



Effective Removal of Fe(III) Ions from Water Sample Using Activated Drinking Water Treatment Sludge: Isotherms and Kinetic Studies

Donya Ansari Moghadam¹, Reza Marandi^{2,*}, Shahrzad Khoramnejadian¹, Saeedreza Asemi Zavareh¹, Shahram Moradi Dehaghi³

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

² Department of Environmental Engineering, North Tehran Branch, Islamic Azad University, Tehran, Iran

³ Faculty of Chemistry, North Tehran Branch, Islamic Azad University, Tehran, Iran

Corresponding Author Email: Gasolin20@yahoo.com

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ABSTRACT

In this study, drinking water treatment sludge was activated and used as an efficient, cheap and cost effective sorbent in the removal of Fe(III) ion from water samples. The prepared material was characterized by Fourier transfer infrared spectroscopy (FT-IR), X-ray powder diffraction (XRD), scanning electronic microscopy (SEM), surface analysis (BET method) and X-ray fluorescence (XRF) analysis. The effects of various parameters such as the solution pH, adsorption time, adsorbent dosage, and initial metal ion concentration upon adsorption were investigated. Equilibrium isotherm studies were carried out with different initial concentrations of Fe(III), and two models (Langmuir and Freundlich isotherms) were utilized to analyze the equilibrium adsorption data. The results revealed that the adsorption process obeyed the Langmuir model, with the maximum monolayer capacity (q_{max}) and the Langmuir constant (KL) calculated as 54.3 mg g⁻¹ and 1.19 L mg⁻¹, respectively. Kinetic studies indicated that the adsorption process followed a pseudo-second-order model. The results showed that activated sludge is an efficient and selective material for adsorption of Fe(III).

1. INTRODUCTION

The problem of toxic-metal-contaminated water has become a great environmental concern and presents significant hazards to the public health and economy [1]. Heavy metals have the negative effect on the soil ecology, agricultural production, and groundwater quality [2]. These toxic pollutants are harmful for human beings and other living species and are toxic if their concentrations exceed certain limits [2]. Thereby, these species should be removed prior to their discharge in water streams [3]. Various methods have been reported for the removal and recovery of heavy metal ions from water and wastewater including ion exchange [4], ion flotation [5], solvent extraction [6], membrane filtration [7], electrochemical treatment [8], biological treatment [9], and adsorption [10]. Among the mentioned methods, adsorption is one of the popular strategy that has been widely utilized for water and wastewater treatment [10]. This method is easy to operate, efficient, and low-cost [11].

Various adsorbents such as carbon nanotubes [12], magnetic chitosan [13], graphene oxide and its composites [14], metal oxide nanoparticles [15], zeolite [16], industrial wastes [17] and drinking water treatment sludge (DWTS) [18] have been evaluated for the adsorption of heavy metals. DWTS is a by-product generated during the production of drinking water [19]. Owing to its high production rate and environmental impacts to landfill, numerous researchers paid attention for using DWTS in various applications [20]. DWTS can be employed as an effective low-cost adsorbent for removal of heavy metals from water and wastewater.

In this paper, we describe the activation of DWTS and its subsequent application as a sorbent to remove Fe(III) ions from water samples. The results reveal that this is a facile, efficient, and environmentally friendly approach for preparation of an efficient sorbent and the as-prepared material can be used as an excellent sorbent for removing Fe(III) ions from water. The physical and chemical properties of the synthesized material were studied, and its performance in the removal of Fe(III) ions from water sample was investigated.

2. EXPERIMENTAL

2.1. Materials and reagents

All reagents and solvents were of analytical reagent (AR) grade and were purchased from Merck (Darmstadt, Germany) and used without further purification. Standard solution of Fe(III) (1000 mg L⁻¹) was purchased from Merck (Darmstadt, Germany) and deionized water used for all solutions.

2.2. Instrumentation

FT-IR spectra of sludge before and after activation were recorded on a Thermo-Nicolet 8700 spectrophotometer in a KBr matrix. X-ray diffraction patterns before and after sludge activation were obtained on a STADIP diffractometer with Cu K α radiation (Germany). Analyses of the morphology and chemical composition of the sludge before and after activation were observed by a scanning electron microscope (SEM) model 1455VP, LEO Co. Identification of elemental combination of the sludge was performed by a Philips X-ray

fluorescence spectroscopy (model PW1410, Netherlands). The surface area of the activated sludge determined by Brunauer-Emmett-Teller (BET) method using BELSORP-mini II (Japan) at 77 K. Fe(III) contents were determined a Varian atomic absorption spectroscopy model AA240. The pH meter was a digital JENWAY, model 3510 equipped with a combined glass-calomel electrode.

2.3. Sorbent preparation and activation

The sludge was obtained from the output of the clearing section of a water treatment center (Tehran, Iran). Afterwards, the sludge was exposed to sunlight for several days in a barrel to evaporate its water content. Afterward, the sludge was placed in an oven at 105 °C for 48 h and then cooled to the laboratory temperature. Finally, the dried sludge was powdered with a mortar and pestle, filtered through sieve shaker with 630-micron size and placed in a desiccator.

To activate the sludge, 2.5 g of sludge powder was stirred with 25 mL 1.0 mol L⁻¹ acetic acid for 4 h at 60 °C. Thereafter, the sludge was filtered through Whatman 40 filter paper, washed with deionized water and dried in an oven at 40-50 °C for 2 h.

2.4. Adsorption ability of activated sludge for Fe(III) removal

The removal of Fe(III) was carried out using batch method. In this procedure, various amounts of adsorbent (0.1 to 0.4 g) was added to 100 mL solution containing different concentrations of Fe(III) (20, 40, and 60 mg/L). The pH was adjusted in the range of 5-9 by drop-wise addition of 0.1 mol L⁻¹ sodium hydroxide and 0.1 mol L⁻¹ hydrochloric acid; and sorbent was added into solutions. The mixture was stirred for a period of time (5-60 min) using a shaker with the speed of 100-200 rpm. Thereafter, the sorbent was separated from the mixture by centrifugation at 3000 rpm for 10 min and amounts of adsorbed iron were estimated from the concentration change of Fe(III) ions in solution, which was determined by flame atomic absorption spectrometer (FAAS). The percent extraction of Fe(III) was calculated from the following equation:

$$\text{Removal\%} = \left(\frac{C_A - C_B}{C_A} \right) \times 100 \quad (1)$$

Where, C_A and C_B are the concentration of iron ions before and after extraction in the solution, respectively.

2.5. Adsorption isotherms and kinetic studies

Equilibrium isotherm studies were carried out with different initial concentrations of Fe(III) ions and Langmuir and Freundlich models were utilized to analyze the equilibrium adsorption data. In the several batch experiments, 0.3 mg portions of the adsorbent were equilibrated with varying concentrations of Fe(III) ion (ranging from 20 to 60 mg L⁻¹) at pH 7.0. The suspensions were agitated for 15 min using a shaker, and then the supernatant solution was removed by centrifugation. The concentration of Fe(III) ions in solution was determined with FAAS, and the amount of the adsorbed Fe(III) ions on the adsorbent was obtained and the adsorption capacity value was calculated.

Investigating the adsorption kinetics of Fe(III) on the activated sludge was performed by adding 0.3 g sorbent to 100 mL of 20 mg L⁻¹ Fe(III) at pH 7.0 with different contact times ranging between 5 and 15 min. The adsorption rate was

determined based on the kinetic equation of Lagergren pseudo first order (Eq. (2)) and pseudo second order (Eq. (3)).

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (2)$$

$$t / q_t = 1 / h + 1 / q_e t \quad (3)$$

3. RESULTS AND DISCUSSION

3.1. Characterization studies

3.1.1. FT-IR spectra

The FT-IR spectra of sludge before and after activation were recorded using KBr plate method (Fig. 1). The FT-IR spectrum of activated DWTS showed some absorption peaks were observed in the wavenumber range from 400-4000 cm⁻¹. DWTS before and after activation exhibited broad band at 3700-2700 cm⁻¹ corresponding to the OH of carboxyl moieties [21]. The bands appearing at 1031 and 1035 are related to Si-O-Si vibration [21]. The band between 400-700 cm⁻¹ are related to the stretching vibration due to the interactions produced between the oxygen and metal contents of sludge such as Fe-O, Ti-O and Al-O.

3.1.2. X-ray diffraction

The identified phases of DWTS were silica (SiO₂), calcite (CaCO₃), and almandine (Al₂Fe₃(SiO₄)₃). (Fig. 1S, Electronic Supporting Information, ESI) The characteristic peaks at $2\theta = 21$ and 26.5 are related to SiO₂. The peaks at $2\theta = 23, 39.2, 43.1, 47.52$ and 48.70 are characteristic of calcite (CaCO₃) and the peaks at $2\theta = 31, 38.2, 48.7, 57.6$ and 60.2 are correspond to the presence of almandine (Al₂Fe₃(SiO₄)₃).

3.1.3. XRF analysis

The results of chemical composition analysis of DWTS are tabulated in Table 1S (ESI) in terms of oxide composition. It is obvious that DWTS composed mainly of silica (SiO₂) and iron oxide (Fe₂O₃).

3.1.4. Scanning electron microscopy

The surface structure of DWTS before and after chemical activation was explored using SEM technique (Fig. 2) [8]. The availability of the pores and internal surface is necessary for an effective adsorbent to separate heavy metal ions from water [21]. The structure of sludge before activation was bulky in shape (Fig. 2a) and after chemical activation, a more porous and rough irregular surface was observed (Fig. 2b). The morphology of the sample consisted to exhibit a relatively high surface area and an associated high adsorption capacity [22].

3.1.5. Surface analysis

N₂ adsorption-desorption isotherm using BET method was employed to determine the surface area of DWTS after activation. The BET surface area of activated DWTS was equal to 127.6 m²g⁻¹ which was higher than reported values [22] for biosorbents. The corresponding values of the total pore volume and average pore diameter were 0.2362 cm³ g⁻¹ and 7.4033 nm, respectively.

3.2. Adsorption studies

3.2.1. Effect of pH

Investigating the influence of pH on the adsorption is important because the metal ions' adsorption from the aqueous solution is dependent on acidity. In several batch experiments, 0.1 g of activated DWTS adsorbent was equilibrated with 100 mL of the buffer solution containing 40 mg L⁻¹ of Fe(III) ion at a pH range of 5-9 for 1 h at a constant shaker speed of 200 rpm. The influence of pH variation on the adsorption of Fe(III) onto activated DWTS adsorbent is shown in Fig. 3a. The adsorption of Fe(III) increases as the pH increases, and in acidic solution, adsorption is very low. This observation is due to protonation of the active sites of the activated DWTS. As the pH increases, the protonation of active sites decreases, and the condition becomes more favorable to complex formation and sorption of Fe(III) ions to the activated DWTS. The adsorption quantity increased up to a pH of 7.0. At pH levels higher than 7.0, Fe(III) ions precipitated out because of the high concentration of OH⁻ ions in the adsorption medium. Besides, it is worth to note that the adsorption efficiency of pH 7 and 9 is not very remarkable and so pH of 7.0 was selected as the optimum value.

3.2.2. Effect of adsorbent dosage

The influence of activated DWTS dosage on Fe(III) adsorption was examined by varying dosages from 0.1 to 0.5 g. In this regards, 100 mL 40 mg L⁻¹ Fe(III) at pH 7.0 with a contact time of 15 min and a constant shaking rate of 200 rpm was employed. Fig. 3b presents a typical set of results obtained by varying adsorbent dosages during Fe(III) adsorption. From the analysis of experimental data obtained for Fe(III) ions, it was observed that the removal efficiency increased with the increase in sorbent dosage. An increase in mass concentration generally increased the amount of or percentage of sorbent metal ions because of an increase in surface area of the sorbent, which in turn increased the binding sites. Maximum adsorption was obtained when the sorbent amount was 0.3 g; beyond this amount, removal efficiency was remained constant.

3.2.3. Effect of Fe(III) initial concentration

The effect of Fe(III) initial concentration the adsorption was explored by varying its concentration from 20 to 60 mg/L. In this regards, the tests were performed by adding 0.3 g sorbent to 100 mL Fe(III) solutions at pH 7.0 with a contact time of 15 min and a constant shaking rate of 200 rpm. The results revealed that the removal efficiency decreased with the increase in the initial concentration (Fig. 3c). This behavior is related to the increase in the ratio of target ions to adsorbent surface area and reactive sites that follow a strong reduce in mass transfer [43].

3.2.4. Isotherms and kinetic

Adsorption isotherm models were widely employed to show the relationship between the equilibrium solute concentration in bulk solution and the amount of adsorbed per unit of adsorbent at a constant temperature. The equilibrium data obtained from the Fe(III) sorption capacity of the adsorbent were fitted to Langmuir and Freundlich isotherms.

The linearized form of the Freundlich adsorption isotherm was used to evaluate the relationship between the concentration of Fe(III) adsorbed by the adsorbent and the

Fe(III) equilibrium concentration in aqueous solution, and is given as:

$$\text{Log } q_e = \text{Log } K_F + \frac{1}{n} \text{Log } C_e \quad (4)$$

Where, q_e is the amount adsorbed, C_e is the equilibrium concentration, and K_F and $1/n$ are empirical constants incorporating all the parameters affecting the adsorption process [24].

The linearized Langmuir adsorption isotherm allows the calculation of adsorption capacities and the Langmuir constants as given by the following equation:

$$\frac{1}{q_e} = \frac{1}{q_{\max}} + \frac{1}{K_L q_{\max}} \frac{1}{C_e} \quad (5)$$

Where, q is milligrams of Fe(III) accumulated per gram of the adsorbent material; C_e is the Fe(III) residual concentration in aqueous solution; q_{\max} is the maximum specific uptake corresponding to the site saturation; and K_L is the ratio of adsorption and adsorption rate [24].

In the several batch experiments, 0.3 g portions of activated DWTS were equilibrated with varying concentrations of Fe(III) ion (initial concentrations ranged from 20 to 60 mg L⁻¹) at pH 7.0 and agitated for 15 min using a mechanical shaker (200 rpm). The obtained correlation coefficients ($R^2_{\text{Langmuir}} = 0.9962$ and $R^2_{\text{Freundlich}} = 0.9449$) showed that Fe(III) adsorption equilibrium data were fitted well to the Langmuir isotherm rather than the Freundlich isotherm (Fig. 4a and Fig. 4b). The maximum monolayer capacity (q_{\max}) and the Langmuir constant (K_L) calculated as 58.1 mg g⁻¹ and 1.11 L mg⁻¹, respectively.

Then the equilibrium adsorption was established within 15 min, and the adsorption rate was determined based on the kinetic equation of Lagergren pseudo first order and pseudo second order.

As shown in Fig. 4c and Fig. 4d, between the two different kinetic models, the pseudo-second order kinetic model has a very high value of R^2 for all kinetic data ($R^2_{\text{First order}} = 0.9028$ and $R^2_{\text{Second order}} = 0.9996$). The pseudo-second order kinetic equation was developed for the adsorption process, and there are three consecutive steps taking place in the sorption of an adsorbate by a adsorbent: (1) migration of the metal ions from the solution to the surface of the adsorbent; (2) migration of the metal ions into the pores of the adsorbent; and (3) adsorption of the metal ions on the interior surface of the adsorbent [25]. The rate of the reaction is mainly controlled by the first two steps. The rate constant of adsorption (k_{ads}) was calculated to be 19.5 g mg⁻¹ min⁻¹, which indicates a second order kinetic.

4. CONCLUSION

In this study, activated DWTS as a cheap, cost effective and efficient adsorbent was used for removal of Fe(III) ions from water sample. The adsorbent was characterized by various techniques such as FT-IR, SEM, XRF, XRD and BET method. The results reveal that this is a facile, efficient, and environmentally friendly approach for preparation of an efficient sorbent and the as-prepared material can be used as an excellent sorbent for removing Fe(III) ions from water. Under the optimal conditions, the Langmuir adsorption plot showed maximum Fe(III) removal with a maximum adsorption capacity of 54.3 mg g⁻¹ and a Langmuir constant (K_L) of 1.19 L mg⁻¹ at the optimal conditions. The pseudo-

second-order model was determined as the best fitting model for kinetic data with a rate constant of adsorption (k_{ads}) equal to $19.6 \text{ g mg}^{-1} \text{ min}^{-1}$. An iron (III) concentration as high as 20 mg/L can be completely removed by the activated DWTS under the optimum conditions which is higher than the maximum permissible concentration of Fe (III) in drinking water (0.3 mg/L) recommended by the World Health Organization (WHO) and the Environmental Protection Agency (EPA).

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