

Adsorption Behavior of Fe(II) and Fe(III) Ions on Polyaniline Coated Sawdust: Batch and Fixed-Bed Studies

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Abstract

The aim of this study is to investigate the suitability of polyaniline coated-sawdust (SD/PAni) as an adsorbent for removal of Fe(II) and/or Fe(III) ions from aqueous solutions. The study includes batch and column tests. With column experiments, the influence of different experimental parameters on the adsorption behavior of Fe(II), Fe(III), and a mixture of both ions were studied and it was found that the optimum adsorption conditions for individual iron species and a mixture of them were similar. The optimal values for pH, flow rate, temperature, and adsorbent mesh size were found to be 4.0, 5.0 mL min⁻¹, 25 °C, and 100 BSS mesh, respectively. Batch experiments were carried out to study the adsorption isotherms at ambient temperature. The results demonstrated that the adsorption isotherms for both iron species were best represented by the multilayer adsorption isotherm model. The adsorption-desorption stability performance of the adsorbent was evaluated and confirmed over 5 cycles.

Keywords: Langmuir; Freundlich; Temkin; Multilayer isotherm; Decoration with polyaniline; Solid phase extraction; Continuous adsorption.

1. Introduction

Water pollution by heavy metals remains a serious environmental problem. Their accumulation in numerous plant and animal organisms occurs easily. Hence, one of the most widely researched topics in environmental science which requires extensive study is the removal of heavy metals from aqueous solutions.¹ Iron is a nutrient element required by living cells.^{2,3} Estimates of the minimum daily requirement for iron depend on sex, age, physiological status, and iron bioavailability, and is approximately 10 to 50 mg/day.⁴ Presence of high levels of iron in drinking water is associated with some problems such as bad taste, discoloration, and high turbidity. World Health Organization (WHO) recommends that the iron concentration in drinking water should be less than 0.3 mg L⁻¹.^{5,6} In anaerobic groundwaters, concentration of iron(II) is usually in the range of 0.5–10 mg L⁻¹, but concentrations up to 50 mg L⁻¹ are also reported. The median iron concentration in rivers has been found to be 0.7 mg L⁻¹.⁷ In countries where water is distributed through galvanized iron pipes concentration of iron may be higher than the normal level.⁵ Thus, removal of iron species from aqueous

media to allowable global limits is essential and has led to an increasing interest in developing efficient methods for this purpose.^{8–11}

In recent investigations, adsorption is being extensively employed for separation of metal ions¹² and elaborate efforts have been continued to find an effective and economic adsorbent. Agricultural wastes like corn stalk, rice waste, peanut, straw, sawdust, and sugarcane bagasse have been proved to be low-cost and most efficient adsorbents in this respect.^{13–15} Sawdust was used as an adsorbent in this study. The cell walls of sawdust principally contain cellulose, lignin, and many hydroxyl groups which all are confirmed to have ion exchange capacities.¹⁶ This feature, together with its abundant availability almost free of charge, makes sawdust most suitable for uptake of heavy metal ions or cationic dyes from aqueous solutions.^{17–21} Modification of sawdust using other materials is also considered by some researchers to improve its sorption performance.²² On the other hand, polymers have gained great importance in environmental applications owing to their easy handling, efficiency, and selectivity.²³ Among them is polyaniline which has been used as metal ions adsorbent.^{24–26} Moreover, polyaniline is a suitable candidate polymer for coating of natu-

ral fibers regarding to its flexibility, low cost, and environmentally safe characteristics.^{27,28} The present research was conducted to study the ability of polyaniline-coated sawdust (SD/PAni) for the removal of Fe(II) and/or Fe(III) ions from aqueous solutions. To the best of our knowledge, no reports are available on the application of SD/PAni as adsorbent for iron species. The removal experiments were carried out in a fixed-bed column to study and optimize the operational conditions including pH, temperature, flow rate, and particle size of adsorbent. The possible mechanism of adsorption was also examined in a batch mode through different isotherm models.

2. Experimental

2. 1. Chemical Reagents

Aniline was purchased from Merck and distilled twice before use. Ammonium persulfate was ACS grade ($\geq 98\%$) and used as received. The stock solutions (1000 mg L^{-1}) of Fe(II) and Fe(III) were prepared from Merck Titra-sol standard solutions in 15% HCl. Working standard solutions were then prepared daily by stepwise dilution of the stock solutions. Other chemicals used in this work were all of analytical reagent grade and prepared in distilled water. pH adjustment was performed using NaOH and HCl solutions. Ammonium acetate buffer solution was prepared by dissolving 38.54 g ammonium acetate in 150 mL distilled water, adding 28.6 mL acetic acid and diluting to 1.0 L with distilled water. Sawdust was obtained from a local carpentry workshop. All vessels used for analysis were kept in dilute nitric acid at least overnight and subsequently washed three times with distilled water.

2. 2. Apparatus

Absorbance measurements at 510 nm were performed by spectrophotometer (Perkin Elmer Lambda 25) with a 1.0 cm glass cell. A Metrohm pH meter (model 691) with a combined double junction glass electrode, calibrated against two standard buffer solutions at pH 4.0 and 7.0, was used for pH measurements. Oxford instrument was used to record scanning electron microscopy (SEM) measurements. Perkin Elmer equipment was employed for FTIR recording. TGA curves were recorded on a STA 1500 (Model Rheometric scientific) at the maximum 800°C . The specific surface areas of the sawdust and SD/PAni were quantified with the Brunauer, Emmitt and Teller (BET) method from the N_2 adsorption/desorption isotherms with a Quantachrome BET instrument (Quantachrome Corporation, USA).

2. 3. Preparation of Sawdust

The raw sawdust obtained from a carpentry workshop was soaked in distilled water for 8 h , followed by rins-

ing with 0.1 mol L^{-1} hydrochloric acid and then with 0.1 mol L^{-1} sodium hydroxide. After that it was thoroughly rinsed with distilled water until the washings showed neutral on litmus paper. To exclude unbound organic materials, the sawdust was washed with 300 mL of acetone and then with 300 mL of methanol. It was then dried at 105°C , ground, and sieved to various mesh sizes (100 , 60 , 40 , and 25 BSS mesh).

2. 4. Synthesis of Polyaniline Polymer

Polyaniline was prepared by the following procedure.²⁹ 5.0 g freshly distilled aniline was dissolved in 250 mL of 1.0 mol L^{-1} HCl. The solution was placed in an ice bath to cool for 20 min . 250 mL of precooled 0.3 mol L^{-1} ammonium persulfate solution in HCl 1.0 mol L^{-1} was slowly added to the above solution under vigorous stirring. The reaction was then allowed to continue overnight at room temperature without stirring. The dark blue polymer formed was filtered and washed with distilled water and dilute HCl solution until the filtrate became colorless, followed by thorough rinsing with methanol and distilled water. The product was dried ($50\text{--}60^\circ\text{C}$), powdered, and stored for processing.

2. 5. Preparation of Polyaniline Coated Sawdust (SD/PAni)

To make PAni soluble in formic acid for coating, it was converted to emeraldine base (EB) form by treating with 0.5 mol L^{-1} NaOH solution for 2 h .³⁰ Following the washing with distilled water, it was dried at 60°C . 0.50 g of the as-prepared EB powder was dissolved in 50 mL of formic acid. Undissolved solids were separated by filtration. To prepare polyaniline-coated sawdust (SD/PAni), 5.0 g sawdust with specified mesh size was mixed with 50 mL EB solution ($1\% \text{ w/v}$) and stirred for 2 h at room temperature. It was then kept at room temperature for another 2 h without stirring. After filtration, it was dried at $\sim 60^\circ\text{C}$ to remove residual solvent.³¹

2. 6. Fixed-Bed Column Adsorption Experiments

For fixed-bed experiments, 10.0 mg of SD/PAni was packed in a burette column (15 cm length) by keeping glass wool at top and bottom. In order to eliminate dissolvable colored materials in SD/PAni column, it was washed with 100 mL of 5% acetone and then with 0.2 mol L^{-1} sodium hydroxide until the exiting liquid became colorless. The column was then rinsed with distilled water. 50.0 mL of a solution containing Fe(II) and/or Fe(III) with concentration of 20 mg L^{-1} was applied to the column using peristaltic pump at specified flow rate under the optimized conditions. The effluent exiting the column was collected and analyzed for the residual analyte(s) by colorimetric

o-phenanthroline method (3500–Fe iron).³² In the case of Fe(II), 2.5 mL of 1,10-*ortho*-phenanthroline 0.1% (w/v) together with 10.0 mL buffer was added to the effluent sample and the absorbance was measured at 510 nm after 10 min.

To evaluate total iron content via the above procedure, reduction of ferric form to the ferrous state is required before the addition of *o*-phenanthroline. Therefore, when ferric ions were present in the effluent sample, reduction to the lower oxidation form was performed by the addition of 2.0 mL hydroxylamine 10% (w/v) and 1.0 mL concentrated hydrochloric acid, followed by heating to boiling to ensure a complete conversion. After cooling, it was treated with 2.5 mL of 1,10-*ortho*-phenanthroline 0.1% (w/v) and 10.0 mL buffer solution and then the absorbance was measured at 510 nm. Fe(III) could be determined as the difference between total iron and Fe(II). All the absorbance measurements were performed in triplicate. Removal percent and capacity of adsorbent (q) were calculated using the following equations:

$$\text{Removal \%} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (1)$$

$$q = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentrations of analyte ion in mg L^{-1} , m and V are mass of adsorbent (g) and volume of the influent (L), respectively.

3. Results and Discussion

In this paper, the potential of polyaniline-coated sawdust as an adsorbent for removal of individual iron species from aqueous solution was investigated through batch and column studies. Simultaneous uptake of ferrous and ferric ions was also examined. Polyaniline was synthesized via an oxidative polymerization approach and then coated on sawdust. The sorbent was characterized by SEM, TGA, and FTIR analysis. The appropriate extraction conditions were estimated by investigating the effect of different parameters by the one-factor-at-a-time approach.

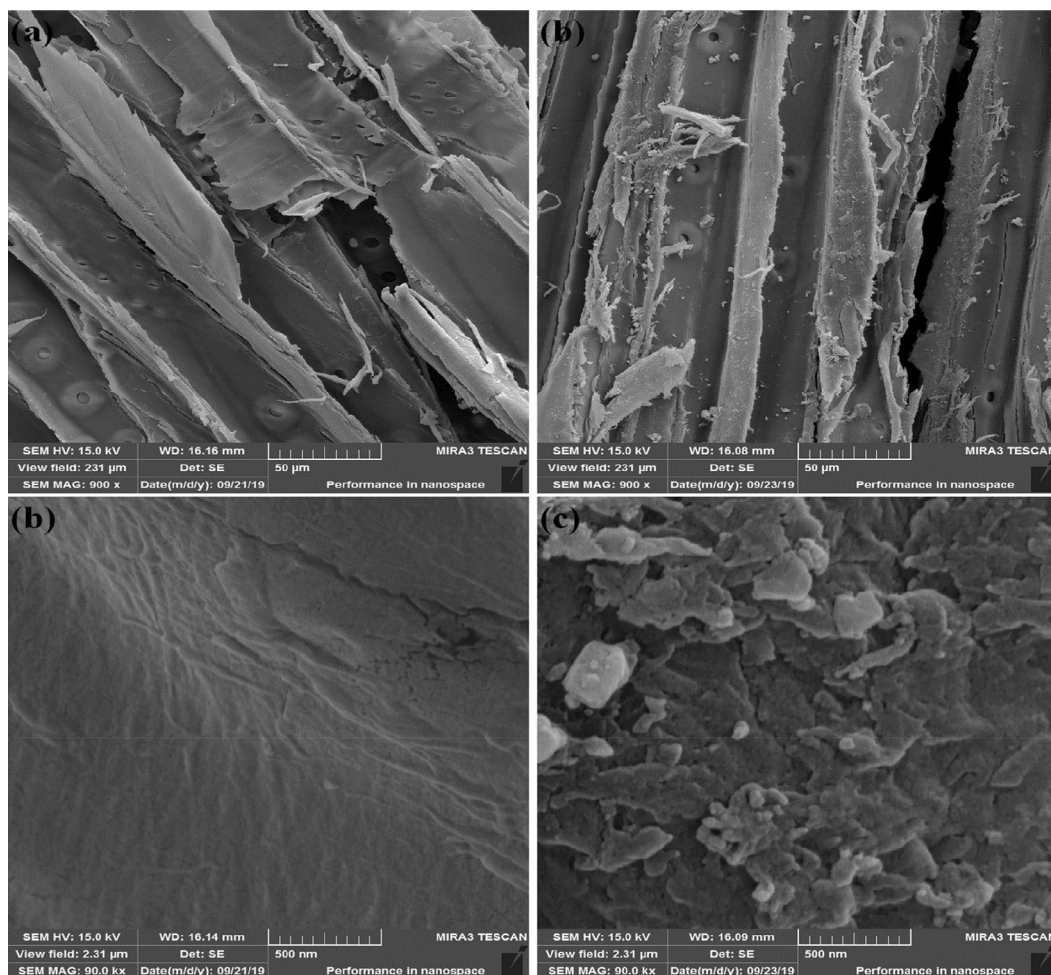


Fig. 1. SEM images of sawdust (a & c) and SD/PANI (b & d).

3. 1. Adsorbent Characterization

SEM measurements of the raw sawdust and SD/PAni are given in Fig. 1. Comparing Figures 1a and 1c with Figures 1b and 1d showed that PAni particles were successfully decorated on the surface of sawdust. Moreover Figures 1b and 1d confirmed that PAni nanoparticles exhibited more or less homogenous shape.

FTIR analysis was carried out to study the surface properties of the raw sawdust and SD/PAni. Fig. 2 shows a broad band at 3287 cm^{-1} for the raw sawdust. This band is related to $-\text{OH}$ stretching vibration. The peak at 2358 cm^{-1} in the same material is stretching vibrations of $\text{N}-\text{H}$ or $\text{C}=\text{O}$ groups probably due to amines and ketones.³³ In the spectrum of SD/PAni, some additional peaks appear, confirming decoration of sawdust with polyaniline. The $\text{N}-\text{H}$ symmetric stretching of polyaniline appears at 3394 cm^{-1} .³⁴ The FTIR spectra of SD/PAni also shows the characteristic peak of nitrogen quinine at 1509 cm^{-1} ,³⁵ and bands appear at 1431 , 1378 , and 1058 cm^{-1} , which correspond to a benzene ring, $\text{C}-\text{N}$ and $\text{C}=\text{N}$ stretching vibrations.³⁶ The peak at 794 cm^{-1} belongs to $\text{C}-\text{H}$ of the polyaniline ring.³⁷

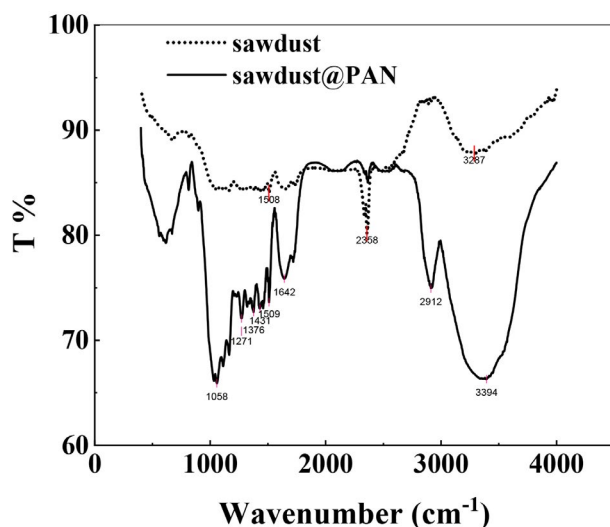


Fig. 2. FTIR spectra of raw sawdust (dot plot) and modified sawdust with polyaniline (solid plot).

The TGA results for the sawdust and SD/PAni presented in Fig. 3 reveal two main steps of weight loss for both adsorbents. The first stage of weight loss for both adsorbents was observed from the beginning of the experiment until the temperature reached about 90°C . This weight loss of around 10% (w/w) was attributed to the loss of physically adsorbed water. The second step occurred between 220 and 400°C , again for both of the adsorbents. This step in the case of raw sawdust was assigned to the transformation of lignin, cellulose, and hemicellulose to gaseous materials and tars.³⁸ For the sawdust decorated with polyaniline, these processes were accompanied with

the production of the facile thermal decomposition of the loaded polyaniline from the surface and, therefore, the weight loss was exacerbated.³⁹ It was also found from TGA results that the surface of sawdust was decorated by PAni with about 5% coating. The specific surface areas for sawdust and SD/PAni were measured using BET surface area analyzer. The values for the specific surface areas and pore diameters for both adsorbents were the same and found to be $0.88\text{ m}^2\text{ g}^{-1}$ and 18.00 nm , respectively.

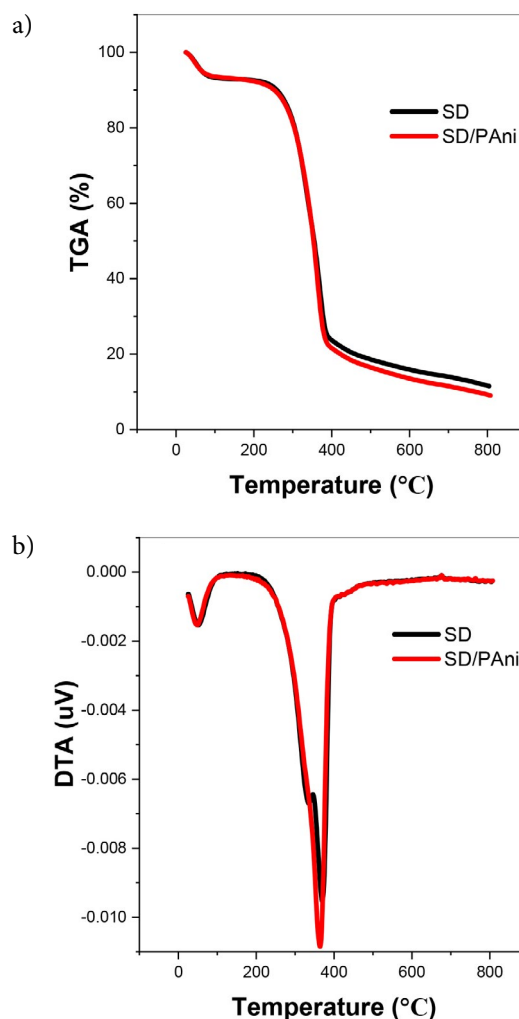


Fig. 3. TGA (a) and DTA (b) curves of sawdust and SD/PAni.

3. 2. Effect of Adsorbent Mesh Size and pH

It is well known that some of the adsorbent properties like its structure, size, and surface chemistry have effect on the adsorption efficiency.⁴⁰ So, the studies were conducted to determine which mesh size of sawdust was suitable to use in the adsorbent preparation step. Fig. 4a depicts the effects of pH and adsorbent mesh size on the removal efficiency. As it is evident, the larger the mesh size of sawdust used for the adsorbent preparation, the

better the adsorption efficiency. This can be contributed to the availability of a larger surface area, providing more adsorption sites which facilitate the adsorption of iron ions.

Another important factor affecting the adsorption process is pH of the sample solution.⁴¹ The effect of pH in the range of 1–4 is depicted in Fig. 4a as well. Higher pH values were not considered due to hydroxide formation of iron ions. In the case of ferrous state, it should be pointed out that iron in the ferrous state can only remain in solution in the absence of oxygen, and generally in acidic media.⁴² Several papers considered only acidic media to prevent the hydroxide formation.^{43,44}

In the present study, optimum pH value was found to be 4.0 for both iron species. At lower pH value, the hydrogen ions compete with the metal ions for the binding sites of the adsorbent. Moreover the protonation of the nitrogen atoms in polyaniline occurred in

acidic solutions.⁴⁵ Consequently, the surface of adsorbent was positive in the highly acidic media and adsorption of the iron ions was suppressed due to the electrostatic repulsion. However, deprotonation of the nitrogen atoms occurs as the pH increases (3–4), leading to the formation of active sites in the adsorbent. Therefore, our further studies were done at pH 4.0. It is worthy to note that the extent of competition of Fe(III) with Fe(II) for the adsorption sites on SD/PAni was also explored. To do this, a solution of mixture of ferric and ferrous ions with initial concentration of 10 mg L^{-1} for each one was passed through the column. Fig. 4b shows that at lower pH values, the extent of competition between iron species was high. However, at optimum pH value, no significant competition might take place. This is mainly due to high adsorption capacity of SD/PAni towards ferrous and ferric ions at $\text{pH} = 4.0$, providing more active sites for the adsorption of the analytes.

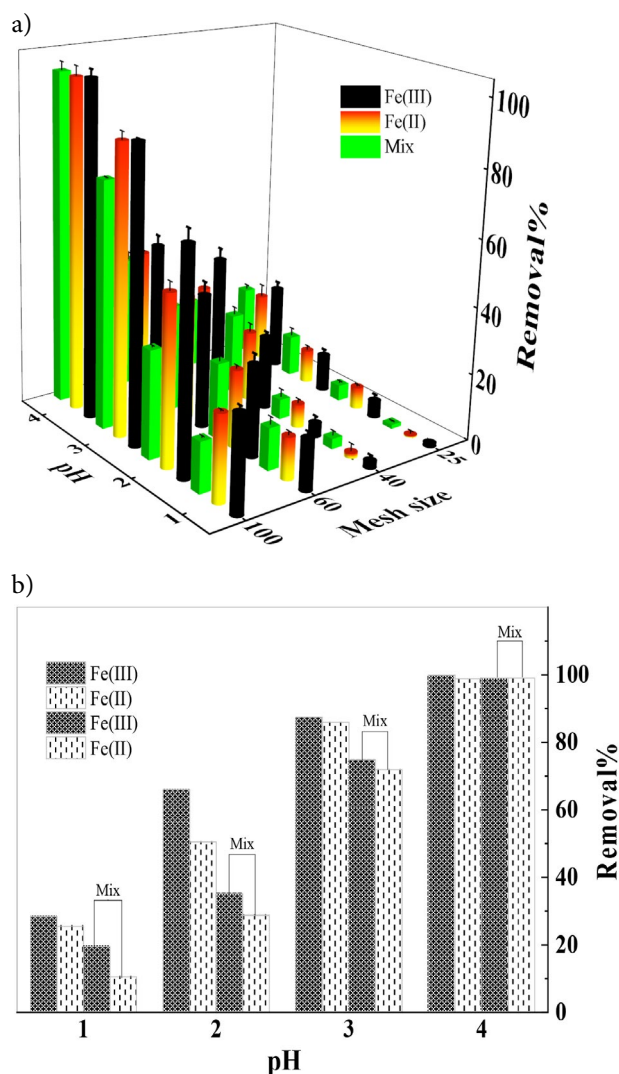


Fig. 4. a) Effect of pH and mesh size on the adsorption of Fe(III) and/or Fe(II); b) pH effect for adsorbent with mesh size of 100. Conditions: $T = 25^\circ\text{C}$; flow rate = 5.0 mL min^{-1} .

3. 3. Effect of Flow Rate

As the adsorption is a time dependent process, the effect of flow rate on the adsorption of iron species was examined at pH 4.0 by passing the influent through packed column at various flow rates. Fig. 5 shows that as flow rate is increased, the adsorption of iron species on SD/PAni decreases. At lower flow rates, there is sufficient contact time between the analyte(s) and the adsorbent and, consequently, the adsorption is brought to completion. In other words, by increasing flow rate the adsorbent has not sufficient time to totally adsorb the analyte(s) well and, as a result, the unretained metal ions leave the column before equilibrium is achieved. Hence, flow rate of 5.0 mL min^{-1} was selected as the best and used in the next experiments. It also can be seen from Fig. 5 that the competition of Fe(I-II) with Fe(II) for the adsorbent is promoted at higher flow rates. Adsorption of Fe(III) becomes most preferable by increasing flow rate.

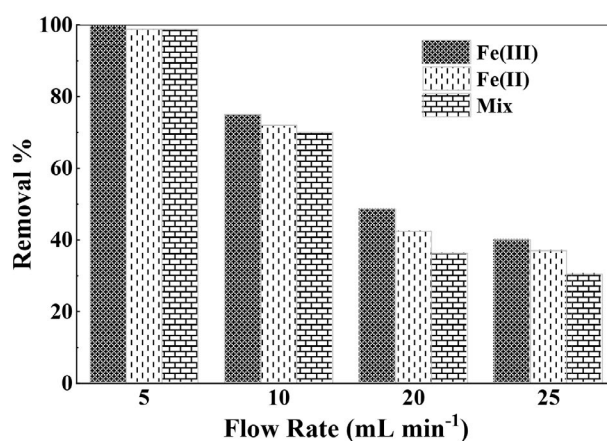


Fig. 5. Effect of flow rate on the adsorption of Fe(III) and/or Fe(II). Conditions: $\text{pH} = 4.0$; $T = 25^\circ\text{C}$; mesh particle size = 100 BSS mesh.

3. 4. Effect of Temperature

The dependence of analytes adsorption on temperature was investigated in the range of 10–75 °C. In accordance to the data shown in Fig. 6, the adsorption increases slightly by increasing in temperature up to 25 °C and then stays at a constant value in the range of 30–55 °C. After that the amounts of removal for both analytes start to decrease, mostly pertaining to the fact that at higher temperature the analyte ions gain more kinetic energy which enables the analytes to overcome the adsorption potential.⁴⁶ Hence, all experiments were performed at ambient temperature. The results in Fig. 6 indicate that ferric ions are favorably adsorbed by SD/PAni at higher temperatures where the experimental conditions are far from optimum.

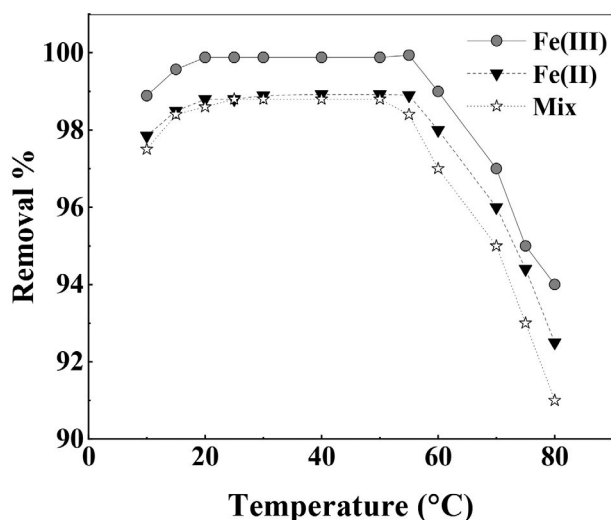


Fig. 6. Effect of temperature on the adsorption Fe(III) and/or Fe(II). Conditions: flow rate = 5.0 mL min⁻¹; pH = 4.0; particle size = 100 BSS mesh.

3. 5. Adsorption Isotherms

Isotherm models are useful to explain the adsorption mechanism and estimate the adsorption capacity of the adsorbent. In other words, the adsorption isotherms explain the relation between the amount of solute adsorbed per unit mass of adsorbent and the amount of the unadsorbed adsorbate at the equilibrium time.⁴⁷

Isotherm experiments were carried out in batch operation by the following procedure: to aliquots of 100 mL solutions of Fe(II)/Fe(III) with initial concentrations ranging from 1 to 7 mg L⁻¹ (pH = 4.0), 10.0 mg SD/PAni was added and the mixture was stirred for 10 min. It should be noted that the adsorption reaches the equilibrium within 10 min. After that, the solution was filtered and residual iron ions was determined. The results are depicted in Fig. 7.

Langmuir adsorption model assumes that adsorption occurs at homogenous monolayer active site of the adsorbent. It also describes that all the adsorption sites have uniform energy and the adsorption takes place at structurally similar sites.⁴⁸ The linearized form of Langmuir adsorption isotherm is given in Eq. 3.

$$\frac{1}{q_e} = \frac{1}{q_m} + \left(\frac{1}{q_m K_L}\right) \frac{1}{C_e} \quad (3)$$

where C_e and q_e are the concentration (mg L⁻¹) and adsorption capacity (mg g⁻¹) at equilibrium, respectively. Langmuir constant (K_L) indicates the affinity of binding sites with the adsorbate. The performance of different adsorbents can be compared using the maximum adsorption capacity (q_m). Langmuir isotherm constants for iron(II) and iron(III) ions were calculated from the intercept and slope of the corresponding

Table 1. Langmuir, Freundlich, Temkin, and multilayer isotherm model constants for the adsorption of Fe(II) and Fe(III) ions

Metal ion		Langmuir isotherm model			
		K_L	q_m	R_L range	R^2
Fe(II)		0.82	35.29	0.15–0.55	0.9982
Fe(III)		0.99	40.65	0.12–0.50	0.9889
		Freundlich isotherm model			Equation
		K_F	n	R^2	
Fe(II)		14.48	1.93	0.9725	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$
Fe(III)		18.33	1.77	0.9917	
		Temkin isotherm model			Equation
		a_t	b_t	R^2	
Fe(II)		16.24	8.07	0.9887	$q_e = a_t + b_t \ln C_e$
Fe(III)		20.82	10.33	0.9722	
		Multilayer isotherm model			Equation
		K_1	K_2	q_m	R^2
Fe(II)		0.94	0.02	31.56	0.9905
Fe(III)		0.88	0.04	39.39	0.9926
					$q_e = \frac{q_m K_1 C_e}{(1 - K_2 C_e)[1 + (K_1 - K_2)C_e]}$

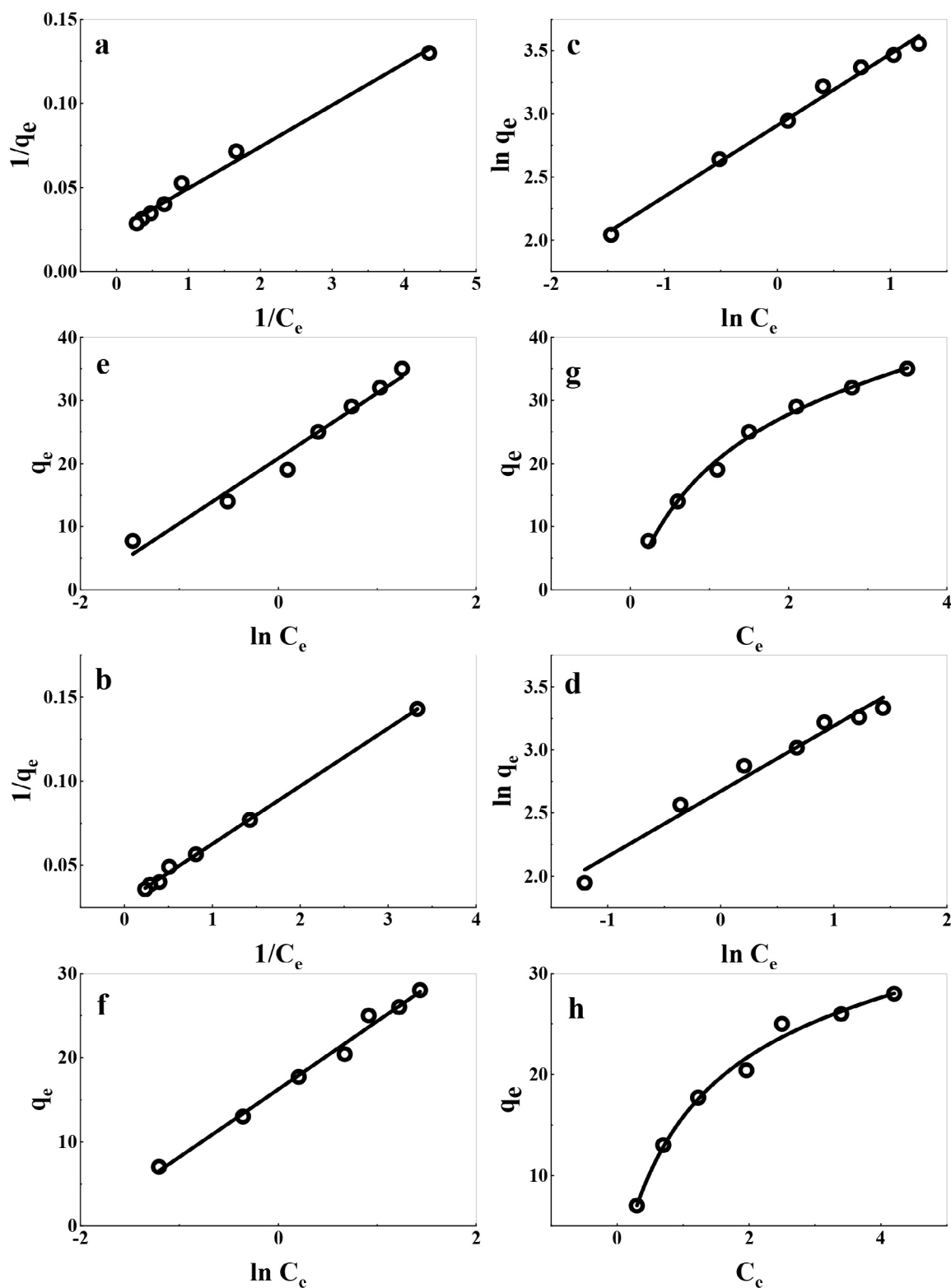


Fig. 7. (a–b) Langmuir; (c–d) Freundlich; (e–f) Temkin and (g–h) multilayer adsorption isotherms for adsorption of Fe(II) and Fe(III) onto SD/PAni; a, c, e, and g represent adsorption data for Fe(III).

linear plot of $1/q_e$ versus $1/C_e$ (Fig. 7a–b). The corresponding parameters are given in Table 1. Both isotherm data sets were well fitted to Langmuir model but

adsorption data of Fe(II) fitted better compared to that of Fe(III). The separation factor which describes the feasibility of the adsorption was calculated by the fol-

lowing equation:⁴⁹

$$R_L = \frac{1}{(1 + K_L C_e)} \quad (4)$$

$R_L > 1$ denotes the unfavorable adsorption; $R_L = 0$, the irreversible adsorption, while $0 < R_L < 1$ indicates the energetically favorable adsorption. R_L -value for iron(II) and iron(III) adsorption is less than 1, indicating SD/PAni as a suitable adsorbent for both analytes.

Freundlich isotherm refers to multilayer and heterogeneous adsorption on the adsorbent surface. This model assumes that the highly energetic sites are firstly occupied by the adsorbate ions and adsorption energy decreases exponentially during the adsorption process.⁵⁰ The linearized form of Freundlich isotherm is displayed below.

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

where n and K_F are called Freundlich isotherm constants. K_F represents the relative adsorption capacity or the amount of adsorbate adsorbed from a solution with unit concentration. $1/n$ denotes heterogeneity of the adsorbent surface. The value of $1/n$ close to or equal to 1 stands for the homogenous binding sites of the adsorbent.⁵⁰ Freundlich isotherm plots of iron(III) and iron(II) ions are depicted in Fig. 7c–d, respectively. K_F and n values were calculated from the corresponding plots and are given in Table 1. The values of n were found to be 1.93 and 1.77 for iron(II) and iron(III) ions, respectively. These values revealed the favorability of iron(II) and iron(III) ions adsorption onto the SD/PAni, since the n values in the range of 1 to 10 represent favorable adsorption. Comparison between calculated correlation coefficients for Langmuir and Freundlich isotherms (given in Table 1) indicated that the adsorption data of Fe(II) was better fitted to Langmuir whilst the experimental adsorption data for Fe(III) was well modeled by Freundlich isotherm.

The adsorbent–adsorbate interaction and heat of the adsorption were assessed by Temkin isotherm model with the following equation (Fig. 7e–f):

$$q_e = a_t + b_t \ln C_e \quad (6)$$

where b_t stands to the heat of the adsorption (J mol^{-1}) and a_t is related to the equilibrium binding constant. The values of a_t and b_t were calculated as 16.24 and 8.07 for Fe(II) and 20.82 and 10.33 for Fe(III), respectively (Table 1). Regarding to the values of a_t obtained for Fe(II) and Fe(III), it was found that ferric ions were preferably adsorbed on the SD/PAni.

Multilayer adsorption isotherm model was also applied to fit the adsorption data:⁵¹

$$q_e = \frac{q_m K_1 C_e}{(1 - K_2 C_e)[1 + (K_1 - K_2)C_e]} \quad (7)$$

where K_1 and K_2 refers to the adsorption affinity constants for the first layer and for subsequent multilayer, respec-

tively. Eq. (7) is reduced to Langmuir equation if K_2 is negligible. Compared the correlation coefficients given in Table 1 for different isotherm models revealed that both the adsorption data for both iron species are well fitted to the multilayer adsorption isotherm. The constant parameters of the multilayer isotherm calculated for both iron ions are given in Table 1. The corresponding curves are depicted in Fig. 7g–h. The data yielded provide convincing evidence that (i) maximum adsorption capacity for Fe(III) is higher than Fe(II); (ii) the tendency of Fe(III) to be bound in multilayer form is higher than that of Fe(II).

3. 6. Adsorption Mechanism

Study of adsorption efficiency at different pH revealed that the uptake of Fe(III) and Fe(II) onto SD/PAni was lower in highly acidic solutions ($\text{pH} < 2$). The maximum removal of analytes was observed at $\text{pH} = 4$ and minimum removal was seen at $\text{pH} = 1$. The lower adsorption behavior of SD/PAni under the highly acidic condition can be explained by taking into account the protonation of the nitrogen atoms present in polyaniline.⁴⁵ As a result, the surface of adsorbent is positive in the highly acidic media and is not able to uptake the iron ions due to the electrostatic repulsion. However, deprotonation of the nitrogen atoms occur as the pH increases (3–4), leading to the formation of active sites in the adsorbent.

Typically, the adsorption of metal ions onto the surface of adsorbent may follow several approaches including ion exchange, chemisorption, and complexation. Ion exchange is the most dominant mechanism by the reaction of metal ions with surface functional groups. The chemisorptive reaction may be formed by participation of a lone pair of electrons of a donor atom with metal ions. Another mechanism is surface adsorption by which metal ions may be bound to the surface of adsorbent. In this mechanism the surface of adsorbent should have a negative charge. That the adsorption isotherms of iron ions onto SD/PAni are well fitted to the Langmuir equation implies the preferential binding of metal ions on all sites of SD/PAni as homogeneous surfaces. This consideration along with the fact that maximum deprotonation of nitrogen atoms occurs at $\text{pH} = 4$, supports the claim that the adsorption mechanism is chemisorption. This is in accordance with the previous literature.³⁹

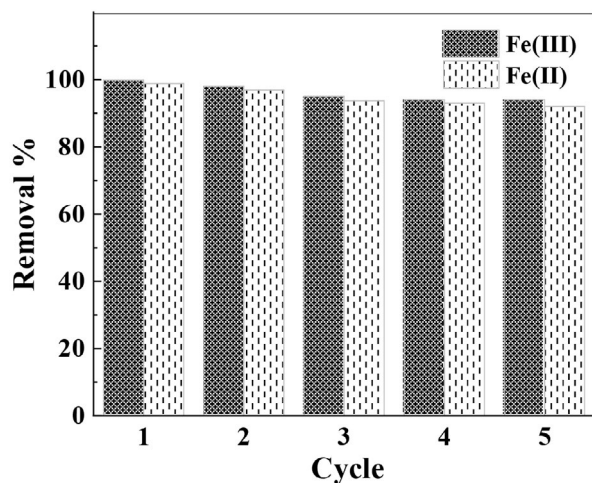
3. 7. Desorption and Reusability

The elution process greatly depends on the type and concentration of the eluent. So, some eluent solutions with different concentrations were employed for desorption of iron(II) and iron(III) ions retained on SD/PAni and the results are given in Table 2. Optimum desorption of both iron ions was observed with 50.0 mL 1.0 mol L⁻¹ HCl. Hence, this solution was considered for regeneration of the used columns.

Table 2. Effect of concentration and type of eluent on the recovery of Fe(II) and Fe(III) ions.

Volume (mL)	Eluent Content	Recovery (%)	
		Fe(II)	Fe(III)
20	0.3 mol L ⁻¹ HCl	87.2	69.0
20	0.3 mol L ⁻¹ HNO ₃	75.7	72.0
20	0.3 mol L ⁻¹ H ₂ SO ₄	63.0	70.3
25	0.5 mol L ⁻¹ HCl	91.2	88.6
30	0.5 mol L ⁻¹ HCl	95.0	94.6
50	1.0 mol L ⁻¹ HCl	98.89	98.3

To check the reusability of SD/PAni for iron ions adsorption, five successive cycles of adsorption and desorption studies were carried out in a batch system. The results are depicted in Fig. 8. The percentage of adsorption of the recycled adsorbent was 98.0% and 96.9% at the first cycle

**Figure 8.** Effect of cycle times on the removal efficiencies of iron ions.

for Fe(III) and Fe(II), respectively. After five adsorption–desorption cycles, the adsorption of Fe(III) and Fe(II) decreased by 5.9% and 6.8%, respectively. The results confirm that SD/PAni is an effective and recyclable adsorbent for the removal of iron ions.

3. 8. Comparison with Other Methods

SD/PAni has satisfactory characteristics in comparison to the previously reported methods for removal of iron(II) and iron (III) ions (Table 3). Adsorption capacity is one of the most important characteristics of an adsorbent. The calculated adsorption capacities (q_m) for the SD/PAni were satisfactory and found to be 31.56 and 39.39 mg g⁻¹ for iron(II) and iron(III) ions, respectively. Operation in continuous mode is another major advantage of the presented method. Additionally, the proposed method can handle reasonable sample volume, and has less normalized extraction time than other methods.^{9,52–59} Normalized extraction time is defined as the time required to extract 1.0 mg of the adsorbate by 1.0 g of the adsorbent. It is worth noting that the efficiency of raw sawdust was checked toward the removal of iron ions. It was found that the efficiency of the sawdust decorated with polyaniline was more than 1.5 times greater than the raw sawdust for the removal of iron ions.

4. Conclusions

SD/PAni was synthesized and employed as an effective adsorbent for removal of Fe(II) and/or Fe(III) ions from aqueous solutions in a fixed-bed column system. To our knowledge, this is the first time that SD/PAni has been used for the removal of iron ions. The data gathered in the study suggest that SD/PAni has a good potential for adsorption of iron(II) and iron(III) ions. The greatest adsorption efficiency was observed at pH 4.0, flow rate of 5.0

Table 3. Comparison of the characteristics of the proposed method with the previously published methods.

Adsorbent	Analyte	Adsorption capacity (mg g ⁻¹)	Extraction time (min)	Normalized extraction time (min mg ⁻¹)	Sample volume (mL)	Reference
Fe(III)–IIP	Fe(III)	40.41	15	600	25	9
Fe(III)-imprinted amino-functionalized silica gel	Fe(III)	25.21	150	150000	150	52
Triton X–100-coated PVC	Fe(III)	2.7	80	8000	450	53
Modified silica gel	Fe(III)	25.76	150	150000	150	55
Functionalized activated carbon	Fe(III)	77.8	100	20000	200	56
SDS-coated alumina	Fe(III)	6.3	437.5	8750	1750	57
Pyridinium IL– modified silica	Fe(III)	11.8	100	20000	200	58
Fe(II)– IIP ^a	Fe(II)	1.57 ^a	30	6000	10	59
Polyaniline coated-saw dust	Fe(II)–Fe(III)	31.56–39.39	10	10	50	This work

^a IIP: ion imprinted polymer

mL min⁻¹, and temperature of 25 °C with adsorbent mesh size of 100 BSS. A closer look at the results indicated that ferric ions are more adsorbed compared to ferrous ions under conditions far from the optimized conditions. However, under optimal conditions where the adsorption efficiency of SD/PAni is as high as possible, no significant competition of adsorption between Fe(II) and Fe(III) ions takes place. Isotherm data of Fe(II) and Fe(III) adsorption were well fitted to multilayer adsorption isotherm model. Adsorption process of both iron species were temperature-independent in the range of 30–55 °C. 50.0 mL 1.0 mol L⁻¹ HCl was efficiently used as an eluent for regeneration of adsorbent.

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5. References

1. D. Fernández-Calviño, J. A. Rodríguez-Suárez, E. López-Periago, M. Arias-Estévez, J. Simal-Gándara, *Geoderma* **2008**, *145*, 91–97. DOI:10.1016/j.geoderma.2008.02.011
2. G. Khayatian, H. A. V. Kolaie, F. Nasiri, B. Atashkar, S. Hassanpoor, *J. Chin. Chem. Soc.* **2010**, *57*, 118–123. DOI:10.1002/jccs.201000019
3. W. S. W. Ngah, S. Ab Ghani, A. Kamari, *Bioresour. Technol.* **2005**, *96*, 443–450. DOI:10.1016/j.biortech.2004.05.022
4. M. Abbasi, M. Zaghari, M. Ganjkanlo, S. Khalaji, *J. Appl. Anim. Res.* **2015**, *43*, 166–176. DOI:10.1080/09712119.2014.928634
5. World Health Organization, Guidelines for drinking-water quality, 2nd ed. Vol. 2. Health criteria and other supporting information. Geneva, **1996**.
6. S. Vasudevan, J. Lakshmi, G. Sozhan, *Clean Soil Air Water* **2009**, *37*, 45–51. DOI:10.1002/clen.200800175
7. National Research Council. Iron. University Park Press: Baltimore, Maryland, **1979**.
8. M. A. Kassem, A. S. Amin, *Food Chem.* **2013**, *141*, 1941–1946. DOI:10.1016/j.foodchem.2013.05.038
9. M. Roushani, T. M. Beygi, Z. Saedi, *Spectrochim. Acta, Part A* **2016**, *153*, 637–644. DOI:10.1016/j.saa.2015.09.029
10. X. Cai, B. Wei, J. Han, Y. Li, Y. Cui, G. Sun, *Hydrometallurgy* **2016**, *164*, 1–6. DOI:10.1016/j.hydromet.2016.04.010
11. A. Bazmandegan-Shamili, A. M. H. Shabani, S. Dadfarnia, M. Saeidi, M. R. Moghadam, *J. Iran. Chem. Soc.* **2016**, *14*, 843–851. DOI:10.1007/s13738-016-1037-1
12. D. Mohan, C. U. Pittman, *J. Hazard. Mater.* **2007**, *142*, 1–53. DOI:10.1016/j.jhazmat.2007.01.006
13. C. Nieto-Delgado, J. R. Rangel-Mendez, *Water Res.* **2012**, *46*, 2973–2982. DOI:10.1016/j.watres.2012.03.026
14. Q. Manzoor, R. Nadeem, M. Iqbal, R. Saeed, T. M. Ansari, *Bioresour. Technol.* **2013**, *132*, 446–452. DOI:10.1016/j.biortech.2013.01.156
15. I. D. Mall, V. C. Srivastava, N. K. Agarwal, I. M. Mishra, *Chemosphere* **2005**, *61*, 492–501. DOI:10.1016/j.chemosphere.2005.03.065
16. A. Shukla, Y.-H. Zhang, P. Dubey, J. L. Margrave, S. S. Shukla, *J. Hazard. Mater.* **2002**, *95*, 137–152. DOI:10.1016/S0304-3894(02)00089-4
17. H. Alidadi, M. Dolatabadi, M. Davoudi, F. Barjasteh-Askari, F. Jamali-Behnam, A. Hosseinzadeh, *Process Saf. Environ. Prot.* **2018**, *117*, 51–60. DOI:10.1016/j.psep.2018.04.007
18. R. Ansari, Z. Mosayebzadeh, *J. Iran. Chem. Soc.* **2010**, *7*, 339–350. DOI:10.1007/BF03246019
19. D. Božić, V. Stanković, M. Gorgievski, G. Bogdanović, R. Kovačević, *J. Hazard. Mater.* **2009**, *171*, 684–692. DOI:10.1016/j.jhazmat.2009.06.055
20. A. Prado, A. Moura, R. Andrade, I. Pescara, V. Ferreira, E. Faria, A. de Oliveira, E. Okino, L. Zara, *J. Therm. Anal. Calorim.* **2009**, *99*, 681–687. DOI:10.1007/s10973-009-0284-0
21. D. Liu, D. Sun, Y. Li, *Sep. Sci. Technol.* **2010**, *46*, 321–329. DOI:10.1080/01496395.2010.504201
22. A. Ostovan, S. Elhami, *J. Water Wastewater* **2018**, *29*, 29–37. DOI:10.22093/WWJ.2017.62973.2253
23. C. McCullagh, G. C. Saunders, *Water Res.* **2005**, *39*, 2799–2806. DOI:10.1016/j.watres.2005.04.045
24. H. Eisazadeh, *J. Appl. Polym. Sci.* **2007**, *104*, 1964–1967. DOI:10.1002/app.25904
25. M. Kumar, M. A. Khan, Z. A. AlOthman, M. R. Siddiqui, *Desalination* **2013**, *325*, 95–103. DOI:10.1016/j.desal.2013.06.022
26. M. R. Samani, S. M. Borghei, A. Olad, M. J. Chaichi, *J. Hazard. Mater.* **2010**, *184*, 248–254. DOI:10.1016/j.jhazmat.2010.08.029
27. M. Idrees, A. Razaq, A. Islam, S. Yasmeen, K. Sultana, M. H. Asif, M. Nadeem, *Synth. Met.* **2017**, *232*, 138–143. DOI:10.1016/j.synthmet.2017.08.009
28. R. Vallerio, R. Keyer, S. Grabania, M. Landis, S. Jansen, Y. Wei, *MRS Online Proceedings Library Archive* **1995**, *413*, 523–528. DOI:10.1557/PROC-413-523
29. R. Ansari, *Acta Chim. Slovenica* **2006**, *53*, 88–94.
30. H. Li, J. Zhou, X. Lu, J. Wang, S. Qu, J. Weng, B. Feng, *J. Mater. Sci. - Mater. Electron.* **2015**, *26*, 7723–7730. DOI:10.1007/s10854-015-3416-2
31. M. S. Mansour, M. E. Ossman, H. A. Farag, *Desalination* **2011**, *272*, 301–305. DOI:10.1016/j.desal.2011.01.037
32. APHA, Standard methods for the examination of water and wastewater. 21st ed.; Andesite Press: Washington DC, **2005**.
33. F. Gode, E. D. Atalay, E. Pehlivan, *J. Hazard. Mater.* **2008**, *152*, 1201–1207. DOI:10.1016/j.jhazmat.2007.07.104
34. M. Bajpai, N. Rai, S. Bajpai, *J. Appl. Polym. Sci.* **2012**, *125*, 1382–1390. DOI:10.1002/app.35289
35. P. X. Thinh, J. K. Kim, D. S. Huh, *Polymer* **2014**, *55*, 5168–5177. DOI:10.1016/j.polymer.2014.08.011
36. R. Kumar, M. Oves, T. Almeelbi, N. H. Al-Makishah, M. A. Barakat, *J. Colloid Interface Sci.* **2017**, *490*, 488–496. DOI:10.1016/j.jcis.2016.11.082
37. M. Bhaumik, R. McCrindle, A. Maity, *Chem. Eng. J.* **2013**,

- 228, 506–515. DOI:10.1016/j.cej.2013.05.026
38. N. T. Abdel-Ghani, G. A. El-Chaghaby, F. S. Helal, *Desalin. Water Treat.* **2013**, *51*, 3558–3575. DOI:10.1080/19443994.2012.750806
39. M. E. Mahmoud, N. A. Fekry, *J. Polym. Environ.* **2018**, *26*, 3858–3876. DOI:10.1007/s10924-018-1263-y
40. H. Eisazadeh, *Chin. J. Polym. Sci.* **2007**, *25*, 393–397. DOI:10.1142/S0256767907002266
41. A. Ghazali, M. Shirani, A. Semnani, V. Zare-Shahabadi, M. Nekoeinia, *J. Env. Chem. Eng.* **2018**, *6*, 3942–3950. DOI:10.1016/j.jece.2018.05.043
42. S. Chaturvedi, P. N. Dave, *Desalination* **2012**, *303*, 1–11. DOI:10.1016/j.desal.2012.07.003
43. Z. Aksu, Ü. Açikel, *Biochem. Eng. J.* **2000**, *4*, 229–238. DOI:10.1016/S1369-703X(99)00053-4
44. M. Al-Anber, Z. A. Al-Anber, *Desalination* **2008**, *225*, 70–81. DOI:10.1016/j.desal.2007.07.006
45. V. Janaki, K. Vijayaraghavan, B.-T. Oh, K.-J. Lee, K. Muthuchelian, A. Ramasamy, S. Kamala-Kannan, *Carbohydr. Polym.* **2012**, *90*, 1437–1444. DOI:10.1016/j.carbpol.2012.07.012
46. R. Ansari, W. E. Price, G. G. Wallace, *Polymer* **1996**, *37*, 917–923. DOI:10.1016/0032-3861(96)87273-9
47. Z. Hu, H. Chen, F. Ji, S. Yuan, *J. Hazard. Mater.* **2010**, *173*, 292–297. DOI:10.1016/j.jhazmat.2009.08.082
48. R. Nadeem, Q. Manzoor, M. Iqbal, J. Nisar, *J. Ind. Eng. Chem.* **2016**, *35*, 185–194. DOI:10.1016/j.jiec.2015.12.030
49. Y. Yoon, W. K. Park, T.-M. Hwang, D. H. Yoon, W. S. Yang, J.-W. Kang, *J. Hazard. Mater.* **2016**, *304*, 196–204. DOI:10.1016/j.jhazmat.2015.10.053
50. A. Dada, A. Olalekan, A. Olatunya, O. Dada, *IOSR J. Appl. Chem.* **2012**, *3*, 38–45. DOI:10.9790/5736-0313845
51. C.-H. Weng, Y.-F. Pan, *J. Hazard. Mater.* **2007**, *144*, 355–362. DOI:10.1016/j.jhazmat.2006.09.097
52. X. Chang, N. Jiang, H. Zheng, Q. He, Z. Hu, Y. Zhai, Y. Cui, *Talanta* **2007**, *71*, 38–43. DOI:10.1016/j.talanta.2006.03.012
53. M. Ghaedi, K. Niknam, A. Shokrollahi, E. Niknam, H. Ghaedi, M. Soylak, *J. Hazard. Mater.* **2008**, *158*, 131–136. DOI:10.1016/j.jhazmat.2008.01.037
54. X. Zhu, X. Chang, Y. Cui, X. Zou, D. Yang, Z. Hu, *Microchem. J.* **2007**, *86*, 189–194.
55. M. Ghaedi, K. Niknam, A. Shokrollahi, E. Niknam, H. R. Rajabi, M. Soylak, *J. Hazard. Mater.* **2008**, *155*, 121–127. DOI:10.1016/j.jhazmat.2007.11.038
56. Z. Tu, Q. He, X. Chang, Z. Hu, R. Gao, L. Zhang, Z. Li, *Anal. Chim. Acta* **2009**, *649*, 252–257. DOI:10.1016/j.aca.2009.07.042
57. M. Ghaedi, H. Tavallali, A. Shokrollahi, M. Zahedi, M. Montazerzohori, M. Soylak, *J. Hazard. Mater.* **2009**, *166*, 1441–1448. DOI:10.1016/j.jhazmat.2008.12.066
58. H. Abdolmohammad-Zadeh, M. Galeh-Assadi, S. Shabkhi-zan, H. Mousazadeh, *Arabian J. Chem.* **2016**, *9*, S587–S594. DOI:10.1016/j.arabjc.2011.07.006
59. M. Mitreva, I. Dakova, I. Karadjova, *Microchem. J.* **2017**, *132*, 238–244. DOI:10.1016/j.microc.2017.01.023

Povzetek

Cilj te raziskave je bil preučiti primernost žagovine s prevleko iz polianilina (SD/PAni) kot adsorbenta za odstranjevanje Fe(II) in/ali Fe(III) ionov iz vodnih raztopin. Raziskava je obsegala šaržne in kolonske poskuse. Pri kolonskih poskusih smo preučevali vpliv različnih eksperimentalnih parametrov na adsorpcijsko obnašanje Fe(II), Fe(III) in zmesi obeh ionov. Ugotovili smo, da so optimalni adsorpcijski pogoji za posamezno zvrst železa in za njuno zmes podobni. Optimalne vrednosti so bile: pH 4,0; pretok 5,0 mL min⁻¹; temperatura 25 °C in velikost delcev adsorbenta 100 BSS mesh. Za študijo adsorpcijskih izoterm pri sobni temperaturi smo izvedli šaržne eksperimente. Rezultati so pokazali, da se adsorpcijski izotermi za obe zvrsti železa najbolje prilegajo večplastnemu adsorpcijskemu izotermnemu modelu. Preverili smo tudi stabilnost adsorbenta pri ponovitvah adsorpcije–desorpcije ter ugotovili, da je stabilen 5 ciklov.



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