The investigation of humic acid adsorption from aqueous solutions onto modified pumice with hexadecyl trimethyl ammonium bromide

Ghorban Asgari, Afshin Ebrahimi[1], Abdolmotaleb Seid Mohammadi, Ghader Ghanizadeh[2]

Department of Environmental Health Engineering, Faculty of Health, Hamadan University of Medical Sciences, Hamadan, Iran, [1]Environment Research Center, Isfahan University of Medical Sciences (IUMS), Isfahan, Iran, and Department of Environmental Health Engineering, School of Health, IUMS, Isfahan, Iran, [2]Health Research Center and Health School, Baqiyatallah University of Medical Sciences, Tehran, Iran

ABSTRACT

Aims: This study was conducted to evaluation humic acid adsorption from aqueous solution using pumice modified with cationic surfactant.
Materials and Methods: The pumice modification was carried out with cationic surfactant of hexadecyl trimethyl ammonium bromide (HDTMA-Br) with a concentration of 3 mmol/l for 48 h using a 150 rpm shaker. The chemical structure of pumice was determined using X-ray fluorescence (XRF) and X-ray diffraction (XRD). For evaluation of the effective parameters, the adsorption of humic acid onto modified pumice was conducted with batch experiments. Humic acid concentration was determined by photometry on 254 nm. Langmuir, Freundlich, and Temkin models and pseudo-first and pseudo-second-order kinetics were used for adsorption isotherm and kinetics studies.
Results: The results showed that humic acid adsorption increased as its initial concentration, the adsorbent dosage, and the contact time increased. Increase in pH within the regions 3-12 resulted in the reduction of adsorption efficiency while the optimum adsorption occurred at pH = 3. The adsorption data followed the Langmuir model (R^2 = 0.99) and second-order kinetic model (R^2 = 0.99). Maximum experimental adsorption and theoretical adsorption capacity of the adsorbent were 22.5 and 29 mg/g, respectively. The Langmuir constant coefficient (b) was determined as 0.8 L/mg.
Conclusions: It was understood from the results of this study that adsorption onto modified pumice is efficient in performance and thus affordable technology for the elimination of humic acid from the polluted water supply.

Key words: Aadsorption, hexadecyl Tteri methyl ammonium bromide, humic acid, pumice stone,

Address for correspondence:
Dr. Afshin Ebrahimi,
Environment Research Center, Hezar Jerib Ave,
Isfahan University of Medical Sciences, Isfahan, Iran.
E-mail: a_ebrahimi@hlth.mui.ac.ir

INTRODUCTION

Different countries in the world often use chlorination to disinfect water and supply drinking water. The major concern regarding water disinfection with chlorine is the formation of potentially health-threatening disinfection by-products (DBPs). During chlorine disinfection, natural organic

material (NOM) reacts with chlorine to form DBPs.[1,2] Since 1974, numerous epidemiological studies have showed the correlation between the consumption of or contact with the chlorinated water and various cancers in humans and animals. Major chlorine disinfection by-products are trihalomethanes (THMs) and haloacetic acids (HAAs) which are toxic, carcinogenic, and mutagenic. THMs cause cancers of bladder, kidney, intestine,[3-5] and include chloroform, bromodichloromethane, dibromochloromethane, and bromoform. Many studies have reported the incidence of cancer in laboratory animals which were exposed to chloroform as an indicator of THMs. Moreover, some researchers have found a relationship between these compounds and stillbirth.[6] Public concern about the dangers of THMs compounds arose when the carcinogenic potential of chloroform was proved and the US Environmental Protection Agency (US-EPA) classified it in the carcinogens taxonomy in 1975. Cancer incidence rate in a 70 kg person drinking 1 L of water containing 1 μg/L of chloroform per day for 70 years has been estimated to be 8.9×10^{-8} with a reliability coefficient of 95 %. When the chloroform concentrations reach 100 μg/L, the cancer incidence rate increases to 1.87×10^{-5}. In other words, being exposed to 100 μg/L the concentration of chloroform results in the increase of 1 person infected with cancer per 56,000 people.[7-9]

About 60 similar reports by 150 researchers across the world about the adverse effects of THMs have been published by the World Health Organization (WHO).[10-12] The presence of organic matters in water resources causes a lot of troubles during treatment processes especially the conventional water treatment. NOM are effective in different aspects of water treatment. The most important effect of these compounds is their reaction with chlorine and producing chlorination by-products. It has been proved that chlorination by-products depend on the concentration of NOM as the main precursor in the formation of these compounds. The conventional water treatment processes remove only 30% of THM precursors.[13-15] Common methods for the removal of THMs and their precursors are the use of activated carbon, membrane processes, advanced flocculation, and air stripping.[6,10-12] However, as reported in the literature, using these methods poses many limitations such as the high operation cost and initial investment, obstruction, and generation of a large amount of sludge, reduction of water pH, production of corrosive water, and the need for reduction operation.[13-15] Therefore, it is necessary to apply more appropriate methods for the removal of THMs and their precursors. Among different methods, the adsorption process is a simple and common method for the removal of organic pollutants like THMs and humic acid. In theory the activated carbon is a best adsorbent for humic acid removal, however in practice it shows low capacity for the removal of high molecular organic compounds such as NOM. Regardingly, some other studies on humic acid adsorption, using vermiculite mineral modified with hexadecyl trimethyl ammonium bromide, showed that the modified type of this mineral matter had a higher potential in humic acid removal than its unmodified one. Modification of glass and nylon granules with polypyrrole also has a desirable potential in humic acid removal.[16]

Other adsorbents such as volatile ash, bentonite, types of biomasses, powder activated carbon, coke, and kaolin are also used in organic pollutants' adsorption.[17,18] However, such adsorbents are expensive, so, recently, the use of cost-effective adsorbents has been attended to and many studies have been done on their feasibility.[18]

The pumice stone is in fact a silica glass with light color.[19] It possesses the specific surface area of 5-22 m²/g, high porosity (85%), silicon of 60-75%, specific dry weight of 500-800 kg/m³. In terms of structure, this stone consists of irregular holes. Layers of pumice stone have been found and recorded by Iran's Geology and Mineral Exploration Organization in mountainous regions of Iran including northwest, west, center, and south. Besides the above regions, this inorganic matter is found around Iran, for instances Taftan mountains in the south, Abali in the north, around Ghazvin, western part of Hamadan, and Tikmedash (western Bostanabad, East Azerbaijan). Italy ranks the first in producing 40% of the total pumice stone, followed by Turkey in manufacturing pumice products. This stone is easily accessible in our country due to its frequency and low cost. It is also applied in water and wastewater industry, especially as a sludge maintenance medium as investigations show that the price per cubic meter of pumice used as a medium is about 2% of the price of a commercial media per cubic meter.[20] Therefore, pumice can be applied as a suitable medium base in water treatment processes. Studies have shown[20] that the medium materials can be used in forms of raw or modified adsorbents with appropriate agents to remove different pollutants in water.

Modification of natural adsorbents with various agents in order to efficiently adsorb organic and inorganic matters has been tested. Regarding the properties of cationic surfactants, these compounds have a high tendency toward negative exchanges which results in the use of these compounds for modification of the outer surface of different materials and promotion of their anion exchange capacity.[21-23] Since the removal of THM precursors from water resources are of special importance, pumice was used as the base adsorbent due to its accessible and cost-effective natural resources. The main objective of this work was to develop and investigate new adsorbent to remove humic acid as a THM precursor from water.

MATERIALS AND METHODS

The study of humic acid adsorption on modified pumice was conducted in a batch system using 250 ml Erlenmeyer flasks and the effect of parameters including pH, humic acid initial concentration, adsorbent dose, and contact time was examined. All of the experiments were carried out at room

temperature and the average of triplicate experiments was reported. The raw pumice was provided from Tikmedash, East Azerbaijan, Iran. Firstly, it was washed with distilled water several times and then dried at 110°C using an oven. Crushing up and granulating the pumice stone was done using an electric mill and ASTM standard sieves with a mesh size of 0.85 mm. The granulated pumice was washed again with distilled water and dried at 110°C. The first modification of pumice was performed with 0.01 M NaCl solution for 24 h using an orbital shaker (3017 GFL) with the speed of 150 rpm. Then, it was rinsed several times with distilled water until silver nitrate became washing out and was dried in an oven at 110°C for 8 h. The final modification of pumice was carried out with a cationic surfactant of HDTMA-Br with a concentration of 3 mmol/L for 48 h using a 150 rpm shaker. The structure of the pumice was determined using a scanning electron microscope (SEM), XRD, and XRF. In all experiments, pumice separation from the solutions used in the modification process was done using a centrifuge with the speed of 2000 rpm for 10 min. After the preparation of adsorbent, 1000 mg/L humic acid stock solution was prepared, and then standard solutions with various concentrations were prepared and studied. The measurement of humic acid concentration in standard and unknown samples was done using a UV visible spectrophotometer (Model PU8700, Philips) at the wavelength of 254 nm.[23-25] The humic acid was provided from Sigma-Aldrich Company, and other materials were provided from Merck Company in Germany. The pH_{ZPC} was determined according to the method presented by other researchers.[19,26,27]

In order to study the effect of pH on humic acid adsorption, samples with initial pH of 3, 7, and 12, humic acid concentration of 50 mg/L, and adsorbent dosage of 0.5 g/100 mL were prepared and the concentration of remaining humic acid was measured after miscibility for 250 min. The effect of humic acid initial concentration was examined using various concentrations (10-100 mg/L). This process of the study was carried out at room constant temperature and mixed at 120 rpm. To evaluate the effect of adsorbent dose, 50 mg/L initial concentration of humic acid was studied along with the adsorbent dose range of 0.1-1 at pH equaling 3. In each process, the adsorption capacity was calculated using equation (1):

$$q_e = \frac{(C_0 - C_e)V}{M},$$ (1)

where

q_e is adsorption capacity (mg/g), C_0 is the humic acid initial concentration (mg/L),

C_e is the equilibrium concentration of humic acid (mg/L),

V is volume of sample (L), and

M is the pumice mass (g).

Once the appropriate contact time, the adsorbent dose, and the adsorption pH were measured, features related to the adsorption isotherm of the given pollutant on the pumice were determined. The experimental data of adsorption equilibrium were studied using Langmuir and Freundlich (equations 2-3):[26,28]

$$\frac{C_e}{q_e} = \frac{1}{Q_{max}b} + \frac{C_e}{Q_{max}}$$ (2)

$$\log q_e = \log k + \frac{1}{n}\log C_e$$ (3)

The adsorption kinetics was analyzed using pseudo-first-order and second-order kinetic models. The pseudo-first-order kinetic linear equation is generally as follows:

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.203}t$$ (4)

The pseudo-second-order kinetic linear equation is generally as follows:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t$$ (5)

In the first-order kinetic equation, parameters of k_1 (constant coefficient (1/min) and q_e (equilibrium adsorption capacity (mg/g)) are calculated by drawing the curve of $\log(q_e - q_t)$ over t, and in the second-order kinetic equation, parameters of q_e and k_2 (rate constant (mg/g min)) are calculated by drawing the curve of t over q_t.[26]

RESULTS

In analysis of the pumice structure using the XRD technique, comparison of the peaks in the curve by standard cards showed that the main part of pumice structure consisted of quartz with the chemical formula of SiO_2 which comprised 74% of the structure. The results by XRF of the sample showed the chemical compositions of pumice as silica, alumina, potassium oxides, and sodium. The pH_{PZC} used in this study was determined as 6.

The results of the effect of pH on humic acid adsorption are shown in Figure 1. According to these results, the adsorption rate at pH values of 3, 7, and 12 was 22.5, 14, and 9 mg/g, respectively, which indicated that the maximum removal of 93.5% occurred at pH 3.

The results of the effect of humic acid concentration on its adsorption on modified pumice are shown in Figure 2. As shown in Figure 2, the adsorption rate (q_e = mg/g) increased as the humic acid concentration increased to 50 mg/L, while further increase of humic acid did not lead to change in the adsorption rate. Based on these results, as the humic acid concentration increased from 10 to 50 mg/L, the adsorption capacity increased from 4 to 22.5 mg/g; however, the higher concentrations of humic acid did not affect the adsorption

capacity as the maximum adsorption capacity was obtained at 50 mg/L concentration.

Figure 3 shows the effect of adsorbent dose on humic acid adsorption. The results showed that the increase of adsorbent dose from 0.1 to 1 g in 100 L resulted in the reduction of remaining humic acid from 6 to 1.8 mg/L. Although the remaining humic acid decreased as the adsorbent dose increased and the total efficiency of humic acid removal increased from 89% to 97%, calculations showed that the adsorbed pollutant decreased per unit mass as the adsorbent mass increased. Therefore, it can be concluded that the optimum dose of adsorbent would be in the range of 0.1-0.2 g in 100 mL that equals to 1-2 g/L.

The results on the determination of the adsorption isotherms are indicated in Figures 4 and 5. Evaluation of the correlation coefficients of the curves of these three models showed that humic acid adsorption on modified pumice followed the Langmuir adsorption isotherm and the values of the constant coefficient of b and theoretical Q_{max} were determined as 0.8 L/mg and 29 mg/g, respectively. The R_L dimensionless parameter is one of the most important parameters which can be determined regarding the results by the Langmuir model and can be used to predict the adsorption conditions. R_L is calculated using equation (6):

$$R_L = \frac{1}{1 + bC_e} \tag{6}$$

According to the performed studies, the correlation between R_L and adsorption conditions was determined according to Table 1. Considering the calculations by equation (6), the R_L of humic acid adsorption on modified pumice was calculated as 0.3 which, regarding Table 1, indicated a desirable adsorption of humic acid on pumice.

The results on the determination of humic acid adsorption kinetics are shown in Figure 6. Comparison of correlation coefficients of the used kinetic models showed that humic acid adsorption on modified pumice followed the pseudo-second-order kinetic model [Figure 6a and b] as the correlation coefficient (R^2) of the second-order kinetic model (0.99) more than that of the first-order one (0.97). Moreover, the adsorption capacity (q_e) obtained from the experimental studies (22.5 mg/g) was more consistent with the q_e calculated by the second-order kinetic model (22.73 mg/g min). The q_e calculated by the second-order kinetic model does not conform to the experimental q_e, if it is equal to 33.36 mg/g.

Table 1: The correlation between R_L and adsorption conditions[26,28]

R_L value	Adsorption condition
<1	Appropriate
1	Linear
0	Irreversible
>1	Inappropriate

DISCUSSION

Considering that in adsorption studies, the dominant phenomenon of interest takes place on the surface of adsorbents to remove pollutants, chemical and surface properties of adsorbents and the effective factors in the status of surface play an important role in adsorption process. Major part of the pumice used in this study consisted of mineral compounds of which quartz with 74% comprised most of the pumice composition. Akbal *et al*, and Kitis *et al*, reported the main compound of pumice as SiO_2.[29,30] The reason of
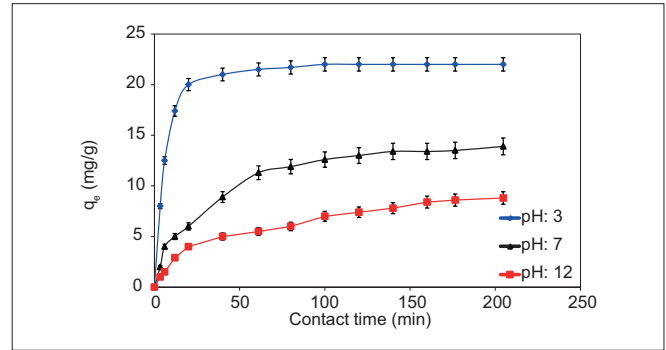

Figure 1: The effect of pH and contact time on humic acid adsorption on pumice (humic acid concentration of 50 mg/L and the adsorbent dose of 0.5 g)
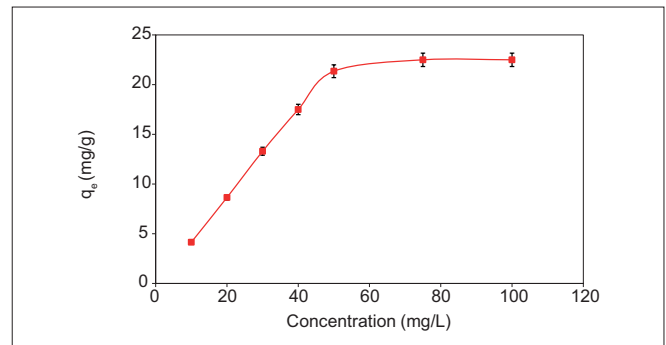

Figure 2: Effect of initial concentration of humic acid on its adsorption on pumice (pH = 3, adsorbent dose = 0.5 g)
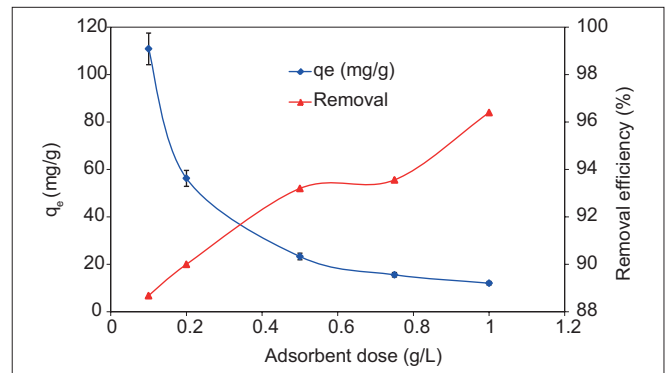

Figure 3: The effect of pumice dose on the efficiency and rate of humic acid adsorption (pH = 3, humic acid concentration = 50 mg/L)

this similarity of the reported results on pumice structure by different researchers may be related to the formation process of this mineral. The pumice products have a uniform structure all over the world due to the natural process of pumice formation (volcanic processes). Furthermore, the main substance of volcanic eruptions which result in pumice formation on the ground is the molten substance or magma which has a rather identical composition in different areas. Therefore, the equality of the major compound of pumice stone used in various studies is normal and inevitable. Another important environmental factor which is effective in the pollutant adsorption rate on solid surfaces is the dispersion of negative and positive surface charges on the adsorbent surface which forms a function of pH of the reaction medium and pH_{ZPC} of a given adsorbent. The results of the present study showed that the medium pH variations and its increase from 3 to 12 reduced the humic acid adsorption rate. Similar results were reported by Capasso *et al*, which confirmed these conditions.[21] These researchers found that the percentage of humic acid adsorption on modified bentonite reduced from 2 to 10 as the pH increased which conformed to the results of this study. The reason of the adsorption rate reduction related to the anionic structure of humic acid and pH_{ZPC} of pumice. Studies have shown that at pH equaling pH_{ZPC}, the electric charges on the adsorbent surface were at equilibrium, while, at pH higher and lower than pH_{ZPC}, the major surface electric charge on adsorbents were positive and negative, respectively, as these conditions along with the anionic and cationic conditions of a given pollutant affected the removal efficiency.[30] Based on the results of pumice pH_{ZPC} (equation 6) in the present study, at pH > 6, the dominant charge on

the pumice surface was negative due to the accumulation of hydroxyl anions on the adsorbent surface and the increase of related negative charge number. Since the humic acid was also of an anionic nature, these conditions led to the reduction of humic acid adsorption rate in the alkaline region. The reason is, on the one hand, the anionic nature of the given pollutant and, on the other hand, the increase of pH subsequent to the accumulation of negative charge on the adsorbent which results in the emergence of the electrostatic repulsion force between the adsorbent and pollutant.[21,27] Moreover, humic acid is present at low pH as molecules which are in a suitable condition to be adsorbed, while, at higher pH, solubility and ionization of humic acid increase through releasing hydrogen ions and these conditions increase the electrostatic repulsion force between the adsorbent and humic acid which results in the reduction of adsorption rate. These results show that adsorbents with rather high pH_{ZPC} are more appropriate for the optimum adsorption of humic acid from aqueous solutions, since, at low pH_{ZPC} (3-5) of the adsorbent, the water on the adsorbent surface has a negative charge at neutral pH and these circumstances lead to the emergence of electrostatic repulsion force between the adsorbent and pollutant and consequently then the reduction of adsorption rate. Such circumstances were seen in the results of the present study as, at pH equaling 7, the adsorption rate was rather high, while, higher pH in the alkaline region resulted in the accumulation of negative charge on the adsorbent surface and then reduction of adsorption rate. Furthermore, in the alkaline region, releasing proton and complete ionization of humic acid into anions became greater which led to the severe reduction of adsorption rate.
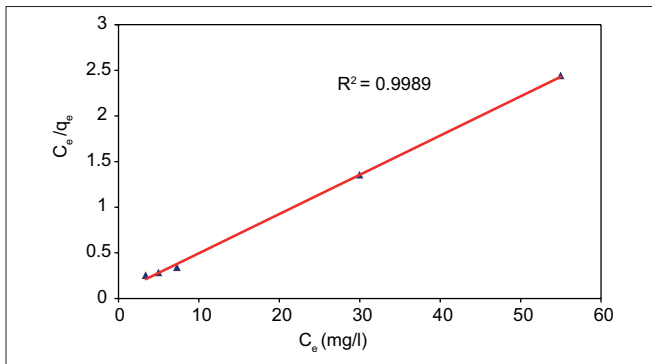

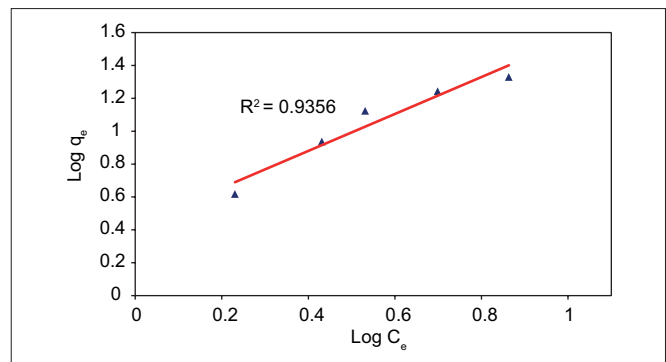**Figure 4:** Langmuir isotherm for humic acid adsorption on pumice

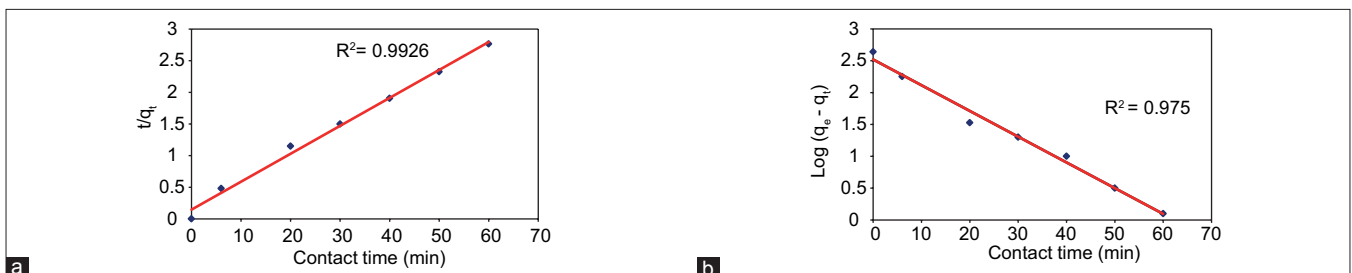**Figure 5:** Freundlich isotherm for humic acid adsorption on pumice

Figure 6: (a) Pseudo-first-order and (b) second-order kinetics for humic acid adsorption on pumice

The effect of initial concentration of the input pollutant of adsorption systems is one of the significant parameters which must be studied. The results showed that as the initial concentration of humic acid increased up to 50 mg/L, the adsorption rate was increased, while increasing the adsorbate concentration higher than 50 mg/L(up to 100 mg/L) the adsorption capacity was not changed. Similar results have been reported by Wang *et al*,[31] on the adsorption of bivalent zinc and copper and humic acid on natural zeolite as the increase of initial concentration of humic acid and the two metals resulted in the increase of their adsorption. The adsorption of humic acid on volatile ash also follows this pattern.[31] This phenomenon may refer to the driving force required for overcoming the existing resistance against the pollutant transmission from the liquid phase toward the solid phase which has also been found by the other researchers.[32] The reason is that the higher initial concentrations, in a specific region, cause a remarkable propulsion which more easily overcomes the resistance to pollutant transmission from the liquid phase toward the solid phase.[30] These circumstances improve the adsorption of pollutants in a specific region, while they may not affect the adsorption rate at higher concentrations. That is because despite the dominance of propulsion over the resistance to pollutant transmission at concentrations higher than a specific limit, the limited available surfaces for adsorption of a given pollutant impedes an adequate adsorption and this phenomenon was also seen in the present study.

The effect of adsorbent dose must be considered in designing large commercial−industrial systems due to the economy of the adsorption process. As shown by the results, although the increase of pumice dose resulted in the increase of humic acid removal efficiency, this increase led to the reduction of humic acid adsorption per unit mass of the adsorbent. The reason may be related to the unsaturated active areas of the surface resulting in the reduction of adsorption rate.[28,33] The increase in removal efficiency is due to the increase of the surface in the system, while the reason of the reduction of adsorbed pollutant per-unit mass of the adsorbent is that the increase of adsorbent mass results in the adsorbent surface overlapping and aggregation of the adsorbent molecules and consequently the effective surface area decreases. Moreover, the increase of adsorbent dose and aggregation of the adsorbent molecules increases the diffusion path during the pollutant diffusion on the adsorbent surface and this in turn decreases the adsorption rate. In such conditions, due to the competition among pollutant molecules to occupy the empty areas of the adsorbent surface, the adsorbent surface is used in its unsaturated form and its valences are not used totally which results in the reduction of adsorbed pollutant per-unit mass of the adsorbent.[34] In this respect, the optimum dose must be determined in order to prevent the unintended adsorbent loss.

The study of humic acid adsorption isotherm for various adsorbents has shown that the adsorption of this pollutant on different adsorbents followed Langmuir and Freundlich isotherms. Most of the studies have applied only these two models for examining the humic acid adsorption isotherm. As the humic acid has a negative zeta potential at pH higher than 1.6, the monolayer adsorption isotherm is more reasonable than the multilayer adsorption isotherm as a result of high electrostatic repulsion force among adsorbed molecules and the molecules being adsorbed.[35-37] Moreover, the substances used for the modification of humic acid cover the adsorbent surface uniformly and make the monolayer adsorption easier.

Kinetics of humic acid adsorption on different adsorbents the same as the adsorption isotherm showed different results which may be due to the adsorbent nature and the conditions of the study.

Analyses of the data using first-order and second-order kinetic models indicated that humic acid adsorption on modified pumice followed the pseudo-second-order kinetic model and the adsorption kinetic constant was calculated as 22.73 mg/g which was more consistent with the adsorption values obtained from adsorption models and batch experiments (22.5 mg/g). The study by Wang *et al*, showed that although there was not a significant difference between the correlation coefficients of humic acid kinetics in the first-order and second-order kinetic models, a comparison of the equilibrium adsorption values showed that the first-order kinetic model has provided better conditions for humic acid adsorption which is different from the results of the present study.[23] Tao *et al*,[16] used first-order and second-order equations to examine humic acid adsorption kinetics and found that humic acid adsorption followed the pseudo-second-order kinetic model as not only the correlation coefficient of the two models but also the calculated adsorption rate was more consistent with the measured rate in adsorption experiments.

CONCLUSIONS

Generally, the results of the present study showed that pumice modified with HDTMA-Br increased the potential of humic acid adsorption. pH_{ZPC} of pumice is 6 and it mainly consists of quartz. The adsorption rate increased as the initial concentration of the pollutant increased to 50 mg/L, while higher initial concentrations did not affect the adsorption rate. Lower pH resulted in the increase of adsorption rate as the optimum pH was 3. Humic acid adsorption on pumice followed the Langmuir isotherm and second-order kinetic model. The maximum adsorption capacity of modified pumice was determined as 29 mg/g. The cost-effectiveness and accessibility of pumice are suggested to be done on this material as an option to improve the adsorbents used in water and wastewater treatment.

ACKNOWLEDGMENT

has been previously published in a local journal in Persian language.

REFERENCES

1. Chiu H, Tsai SS, Wu TN, Yang CY. Effect modification of the association between trihalomethanes and pancreatic cancer by drinking water hardness: Evidence from an ecological study. Environ Res 2010;110:513-8.
2. Tripathy GK, Bersillon SJ, Dubey SP. Chlorination byproducts, their toxicodynamics and removal from drinking water. J Hazard Mater 2007;140:1-6.
3. Babi K, Koumenides KM, Nikolaou AD, Makri CA, Tzoumerkas FK, Lekkas TD. Pilot study of the removal of THMs, HAAs and DOC from drinking water by GAC adsorption. Desalination 2007;210:215-24.
4. Capar G, Yetis U. Removal of THM precursors by GAC: Ankara case study. Water Res 2002;36:1379-84.
5. Koparal A, Yildiz YS, Keskinler B, Demircoglu N. Effect of initial pH on removal of humic substances from wastewater by electro coagulation. Sep Purifi Technol 2008;59:175-82.
6. Bitton G. *Wastewater microbiology*. 3rd ed. New York, USA: John Wiley and Sons Inc; 2005.
7. Samadi M. *Application of membrane technology THMS from drinking water* [Thesis in Environmental Health]. Tehran: Tarbiat Modarres University; 2003. [In Persian]
8. Masters G, Ela WP. *Introduction to environmental engineering and science*. 3rd ed. USA: Prentice–Hall; 2004. p. 651.
9. AWWA. *Water quality and treatment*. 5th ed. America: McGraw Hill Publishing Co; 1999.
10. Hamidie M. *Adsorbent filters performance evaluation of debris removal from drinking water at the point consumption* [MSc Thesis]. Tehran: Tarbiat Modarres University; 1997. [In Persian]
11. Daei M. *Review the possibility of THMs formation in drinking water* [MSc thesis]. Tehran: Tehran University; 1991. [In Persian]
12. WHO. *Guidelines for drinking water quality, Health criteria and other supporting information*. Vol. 1. 2nd ed. Geneva: WHO; 1996.
13. Simpson D. Biofilm processes in biologically active carbon water purification. Water Res 2008;42:2839-48.
14. Kawamura S. *Integrated design and operation of water treatment facilities*. 2nd ed. USA: John Wiley and Sons Inc; 2000.
15. Crittenden J, Rhodes R, Hand DW, Tchobanoglous G. *Water treatment: Principales and design*. 2nd ed. USA: John Wiley and Sons Inc; 2005.
16. Tao Q, Xu Z, Wang J, Liu F, Wan H, Zheng S. Adsorption of humic acid to aminopropyl functionalized SBA-15. Microporous Mesoporous Mater 2010;131:177-85.
17. Mohan D, Pittman Jr CU. Activated carbons and low cost adsorbents for remediation of tri-and hexavalent chromium from water. J Hazard Mater 2006;137:762-811.
18. Garg U, Kaur MP, Sud D, Garg VK. Removal of haxavalent chromium from aqueous solution by adsorption on treated sugarcane bagasse using response surface methodological approach. Desalination 2009;249:475-9.
19. Asgari G, Roshanib B, Ghanizadeh G. The investigation of kinetic and isotherm of fluoride adsorption onto functionalize pumice stone. J Hazard Mater 2012;217- 218:123-32.
20. Mineral. NGDoI-M. Available from:http://www.ngdir.ir/minemineral/Mine Mineral/.
21. Capasso S, Salvestrini S, Coppola E, Boudonno A, Colello C. Sorption of humic acid on zeolitic tuff: A preliminary investigation. Appl Clay Sci 2005;28:159-65.
22. Anirudhan T, Ramachandran M. Surfactant-modified bentonite as adsorbent for the removal of humic acid from wastewaters. Appl Clay Sci 2007;35:276-81.
23. Wang S, Gong WX, Liu XW, Gao BY, Yue Q, Zhang DH. Removal of fulvic acids from aqueous solution via surfactant modified zeolite. J Chem Res Chinese U 2006;22:566-70.
24. Asgari G, Mohammadi AS, Ebrahimi A, Hosseinzadeh E. Adsorption of phenol from aqueous solution by modified zeolite with FeCl3. Int J Environ Health Eng 2012;1:1-6.
25. American Public Health A, American Water Works A, Water Environment F. *Standard Methods for the Examination of Water and Wastewater*. 21st ed. Washington D.C: American Public Health Association; 2005.
26. Asgari G, Ghanizadeh GH. Adsorption kinetic and isotherm of methylene blue and its removal from aqueous solution using bone charcoal. *React Kinet Mech Catal* 2011;102:127-42.
27. Orfão JJ, Silva AI, Pereira JC, Barata SA, Fonseca IM, Faria PC, Pereira MF. Adsorption of a reactive dye on chemically modified activated carbons:influence of pH. J Colloid Interface Sci 2006;296:480-90.
28. Hameed B, Ahmed AA, Aziz N. Isotherms, kinetics and thermodynamics of acid dye adsorption on activated plam ash. Chem Eng J 2007;133:195-203.
29. Akbal F. Adsorption of basic dyes from aqueous solution onto pumice powder. J Colloid Interface Sci 2005;286:455-8.
30. Kitis M, Karakaya E, Yigit NO, Civelekoglu G, Akcil A. Heterogeneous catalytic degradation of cyanide using copper-impregnated pumice and hydrogen peroxide. Water Res 2005;39:1652-62.
31. Wang S, Terdkiatburana T, Tade MO. Adsorption of Cu(II), Pb(II) and humic acid on natural zeolite tuff in single and binary systems. Sep Purif Technol 2008;62:64-70.
32. Hameed B, Ahmad AA. Batch adsorption of methylene blue from aqueous solution by garlic peel, an agricultural waste biomass. J Hazard Mater 2009;164:870-5.
33. Sulak M, Demirbas E, Kobya M. Removal of Astrazon Yellow 7GL from aqueous solutions by adsorption onto wheat bran. Bioresour Technol 2007;98:2590-8.
34. Chen S, Yue Q, Gao B, Xu X. Equilibrium and kinetic adsorption study of the adsorptive removal of Cr(VI) using modified wheat residue. J Colloid Interface Sci 2010;349:256-64.
35. Zhang X, Bai R. Machanisms and kinetics of humic acid adsorption onto chitosan -coated granules. J Collid Interface Sci 2003;264:30-8.
36. Chang M, Juang RS. A dsorption of tannic acid, humic acid, and dyes from water using the composite of chitosan and activated clay. J Collid Interface Sci 2004;278:18-25.
37. Wan W, Hanafiah M, Yong SS. Adsorption of Humic acid from aqueous solutions on crosslinked chitosan- epichlorohydrin bead: Kinetics and isotherm studies. Colloids Surf B Biointerfaces 2008;65:18-24.