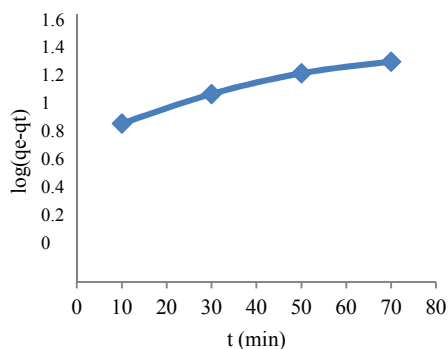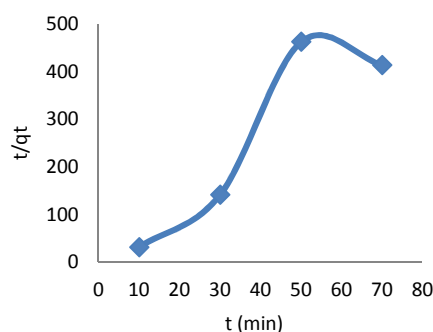
Fig. 9. Pseudo-first-order model

Fig. 10. Pseudo-second-order model

Table 3. Rate of adsorption kinetic model constants for copper ion removal

Pseudo-first order			Pseudo-second order		
q_e (mg/g)	K (1/min)	R^2	q_e (mg/g)	K (g/mg min)	R^2
9.208	0.0147	0.9642	0.148	0	0.823

Conclusion

According to the results, Fe_3O_4-AC with an average particle diameter of 34 nm could be effectively used an as adsorbent for the removal of copper ions from aqueous solutions. The experimental results also indicated the optimal conditions for the removal of copper ion to be the pH of 7, adsorbent dosage of 0.1 g/l, and Cu (II) initial concentration of 10 mg/l. The removal rate was estimated at 96.37% for Fe_3O_4-AC after 25 minutes, while it was 61.52% for AC after 25 minutes. In addition, the equilibrium data were well fitted in the Temkin adsorption model, and the kinetics of copper ion adsorption onto Fe_3O_4-AC followed the pseudo-first-order model.

Acknowledgements

References

1. Hao YM, Man C, Hu ZB. Effective removal of Cu (II) ions from aqueous solution by amino-functionalized magnetic nanoparticles. J Hazard Mater 2010; 184(1-4): 392-9.

2. Eren E, Tabak A, Eren B. Performance of magnesium oxide-coated bentonite in removal process of copper ions from aqueous solution. Desalination 2010; 257: 163–169.

3. Dai J, Yan H, Yang H, Cheng R. Simple method for preparation of chitosan/poly (acrylic acid) blending hydrogel beads and adsorption of copper (II) from aqueous solutions. Chem Eng J 2010; 165(1): 240-9.

4. Chen JJ, Ahmad AL, Ooi BS. Poly (N-isopropylacrylamide-co-acrylic acid) hydrogels for copper ion adsorption: Equilibrium isotherms, kinetic and thermodynamic studies. J Environ Chem Eng 2013; 1(3): 339-48.

5. Hasfalina CM, Maryam RZ, Luqman CA, Rashid M. Adsorption of Copper (II) From Aqueous Medium in Fixed Bed Column by Kenaf Fibres. APCBEE Procedia 2012; 3: 255-63.

6. Peng Q, Liu Y, Zeng G, Xu W, Yang C, Zhang J. Bio sorption of copper(II) by immobilizing Saccharomyces cerevisiae on the surface of chitosan-coated magnetic nanoparticles from aqueous solution. J Hazard Mater 2010; 177(1-3): 676-82.

7. Ghaee A, Shariaty- Niassar M, Barzin J, Matsuura T. Effects of chitosan membrane morphology on copper ion adsorption. Chem Eng J 2010; 165(1): 46-55.

8. Wan MW, Kan CC, Rogel BD, Dalida ML. Adsorption of copper (II) and lead (II) ions from aqueous solution on chitosan-coated sand. Carbohydrate Polymers 2010; 80(3): 891-9.

9. Al-Qodah Z. Biosorption of heavy metal ions from aqueous solutions by activated sludge. Desalination 2006; 196(1-3): 164-76.

10. Lim SF, Zheng YM, Zou SW, Chen JP. Removal of copper by calcium alginate encapsulated magnetic sorbent. Chem Eng J 2009; 152(2-3): 509-13.

11. Oliveira LC, Rios RV, Fabris JD, Sapag K, Garg VK, Lago RM. Clay -iron oxide magnetic composites for the adsorption of contaminants in water. App clay Sci 2003; 22(4): 169-77.

12. Oliveira LCA, Petkowicz DI, Smaniotto A, Pergher SB. Magnetic zeolites: a new adsorbent for removal of metallic contaminants from water. Water Res 2004; 38(17):3699-704.

13. Sai Krishna Y.V.S, Ravichandra Babu R. Adsorption of Copper and Lead ions from aqueous solutions using Nickel oxide nanostructure. Int J of Eng Res Gen Sci 2015; 3, (5) :77-84.

14. Adeli M, Yamini Y, Faraji M. Removal of copper, nickel and zinc by sodium dodecyl sulphate coated magnetite nanoparticles from water and wastewater samples. Arab J Chem 2017; 10, Supl 1:s514-s521.

15. Ozmen M, Can K, Arslan G, Tor A, Cengeloglu Y, Ersoz M. Adsorption of Cu(II) from aqueous solution by using modified Fe_3O_4 magnetic nanoparticles. Desalination 2010; 254(1-3): 162-9.

16. Laurent S, Forge D, Port M, Roch A, Robic C, Vander Elst L, et al. Magnetic iron oxide nanoparticles: synthesis, stabilization, vectorization, physicochemical characterizations and biological applications. Chem Rev 2008; (108): 2064–2110.

17. Liu Y, Chen M, Hao Y. Study on the adsorption of Cu(II) by EDTA functionalized Fe_3O_4 magnetic nano-particles. Chem Eng J 2013; 218: 46–54.

18. Sheng G D, Shao D D, Chen C L, Chen Y X, Wang X K. Adsorption of copper (II) on multi walled carbon nanotubes in the absence and presence of humic or fulvic acids. J Hazard Mater 2010; 178: 333-340

19. Repo E, Warchol J, Bhatnagar A, Sillanpaa M. Heavy metals adsorption by novel EDTA-modified chitosan–silica hybrid materials. J Colloid Interface Sci 2011; 358: 261–267.

20. Kaur R, Singh J, Khare R, Cameotra SS, Ali A. Batch sorption dynamics, kinetics and equilibrium studies of Cr (VI), Ni (II) and Cu (II) from aqueous phase using agricultural residues. App Water Sci 2013; 3: 207–18.

21. Liu J F, Zhao Z S, Jiang G B. Coating Fe_3O_4 magnetic nanoparticles with humic acid for high efficient removal of heavy metals in water. Environ Sci Technol 2008; 42: 6949–54.

22. Chang Y C, Chen D H. Preparation and adsorption properties of monodisperse chitosan-bound Fe_3O_4 magnetic nanoparticles for removal of Cu (II) ions. J Colloid Interface Sci 2005; 283: 446–451.

23. Zhu S M, Yang N, Zhang D. Poly (N, N-dimethylaminoethyl methacrylate) modification of activated carbon for copper ions removal. Mater Chem Phys 2009; 113: 784–789.

24. Araneda C, Fonseca C, Sapag J, Basualto C, Yazdani-Pedram M, Kondo K, et al. Removal of metal ions from aqueous solutions by sorption onto microcapsules prepared by copolymerization of ethylene glycol dimethacrylate with styrene. Sep Purif Technol 2008; 63: 517–523.

25. Ossman M E, Mansour M S. Removal of Cd (II) ion from wastewater by adsorption onto treated old newspaper: kinetic modeling and isotherm studies. J Ind Chem 2013; 4: 13.

26. Örnek A, Özacar M, Şengil İA. Adsorption of lead onto formaldehyde or sulphuric acid treated acorn waste: equilibrium and kinetic studies. Biochem Eng J 2007; 37: 192-200.