

Fe(III) SORPTION FROM AQUEOUS SOLUTIONS ON CHITOSAN

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Abstract. The present work aims to use chitosan in Fe(III) removal from aqueous solutions and evaluates their sorption capacity. Experiments were carried out as function of contact time, agitation rate, pH and the concentration Fe(III) ions in initial solution. The Langmuir and Freundlich adsorption models were applied to describe the isotherms and isotherm constants. Equilibrium data agreed very well with the Langmuir model. Results also showed that chitosan is Fe(III) favourable adsorbent.

Keywords: Fe(III) removal, chitosan, sorption, wastewaters.

AIMS AND BACKGROUND

Improper disposal of dangerous pollutants from industrial wastes is the most important global issues due its effects on environment and life. This problem is too evident in the recent years. Wastewaters containing heavy metals have noxious environmental consequences. As other elements iron can be present in different forms with different chemical behaviour, toxicity and bioavailability. For example As(III), As(V) and Cr(VI) are carcinogens, while Mn(II), Mn(VII), Cr(III), Fe(II) and Fe(III) are essential micronutrients for plants and organisms. At higher levels these micronutrients become toxic.

Iron is present in wastewaters from steel tempering, coal coking and mining industries¹. For iron removal from wastewaters many conventional methods can be applied, like: chemical precipitation, ion exchange, coagulation, solvent extraction, membrane processes, and adsorption^{2–9}. Adsorption is the most economically feasible alternative. The most common adsorbent used for the removal of metal ions from aqueous solution is activated carbon¹⁰. For the removal of heavy metals from wastewater is needed higher quality activated carbon which is obtaining with expensive costs, consequently many researches are made to obtain alterna-

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tive adsorbents. Natural materials such as zeolites, clays, waste products from industrial operations such as fly ash, coal and oxides and chitosan are considered low-cost adsorbents¹¹.

Chitosan is a derivative of N-deacetylation of chitin, a naturally occurring polysaccharide from crustacean and fungal biomass. Most interest and research have been generated by the ability of chitosan to remove metal ions from wastewaters by the process of adsorption¹². Chitosan has been successfully used for lead, vanadium, platinum, silver, cadmium, gold, mercury, chromium, zinc and copper removal from wastewaters¹³⁻²¹. Its ability to remove heavy metals from wastewaters is due to the presence on its chain of amino and hydroxyl groups which can participate in forming chelating bonds with heavy metal ions. The free electron doublet of nitrogen on amine groups is responsible for the sorption of metal cations. The protonation of amine groups in acidic solutions is responsible for the electrostatic attraction of metal anions¹.

The basic objectives of the present research were to study the adsorption mechanism of Fe(III) ions on chitosan and contribute to the understanding and modelling the equilibrium of the adsorption processes. The sorption capacity of Fe(III) was examined by varying experimental conditions such as contact time, agitation rate, pH and concentration of Fe(III) ions in initial solution. The experimental data were correlated to different kinetic and adsorption models and the corresponding parameters were determined. These parameters are considered fundamental for further studies involving the scale-up of the process for continuous studies.

EXPERIMENTAL

Samples of chitosan used in this study were purchased from Sigma Aldrich Chemie GmbH. It has a value of viscosity > 200 cP (1% in 1% acetic acid), and a concentration of total impurities ≤ 1%.

Stock solutions of 1 g/l of Fe(III) were prepared by dissolving the corresponding salt (FeCl₃•6H₂O) (Merck a.r. grade) in distilled water. From this solution, 2 stock solutions of 100 mg of Fe(III)/l and 200 mg of Fe(III)/l were prepared.

Sorption experiments were carried out by batch method by using an IKA RTC basic stirrer. The quantity of chitosan was 0.1 and 0.2 g, and the agitation rate was 550 rpm (revolutions per minute). The solution volume used was 50 ml, and the iron concentration in the solution was 100 and 200 mg/l.

Metallic ion concentration in the initial solution, and in the solution after the adsorption on chitosan, was determined by spectrophotometric method using a T90 + UV/VIS spectrometer (PG Instruments Ltd.).

Chemical composition of chitosan was determined using an ARL 9800 XP – simultaneous/sequential X-ray fluorescence spectrometer.

pH values were determined using a pH 315i Instruments and conductivity was determined using a Constant C862-multi-parameter analyser.

RESULTS AND DISCUSSION

Chitosan characteristics were determined in an authorised laboratory. Grain density (effective bulk density, g/cm³), bulk density (g/cm³), water adsorption capacity (%) and swelling capacity with humidity (%) of chitosan were evaluated. Results obtained are presented in Table 1. From this table it can be seen that chitosan samples used have a great capacity to absorb water.

Table 1. Chitosan characterisation

Properties	Units of measurement	Value	Standard
Effective bulk density	g/cm ³	0.391	SR EN 1097-6/2002
Bulk density	g/cm ³	0.229	SR EN 1097-3/2002
Water adsorption	%	WA ₂₄ = 35.53	SR EN 12087/2002 Chapter 4.3.6.1
Swelling with humidity	%	16.66	SR EN 12088/2002 Chapter 4.3

The chemical composition of chitosan presented in Table 2 indicates the presence of some metallic and non-metallic ions such as: Al, Fe, Na, Zn, Si and S. Chitosan composition was presented as oxides. Value till 100% represents carbon and hydrogen from organic composition.

Table 2. Chitosan composition

Component	Al ₂ O ₃	FeO	Na ₂ O	ZnO	Si	S
%	0.18	1.19	2.44	1.73	0.03	0.016

Variation of solution pH with iron concentration in solution was determined (Fig. 1). Figure 1 indicates the fact that pH value decreases with increasing of iron concentration in solution.

Effect of contact time on iron removal from aqueous solution. Experiments in which were used solutions with 100 mg of Fe(III)/l concentration were performed in order to determine the time influence on the iron removal by chitosan.

Time varied in the range of 0–360 min, solution volume used was 50 ml. Iron removal percentage by chitosan function of time is presented in Fig. 2.

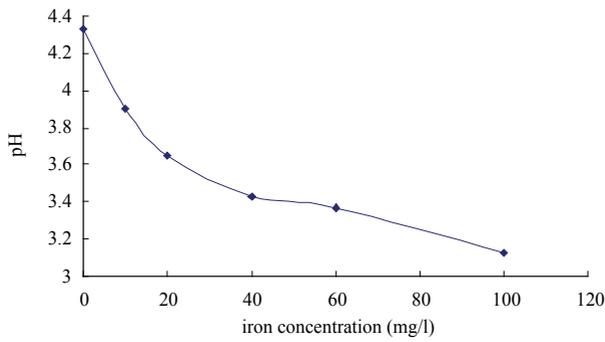


Fig. 1. pH value function of iron concentration in solution

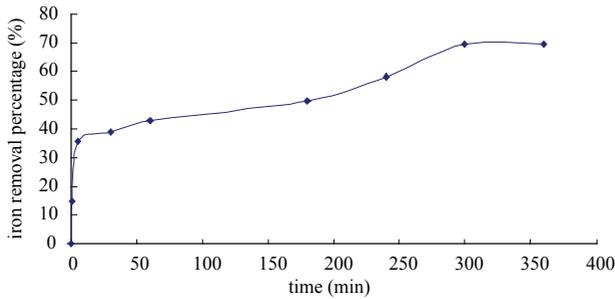


Fig. 2. Time effect on iron removal by chitosan

The percent removal of Fe(III) was calculated as follows:

$$\% \text{ removal of Fe(III)} = \frac{C_{\text{initial}} - C_{\text{final}}}{C_{\text{initial}}} \times 100 \quad (1)$$

where C_{initial} and C_{final} are the initial and final Fe(III) concentrations, respectively.

From this figure it can be seen that the iron removal percentage increases with the increasing of time and the maximum value of this percentage being 69.79%. Iron removal process is one slow process because the equilibrium was reached after 300 min.

Effect of contact time on solution of pH in iron removal process. Experiments in which were followed solution of pH and conductivity with contact time between chitosan and Fe(III) solutions were performed. Results obtained are presented in Figs 3 and 4.

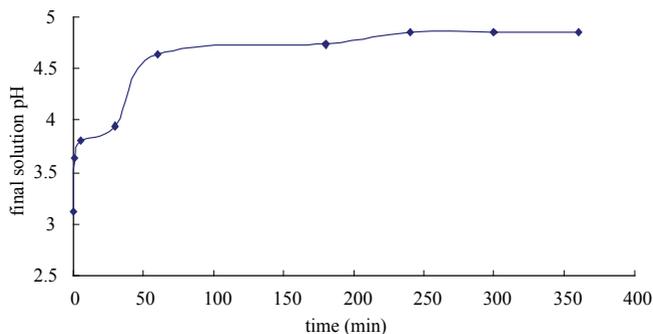


Fig. 3. Final solution pH function of contact time between chitosan and Fe(III), 100 mg/l solution

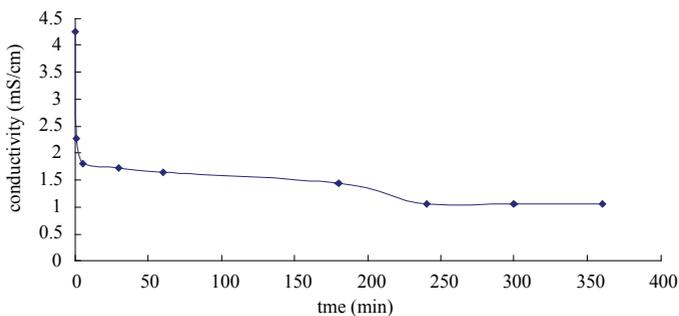


Fig. 4. Final solution conductivity function of contact time between chitosan and Fe(III), 100 mg/l solution

Variation of pH solution obtained after contact between two phases in function of contact time indicates that iron removal process by chitosan involves chemical reaction between chitosan and iron. This result is sustained by conductivity variation with the contact time.

Effect of initial concentration. Fe(III) concentration in initial solution effect to the Fe(III) removal process by chitosan was determined performing experiments in which were used aqueous solutions with concentrations: 100, 200, 300 and 400 mg/l. Solution volume used was 25 ml, contact time varied between 0 and 360 min, and rotation speed was 550 rpm.

The sorption curves of Fe(III) from aqueous solutions containing different initial concentrations are presented in Fig. 5.

It can be observed from this figure that the sorption process of Fe(III) by chitosan depends on the initial concentration of iron. Lower iron concentrations are characterised by lower Fe(III) to chitosan ratio. At higher concentrations the available sites of sorption become fewer and hence the percentage removal of Fe(III) is dependent on the initial concentration.

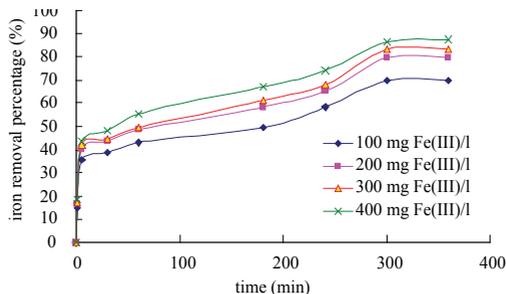


Fig. 5. Effect of initial iron concentration to the sorption Fe(III) process by chitosan

The maximum value of iron removed percentage was obtained for the solution with 400 mg of Fe(III)/l concentration, and this value is 87.5%.

Adsorption isotherms. There are many theoretical models to describe the adsorption process of heavy metal ions by sorbents. Among these models, the Langmuir and Freundlich equilibrium models have been applied in this study. Data obtained from iron retaining on chitosan are correlative with the Freundlich and Langmuir models in function of the next equations:

$$Q = K_f C_e^{1/n} \text{ (the Freundlich equation)} \quad (2)$$

or

$$Q = \frac{K_L C_e}{1 + a C_e} \text{ (the Langmuir equation)} \quad (3)$$

where Q is the adsorption capacity at equilibrium (mg g^{-1}); C_e – the equilibrium concentration of metal ion (mg l^{-1}); K_f and $1/n$ – adsorption isotherm parameters (capacity and intensity); K_L and a – the Langmuir model parameters. The next equation was obtained by logarithmation:

$$\lg Q = \lg K_f + n \lg C_e \quad (4)$$

The next equation represents the linear form of equation (3):

$$\frac{C_e}{Q} = \frac{1}{K_L} + \frac{a}{K_L} C_e \quad (5)$$

The Freundlich isotherm is an empirical expression that takes into account the heterogeneity of the surface and multilayer adsorption to the binding sites located on the surface of the sorbent.

The Langmuir model assumes a monolayer adsorption of solutes onto a surface comprised of a finite number of identical sites with homogeneous adsorption energy.

For the determination of adsorption isotherms synthetic solutions (solutions made in laboratory in order to simulate real wastewaters) with 50, 100, 200, 300 and 400 mg/l iron concentrations were used. The solution volume used was 25 ml, the chitosan quantity used was 0.1 g, the contact time was 360 min, and the temperature was $22\pm 2^\circ\text{C}$.

The adsorbed amount of Fe(III) ions per unit weight of chitosan at time t , $Q(t)$ (mg g^{-1}) was calculated from the mass balance equation as follows:

$$Q = \frac{(C_i - C_f) V}{w} \quad (6)$$

where C_i and C_f (mg/l) are the initial Fe(III) ions concentration and the Fe(III) ion concentrations at any time t , respectively; V – the volume of the Fe(III) ion solution, and w – the weight of chitosan.

The linearised Langmuir and Freundlich adsorption isotherms for Fe(III) using chitosan are shown in Figs 6 and 7. The Freundlich constants, K_F and $1/n$ are obtained from the slope and the intercept of the plot $\lg Q_e$ versus $\lg C_e$, respectively (Fig. 6), and the Langmuir constants from the slope and the intercept of the plot C_e/Q versus C_e (Fig. 7).

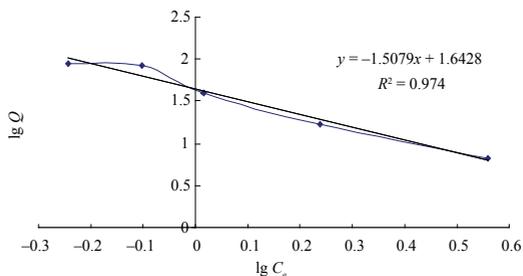


Fig. 6. The Freundlich isotherm for Fe(III) sorption by chitosan

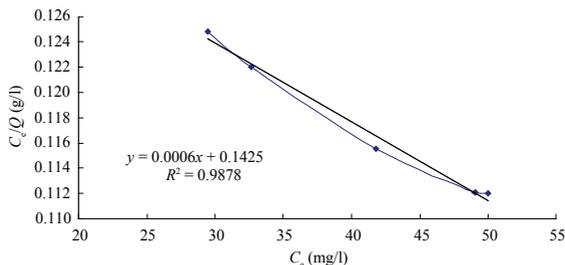


Fig. 7. The Langmuir isotherm for Fe(III) sorption by chitosan

The isotherm constants, and correlation coefficient (R^2) of these models for sorption of Fe(III) on chitosan are presented in Table 3.

Table 3. The Langmuir and Freundlich parameters for iron removal

The Freundlich parameters	The Langmuir parameters
$K_F = 43.9339$	$K_L = 7.0175$
$n = -1.5079$	$a = 4.2105 \times 10^{-3}$
$R^2 = 0.9740$	$R^2 = 0.9876$

From Figs 6 and 7 it can be seen that in case of Fe(III) adsorption on chitosan, the correlation parameter between experimental and the data obtained by the Freundlich linearised isotherm is $R^2 = 0.9740$, and for the Langmuir isotherm is $R^2 = 0.9878$. This fact leads to the conclusion that Fe(III) adsorption on chitosan may be the best described by the Langmuir isotherm:

$$Q = \frac{K_L C_e}{1 + a C_e} = \frac{7.0175 C_e}{1 + 4.2105 \times 10^{-3} C_e} \quad (7)$$

According to the Langmuir model the uptake of metal ions involves one chemical reaction.

CONCLUSIONS

The experimental results showed that the adsorption of Fe(III) by chitosan is a slow process because the equilibrium was reached after 300 min. Sorption of Fe(III) involves one chemical interaction between Fe(III) and chitosan due to the fact that solution of pH varied with the contact time between the two phases. It was shown that the sorption process of Fe(III) by chitosan depends on iron concentration in aqueous solution. The Fe(III)–chitosan system follows the Langmuir isotherm which indicates the governance of chemisorption.

The maximum removal percentage of iron by chitosan was 87.5% and this result suggests that chitosan can be successfully used in iron removal from wastewaters.

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