

Kinetics modeling and Adsorption isotherm studies for Cr(III) removal using Boehmite Nano-powder

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Abstract

Kinetics and equilibrium experiments were conducted to evaluate the adsorption characteristics of Cr (III) onto boehmite. Results show that boehmite can remove Cr (III) effectively from aqueous solution. The operating variables that have been studied were contact time, initial Cr (III) concentration, pH and adsorbent dose. Adsorption studies showed that the adsorption of Cr(III) onto boehmite is affected by changes in pH. Langmuir and Freundlich isotherms can be used to describe the adsorption equilibria of Cr(III) onto boehmite. It was found that equilibrium adsorption data more fitted Freundlich isotherm than Langmuir model. The kinetics of the adsorption was found to be fitted with pseudo second order model. The results of multiple linear regressions conducted for the second order response surface model implied that the linear effects of pH, sorbent dosage and Cr (III) concentration are more significant factors.

Keywords: Kinetics, equilibrium, Chromium, adsorption, waste water treatment, and Nano-powder

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1. Introduction

Leather is a material that has a reasonable mechanical resistance, good chemical stability and acceptable thermal behavior. This material is obtained by means of specific reactions among carboxylic groups of the protein fiber network of animal skin (collagen) and tanning reagents. The basic chromium (III) sulfate $[\text{Cr}(\text{OH})(\text{H}_2\text{O})_5\text{SO}_4]$ is a primary tanning agent widely used at the present time [1]. During the tanning process, large amounts of wastewater; sludge; and solids containing chromium, sodium, chloride and sulfate are produced. In all these wastes the chromium is present only in the trivalent form since the tanning process not generates chromium (VI) [1, 2]. Industrial wastewater containing chromium (III) has received much attention [3] due to the major environmental impact associated with the two most common chromium oxidation states, Cr(III), and Cr(VI). Chromium (VI) has greater environmental impact because soluble Cr(VI) is usually absorbed more easily and crosses body cell membranes more readily. It is therefore more toxic and more stable than chromium (III) [4]. Hafez *et al.*[5] and Chaudry *etal* .[6] reported that the chromium ions concentration in the tanning wastewater varies from 2500 to 8000 ppm and 1300 to 2500 ppm, respectively. International environmental standards require that chromium in

wastewater should not exceed 5mg L^{-1} for Cr(III) and 0.05 mg L^{-1} for Cr(VI) [5,6]. Several methods are cited in the literature for the removal of chromium (III), from wastewater. These include chemical precipitation [7], ion exchange [8,9], adsorption [10-14], membrane separation [15], and biosorption [16]. Owing to the high concentrating ability of typical adsorbents, adsorption is proved to be one of the most attractive and effective techniques to remove heavy metals from aqueous streams in water/wastewater treatment.

In recent years, the use of inorganic materials in the adsorption process as adsorbent for removing heavy metals from polluted wastewater has come to the forefront [17-19]. Inorganic materials have proved to be useful and of common use due to their low costs and high effectiveness [20]. A universal adsorbent has not been found yet, neither a perfect adsorbent for any given purpose has been developed. Recently, nanotechnology has introduced different types of nanomaterials to water industry that can have promising outcomes. Nanosorbents such as CNTs (carbon nanotubes), polymeric materials (e.g. dendrimers). Boehmite (AlOOH), which is widely used in ceramic materials, can be used in water applications [21]. However, the nano-size form of this alumina is anticipated to be more catalytically active than its presently more commonly used forms and if indeed sorption is the key mechanism, then the substantial increase

in surface area of the nano form would increase capacities very significantly. There is therefore scope for development of such nano-boehmite materials for sorption of pollutants. Boehmite was thought to exist under two distinct forms, well-crystallized boehmite and pseudoboehmite with significantly different morphologies, porosity and surface areas but it was found that pseudoboehmite is simply micro- or rather nano-crystallized boehmite [22]. Thus, boehmite was selected as a model adsorbent because it possesses well-defined properties and has been extensively utilized as a representative aluminum oxyhydroxide phase (α -AlOOH) [23]. This aim of this work is to study the possibility of using Boehmite nanopowder for removal of trivalent chromium Cr(III) from waste water and study the variables that affecting the removal process such as; initial concentration, pH, and weight of adsorbent. Additionally some of the kinetic were determined to interpret and elucidate how the adsorption mechanism of chromium ions works.

2. Materials and Methods

2.1. Adsorbent preparation

Aluminum nitrate {Al (NO₃)₃·9H₂O, 99.5%} (Aldrich), sodium hydroxide solution {NaOH, 98%} (Junsei) and deionized water were used as starting chemicals. Aluminum nitrate {Al (NO₃)₃·9H₂O, 99.5%} was dissolved into distilled water (200ml). 2 Sodium hydroxide solution was added to the aluminum nitrate solution (2mol/l) drop by drop to precipitate Al cations in the form of hydroxides. A white precipitate was obtained under various pH values (4.5-10). After stirring at (500 rpm) for 20h at room temperature, the gelatinous solution was filtered and the filter cake was heated at 200°C for 20h. The filtered cake finally washed with water first (three times) followed by ethanol (one time) to avoid contamination of Na ions; and air dried at room temperature. The air dried precipitate was calcinated in a programmable furnace at 550 °C with heating rate of 2°C/min for 5 h to produce nano-sized γ -Al₂O₃ nanopowder.

2.2. Batch experiments

Adsorption experiments were carried out in batch mode by mixing (0.1-0.5 g) of boehmite, various pH (4-9) and 20mL of chromium solution (-conc. 4000 -10000 ppm) in closed vials, continuously shaking at different time intervals to attain equilibrium. The amount of solute adsorbed per unit gram of adsorbent q_e (mg/g), was evaluated from the equation:

$$q_e = (V(C_0 - C_e))/M \quad (1)$$

Where; V is the volume of the solution (in l), C_0 is the initial concentration of the adsorbate solution (mg/l), C_e is the concentration of the solute in the bulk phase at equilibrium (mg/l) and M is the mass of the adsorbent (mg).

3. Results and discussion

3.1. Characterization of boehmite

A scanning electron microscope (SEM) by Jeol JSM-6360 LA was used to examine the surface of the adsorbent. Fig. 1 shows porous morphology of the adsorbent

with pores of different sizes. The prepared nano structured alumina has obtained by the line fitting method with Origin program. The size of these nanocrystallinities ranged from 11 to 21 nm.

X-ray diffraction patterns showed that boehmite was obtained in the synthesized samples. This synthesis produces a fine white powder of nano crystalline boehmite. The X-ray diffraction pattern of the synthesized boehmite sample is shown in Fig. 2. According to this synthesis, the boehmite sample showed a typical boehmite type pattern when the compound compared with the Shimadzu XRD-7000 card in the conventional way. The presence of sharp and intense lines at low values of 2θ angles and less intense and fairly asymmetric lines at higher angular values, shows a moderate broadening of the lines due to crystallite size (100-300 Å).

3.2. Effect of contact time

In order to establish equilibration time for maximum uptake and to know the kinetics of adsorption process, the adsorption of Cr(III) on boehmite nanopowder as adsorbent was studied as a function of contact time. Fig. 3 shows that the rate of uptake of the Cr(III) is rapid in the beginning and 50% adsorption is completed within 20 min. and the time required for equilibrium adsorption is 70 min. The effect of concentration on the equilibration time was also investigated as a function of initial Cr(III) concentration and the results are shown in Fig. 3. It was found that time of equilibrium is independent of initial concentration.

3.3 Effect of pH

pH is an important parameter that affects the adsorption of metal ions. A set of experiments was conducted to determine the optimum pH for Cr (III) removal. It was reported from previous studies that the pH_{zpc} (point of zero charge) of boehmite equal (8.4) [21] and at lower pH values than this value the boehmite surface is positively charged and is suitable for anions adsorption while the reverse takes place at higher pH values In this study, the pH was varied from 4-9 to determine the optimum value for Cr (III) adsorption on boehmite. The results are shown in Fig.4. It was found that by increasing the pH values from 2 to 8.4 the electrostatic repulsion between Cr (III) and boehmite surface increased so the adsorption is negligible until reach a pH value of (8.4) and at pH higher than 8.4 the adsorption and precipitation of Cr(III) on the solid surface took place and that was clearly shown through the SEM Fig. (5-a, 5-b). So negligible adsorption occurs at a high acidic pH values and a sharp increase in removal in alkaline media due to adsorption and precipitation of Cr(III). Therefore, for anionic chemical species, adsorption decreased when alkaline media is increased [22]. So, it would be expected that the maximum adsorption of chromium ions could occur at higher acid pH values, because, at initial acid media the chromium ions form negatively charged hydrolyzed species. Both adsorption and precipitation of Cr (III) takes place and therefore the % removal is higher than the other points. The adsorption of the studied metal cation increased as pH increases and recorded its minimum values at acidic pH. This can be justified on the basis that at lower pH values, the H⁺ ions compete with the metal cation for the adsorption sites in the

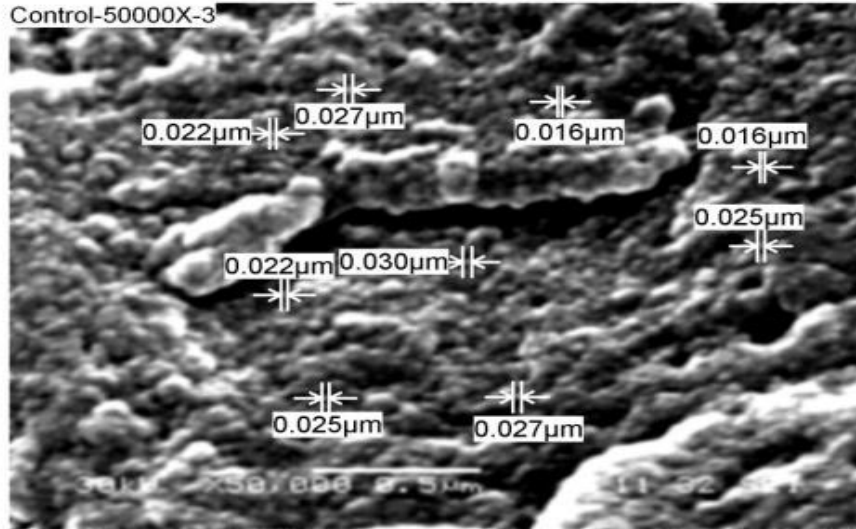


Fig. 1. The SEM scans of boehmite nano powder before adsorption

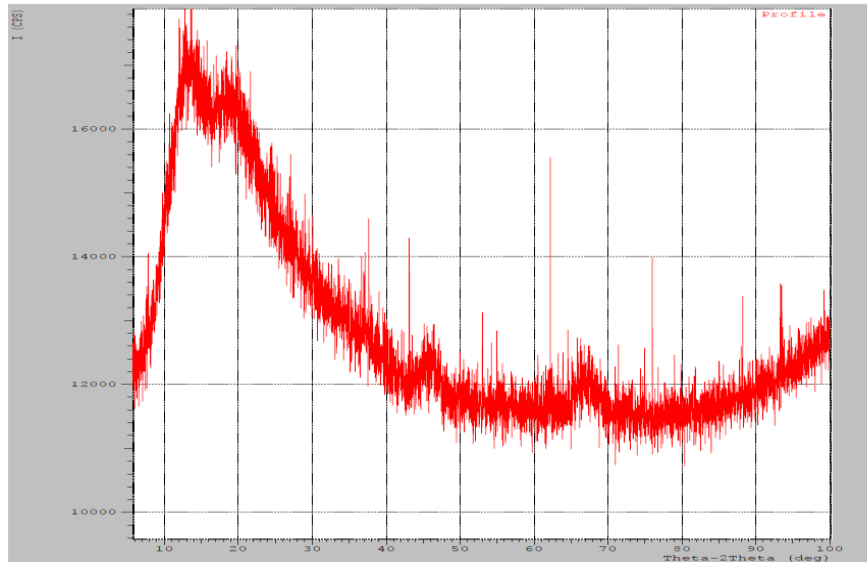


Fig. 2. X-ray diffraction (XRD) pattern of the synthesis boehmite sample

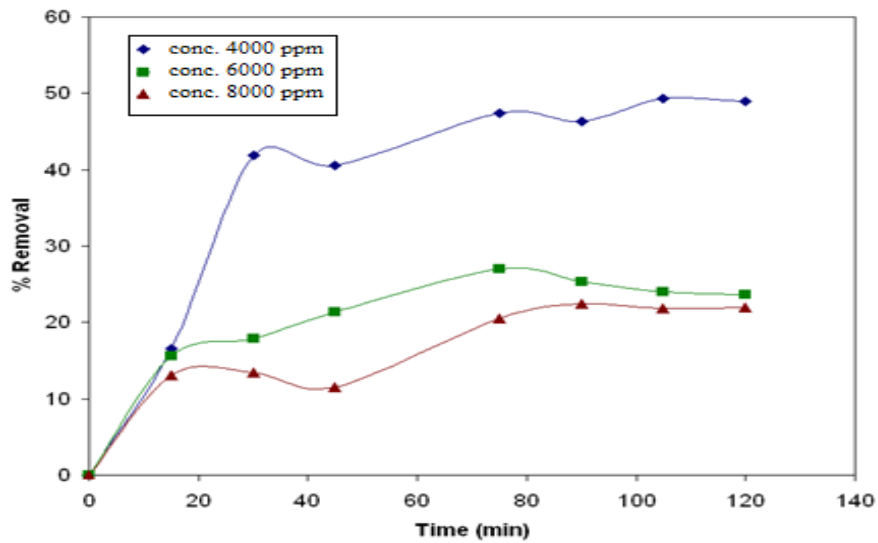


Fig. 3. Effect of Contact time on % Removal of Cr(III) at different concentrations

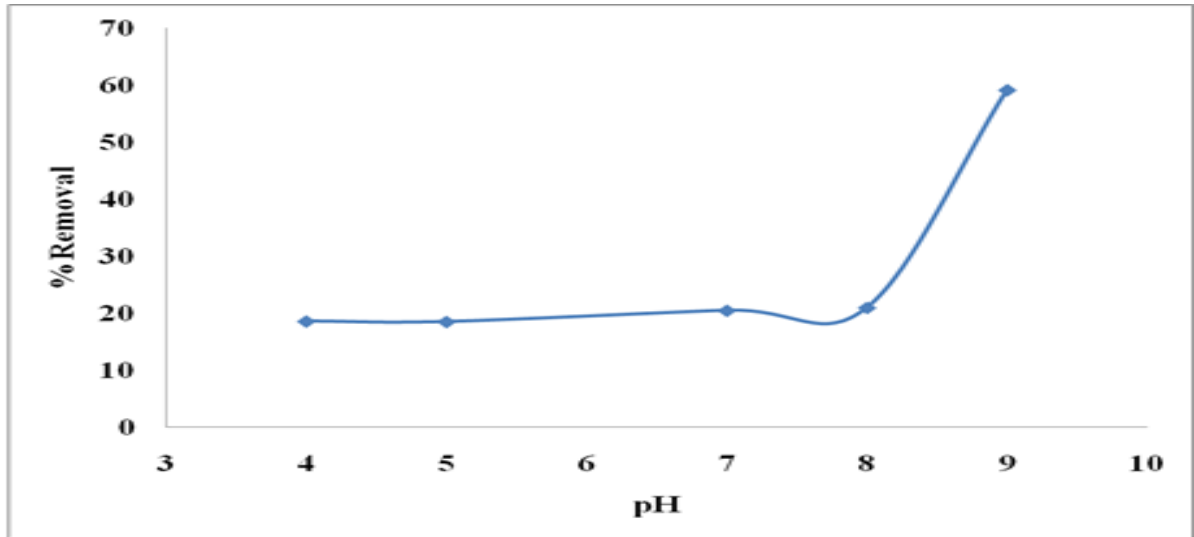


Fig. 4. Effect of pH on % removal for Cr(III) at different weight of adsorbent.

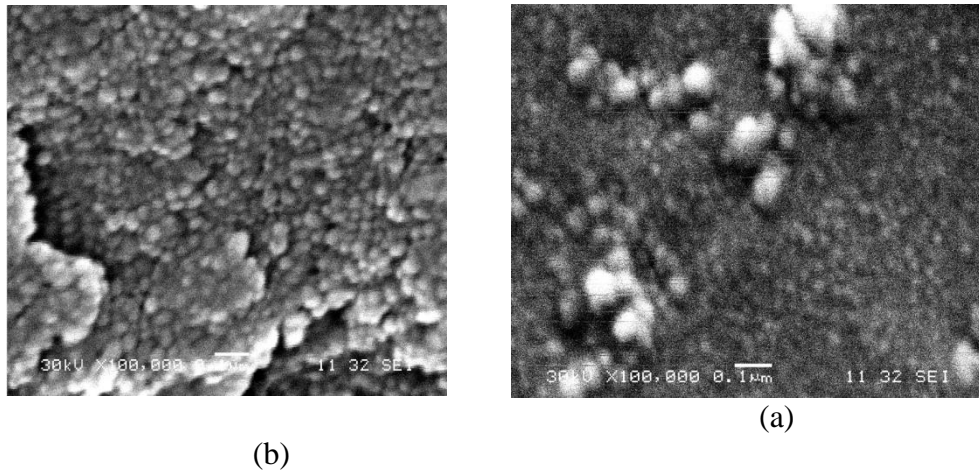


Fig. 5. The scan of boehmite after adsorption. (a) At pH = 4, (b) at pH = 9

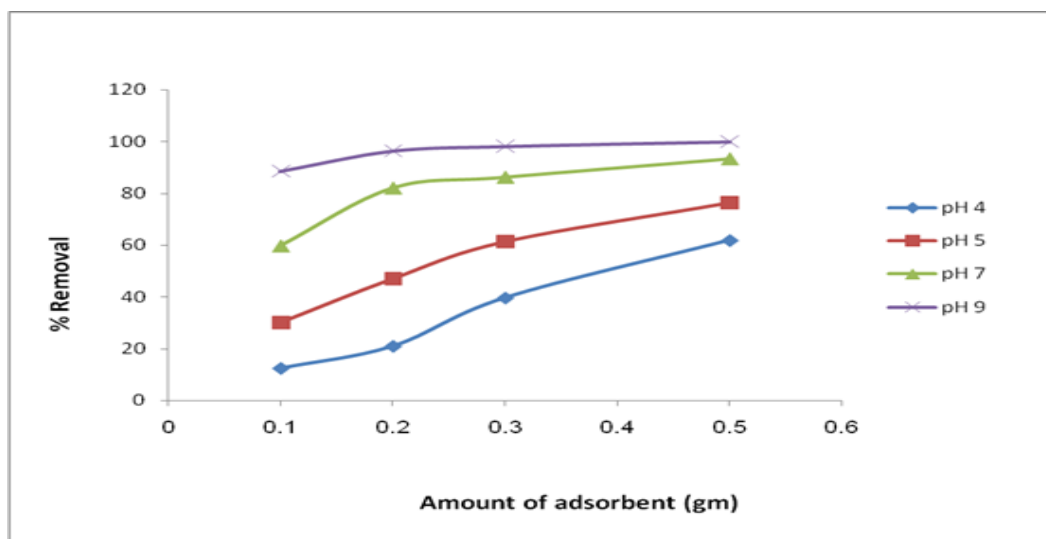


Fig. 6. Effect of changing the amount of adsorbent on % removal for Cr(III) at different pH

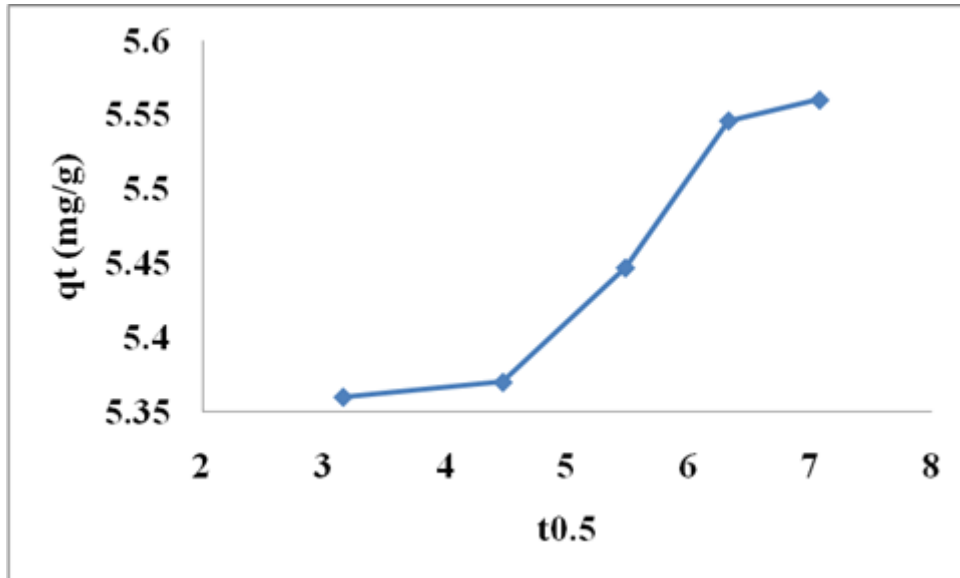


Fig.7. Intraparticle diffusion model

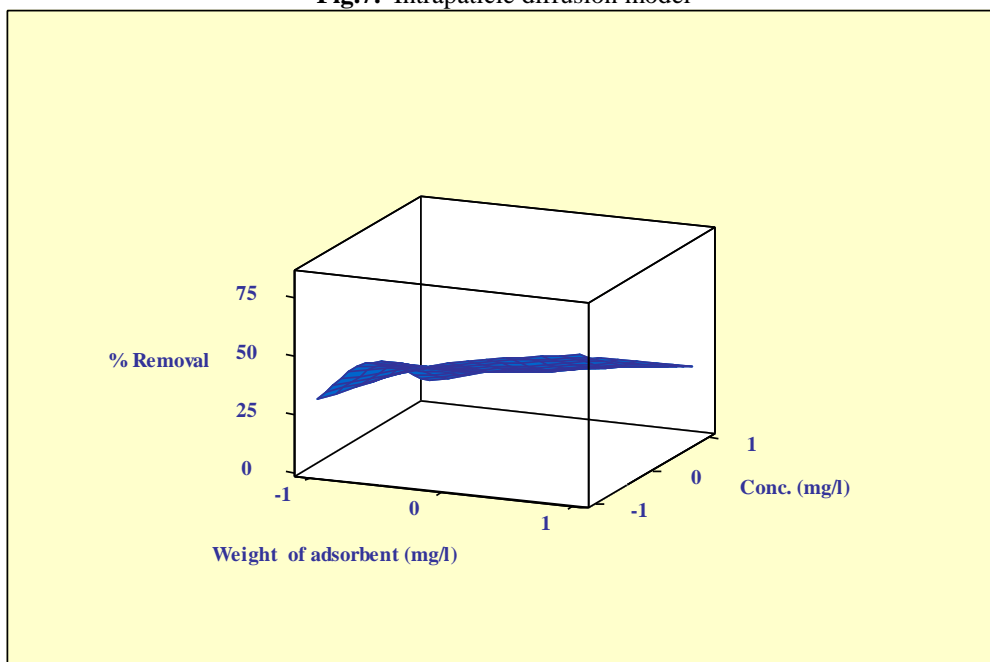


Fig. 8. Surface response of % Removal vs. Conc. And weight of adsorbent

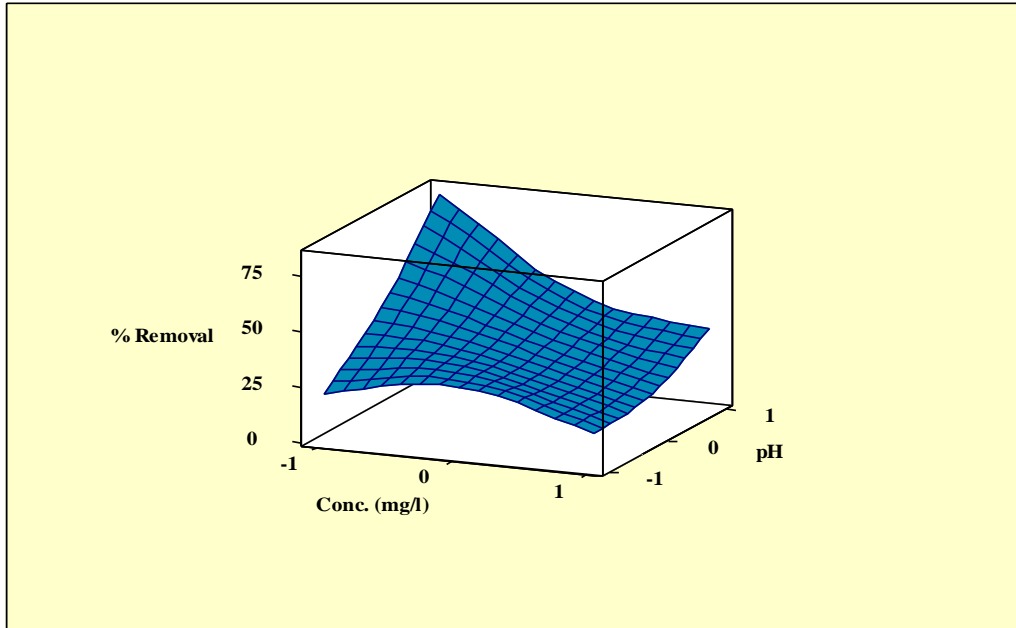


Fig. 9. Surface Plot of % Removal vs pH and Conc.

Table 1: Langmuir and Freundlich isotherm constants for adsorption of Cr(III) onto boehmite

Isotherm model	Value of constants
Langmuir	
Q_m (mg/g)	200
K_a (l/mg)	3.8×10^{-3}
R^2	0.78
Freundlich	
KF	2.1727
1/n	0.702
R^2	0.980

Table 2: Kinetic models parameters by linear regression method for the sorption of Cr(III) by boehmite at 6000 ppm initial Cr(III) concentration

kinetic model	R^2	Parameters
1) Elovich	0.839	$\beta=0.136\text{g/mg}$ $\alpha=7.353\text{mg/g.min}$
2) Fractional power	0.8412	$K=5.03\text{mg/g.min}^v$ $v=0.0249$
3) Zero Order	0.9318	$q_e=5.28\text{mg/g}$ $K_0=-0.0058\text{mg/g.min}$
4) First Order	0.926	$q_e=1.66\text{mg/g}$ $K_1=-0.0011\text{min}^{-1}$
6) Second Order	0.932	$q_e=5.288\text{mg/g}$ $K_{2p}=-0.002\text{g/mg.min}$
7) Pseudo-second order		
Type (I)	0.9998	$q_e=5.637\text{mg/g}$ $K_{2p}=0.2282\text{g/mg.min}$
Type(II)	0.672	$q_e=5.565\text{mg/g}$ $K_{2p}=0.404\text{g/mg.min}$
Type (III)	0.663	$q_e=5.567\text{mg/g}$ $K_{2p}=0.402\text{g/mg.min}$
Type (IV)	0.663	$q_e=5.562\text{mg/g}$ $K_{2p}=0.264\text{g/mg.min}$

Table 3: Experimental range and levels of independent process variables

Independent variable	Range and level		
	-1	0	1
pH (A)	3	5	7
Cr(III) concentration (C) mg/l	6000	8000	10000
Sorbent dosage (B) g/l	0.4	0.8	1.2

Table 4: Analysis of variance (ANOVA) for response surface quadratic model

Predictor	Coef	SE Coef	T	P
Constant	32.530	5.001	6.50	0.001
A	13.591	3.228	4.21	0.008
B	-13.131	3.481	-3.77	0.013
C	8.518	3.481	2.45	0.058
A*B	-10.677	4.566	-2.34	0.066
A*C	1.960	4.566	0.43	0.686
C*B	-3.840	5.255	-0.73	0.498

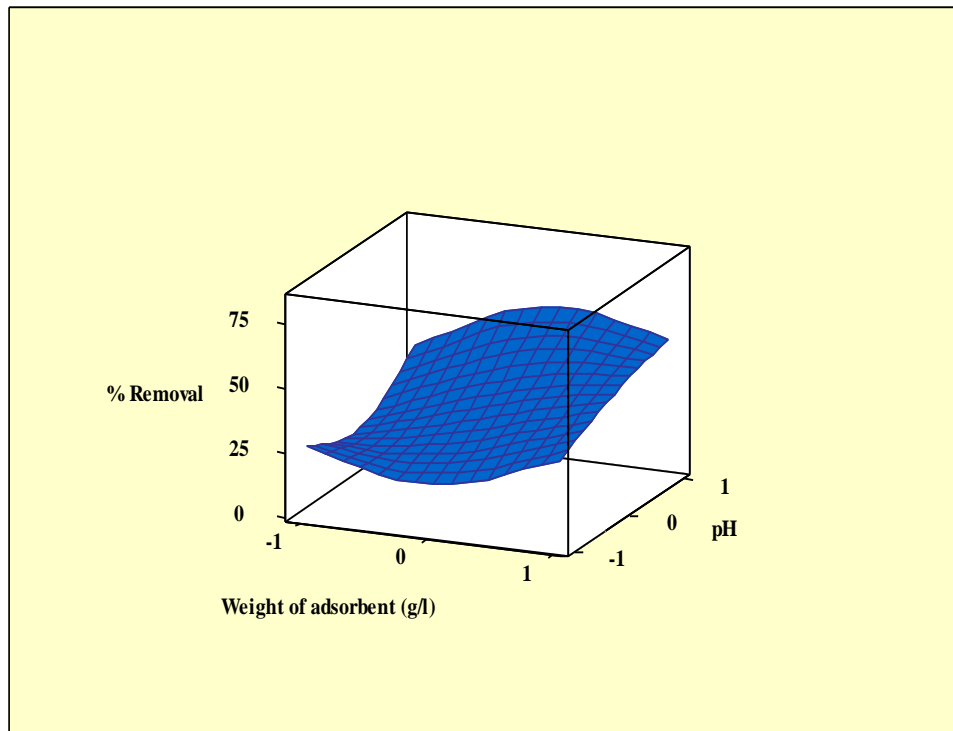


Fig. 10. Surface Plot of % Removal vs pH and weight of adsorbent

system, which in turn leads to partial releasing of the later. The heavy metal cations are completely released under extreme acidic conditions [24]. These results are in agreement with previous studies. [25-27].

3.4. Effect of amount of adsorbent

The results of the experiments with varying adsorbent dosage are presented in Fig. 6. It was found that

with an increase in the adsorbent dosage from 0.5 to 2.5 g/L, the adsorption capacity of boehmite increases from 50 mg/g to 90 mg/g at pH 7. This may be explained by the increase of adsorption sites with increasing the amount of adsorbent.

3.5. Modeling of adsorption isotherm

The analysis of the isotherm data is important to develop an equation which accurately represents the results

and could be used for design purposes. In order to investigate the adsorption isotherm, the adsorption data can be interpreted using several relationships which describe the distribution of Cr(III) between the aqueous and solid phases. In order to investigate the adsorption isotherm, the experimental data of equilibrium isotherms were interpreted using two equilibrium models; the Freundlich and the Langmuir isotherm Eqs.(2), (3). This modeling permits us to determine the maximal capacity of removal. The Langmuir isotherm predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The isotherm equation assumes that adsorption takes place at specific homogeneous sites within the adsorbent and there is no significant interaction among adsorbed species. The rate of adsorption to the surface should be proportional to a driving force, which times area. A linear expression of Langmuir equation is:

$$\frac{C_e}{q_e} = \frac{1}{K_a Q_m} + \frac{1}{Q_m} \times C_e \quad (2)$$

Where C_e is the concentration of the solute in the bulk phase at equilibrium (mg/l), q_e is the amount of solute adsorbed per unit gram of adsorbent (mg/g), Q_m is the maximum adsorption capacity (mg/g); K_a is adsorption equilibrium constant (l/mg). A plot of specific sorption (C_e/q_e) versus C_e gives a straight line of slope ($1/Q_m$) and intercepts ($1/Q_m K_a$). The values of Q_m and K_a can be calculated from the slope and intercept of the plot of C_e/q_e versus C_e . Freundlich isotherm describes the adsorption equation for non-ideal adsorption that involves heterogeneous adsorption. This empirical isotherm is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \quad (3)$$

The equation is conveniently used in the linear form by taking the logarithm of both sides as

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

Freundlich constants, K_F and $1/n$, are related to adsorption capacity and intensity of adsorption, respectively. The values of n and K_F can be calculated from the slope and intercept of the plot of $\log q_e$ versus $\log C_e$ derived from Eq. (4). The magnitude of the exponent $1/n$ gives an indication of the favorability of adsorption. A comparison of correlation coefficients for the isotherms is listed in Table 1. The correlation coefficient, R^2 , for the Freundlich isotherm is greater than that for the Langmuir isotherm. It is clear that the Freundlich isotherm has best fitted for the adsorption data of Cr (III) onto Boehmite. Freundlich plots have high linearity (>0.980) which indicate that the process conformed to the empirical Freundlich pattern of adsorption on non-specific, energetically non-uniform, heterogeneous surface in terms of functional groups.

3.7. Kinetics of adsorption

Kinetics of adsorption is one of the most important characteristics to be responsible for the efficiency of adsorption. The adsorbate can be transferred from the solution phase to the surface of the adsorbent in several steps and one or any combination of which can be the rate-controlling

mechanism: (i) mass transfer across the external boundary layer film of liquid surrounding the outside of the particle; (ii) diffusion of the adsorbate molecules to an adsorption site either by a pore diffusion process through the liquid filled pores or by a solid surface diffusion mechanism; and (iii) adsorption (physical or chemical) at a site on the surface (internal or external) and this step is often assumed to be extremely rapid.

The overall adsorption can occur through one or more steps. In order to investigate the mechanism of process and potential rate controlling steps, the experimental kinetic data for the uptake of Cr(III) at different initial concentration which modeled by different kinetic models as follows First order model which expressed as follows;

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303} t \quad (5)$$

Pseudo first order model;

$$\ln(q_e - q_t) = \ln(q_e) - k_1 t \quad (6)$$

Second order model;

$$\frac{1}{q_t} = \frac{1}{q_e} + k_2 t \quad (7)$$

While the pseudo second order can be modeled by different forms as follows:

$$\text{Type (I)} \quad \frac{t}{q_t} = \frac{1}{k_{2p} q_e^2} + \frac{t}{q_e} \quad (8)$$

$$\text{Type (II)} \quad \frac{1}{q_t} = \left(\frac{1}{k_{2p} q_e^2} \right) \left(\frac{1}{t} \right) + \frac{1}{q_e} \quad (9)$$

$$\text{Type (III)} \quad q_t = q_e - \left(\frac{1}{k_{2p} q_e} \right) \frac{q_t}{t} \quad (10)$$

$$\text{Type (IV)} \quad \frac{q_t}{t} = k_{2p} q_e^2 - k_{2p} q_e q_t \quad (11)$$

The Elovich equation is generally expressed as follows:

$$q_t = \beta \ln(\alpha\beta) + \beta \ln t \quad (12)$$

The fractional power model can be expressed as follows

$$\ln q_t = \ln k + \nu \ln t \quad (13)$$

The zero order models expressed as:

$$q_t = q_e - k_0 t \quad (14)$$

A comparison of the rate constants, calculated and experimental q_e values with the correlation coefficients for different Cr(III) concentrations and for the different kinetic models are presented in Table 2. The calculated q_e values agree very well with the experimental data in the case of pseudo-second-order kinetics. According to the pseudo-second-order model, the adsorption rates become very fast and the equilibrium times are short, which are confirmed by the experimental results.

The Lagergren first-order, pseudo-second order and Elovich models cannot identify the diffusion mechanism and the kinetic results were then subjected to analyze by the intraparticle diffusion model and it may be the rate-controlling step. If this does occur, then the plot of uptake, qt , vs. square root of time, $t^{0.5}$, should be linear and if it passes through the origin then the intraparticle diffusion will be the sole rate-limiting process. In the present study, it was found

that the plots of qt vs. $t^{0.5}$ exhibited an initial linear portion followed by a plateau which occurred after 15 min for boehmite Fig. 7. Initial curved portion of the plots seems to be due to the boundary layer adsorption and the linear portion to the intraparticle diffusion, with the plateau corresponding to the equilibrium. However, neither plot passed through the origin. This indicates that although intraparticle diffusion was involved in the adsorption process, it was not the rate-controlling step. The linear regression method of least squares was used to determine the parameters of the kinetic models. The relative parameters were obtained from the plots between $[qt$ vs. $\ln t]$, $[\ln qt$ vs. $\ln t]$, $[qt$ vs. $t]$, $[\ln(qt)$ vs. $t]$, $[\ln(qe^{-qt})$ vs. $t]$, $[qt^{-1}$ vs. $t]$, $[t/qt$ vs. $t]$, $[1/qt$ vs. $1/t]$, $[qt$ vs. $qt/t]$ and $[qt/t$ vs. $qt]$, respectively.

3.8. Experimental design by RSM

A full factorial design, which includes all possible factor combinations in each of the factors, is a powerful tool for understanding complex processes for describing factor interactions in multifactor systems. RSM is an empirical statistical technique employed for multiple regression analysis by using quantitative data obtained from properly designed experiments to solve multivariate equations simultaneously. The experiments with different pH, adsorbent dosage and initial metal concentration were employed simultaneously covering the spectrum of variables for the removal of Cr (III) in the Central composite design. In order to describe the effects of pH, adsorbent dosage and initial nickel concentration on percentage removal of Cr (III) batch experiments were conducted. The coded values of the process parameters were determined by the following equation.

$$x_i = \frac{X_i - X_0}{\Delta x}$$

Where x_i - coded value of the i th variable, X_i - uncoded value of the i^{th} test variable and X_0 - uncoded value of the i th test variable at center point. The range and levels of individual variables were given in Table 1. The experiment design was given in Table 2 along with experimental data and predicted responses. The regression analysis was performed to estimate the response function as a second order polynomial

$$Y = \beta_0 + \sum_{i=1}^k X_i + \sum_{i=1}^k \beta_{ii} X_i^2 + \sum_{i=1}^{k-1} \sum_{j=2}^k \beta_{ij} X_i X_j$$

Where Y is the predicted response, β_0 , β_i , β_{ij} are coefficients estimated from regression, they represent the linear, quadratic and cross products of X_1 , X_2 and X_3 on response. A statistical program package Minitab 14, was used for regression analysis of the data obtained and to estimate the coefficient of the regression equation. The equations were validated by the statistical tests called the ANOVA analysis. *An ANOVA is an analysis of the variation present in an experiment. It is a test of the hypothesis that the variation in an experiment is no greater than that due to normal variation of.* The significance of each term in the equation is to estimate the goodness of fit in each case. The goodness of fit is examined by using the determination coefficient (R^2). The coefficient of determination (R^2) was calculated to be 0.9086.

The experimental results are analyzed through RSM to obtain an empirical model for the best response. The mathematical expression of relationship to the response with variables is shown below;

$$Y = 32.530 - 13.591*A - 13.131*B + 8.518*C - 10.677*A*B + 1.96 *A*C - 3.84*B*C - 4.378*A^2 + 0.197*B^2 + 1.259*C^2$$

Where Y is the percentage removal of Cr (III).

The results of multiple linear regressions conducted for the second order response surface model are given in Table 4. The significance of each coefficient was determined by Student's t -test and p -values, which are listed in Table 4. The larger the magnitude of the t -value and smaller the p -value, the more significant is the corresponding coefficient. In this case, A, B, C and AB are significant model terms for the sorption of Cr (III). Values greater than 0.10 indicate the model terms are not significant. This implies that the linear effects of pH, sorbent dosage and Cr (III) concentration are more significant factors.

4. Conclusion

The adsorption behavior of Cr(III) onto the boehmite nano powder from aqueous solution has been investigated in this study. The method that used to prepare boehmite nanopowder resulted in a significant increase in the specific surface area (SSA) of boehmite. Adsorption studies showed that the adsorption of Cr(III) onto boehmite is affected by changes in pH. Langmuir and Freundlich isotherms can be used to describe the adsorption equilibria of Cr(III) onto boehmite. It was found that equilibrium adsorption data more fitted Freundlich isotherm than Langmuir model. The kinetics of the adsorption was found to be fitted with pseudo second order model. The results of multiple linear regressions conducted for the second order response surface model implied that the linear effects of pH, sorbent dosage and Cr (III) concentration are more significant factors. The study presented revealed that boehmite can be a promising adsorbent for the removal of Cr(III) from tanning wastes.

References

- [1] F.H. Rutland. (1991). Environmental compatibility of chromium product wastes at land disposal sites. *Journal-American Leather Chemists Association*. 86: 364-374.
- [2] R.J. Langlais. (1991). Aluminium toxicity versus chromium toxicity: a review plus some pertinent observations. *Journal-American Leather Chemists Association*. 86: 413.
- [3] C. Kornhauser, K. Wrobel, J. M. Malacare, L.E. Nava, L. Gómez, and R. González. (2000). Possible adverse effect of chromium in occupational exposure of tannery workers. *Industrial Health*. 40 :207 – 213.
- [4] S. M. Bradberry, and J. A.Vale. (1999). Therapeutic review: Is ascorbic acid of value chromium poisoning and chromium dermatitis. *Journal of Toxicology-Clinical Toxicology*. 37: 195 –200.
- [5] A. I. Hafez, M. S. El-Manharawy and M. A. Khedr. (2002). RO membrane removal of unreacted

- chromium from spent tanning effluent. A pilot scale study, part 2. *Desalination*. 14: 237-242.
- [6] C. Ashraf, M. S. Ahmad and M.T. Malik. (1998) Supported liquid membrane technique applicability for removal of chromium from tannery wastes. *Waste Management*. 17: 211-218.
- [7] E. Abass, M. Alireza, and V. Reza. (2005) Chromium (III) Removal and Recovery from Tannery Wastewater by Precipitation Process. *American Journal of Applied Sciences Vol. (10)* 1471-1473.
- [8] M. A. S. Barros, I. F. Araújo Jr, P. A. Arroyo, E. F. Sousa-Aguiar and C. R. G. Tavares. (2003). Multi-component ion exchange isotherms in NaX zeolite. *Latin American Applied Research*. **33**: 339-344.
- [9] G. Tiravanti, D. C. Petruzzelli, R. Passino. (1997). Pretreatment of tannery wastewaters by an ion exchange process for Cr(III) removal and recovery. *Water Science and Technology*. 36: 197-207.
- [10] D. De Casto, T. N. Dantas Neto, and M. C. P. Moura. (2001). Removal of chromium from aqueous solution by diatomite treated with micro emulsion. *Water Research*. 35: 2219- 2224.
- [11] M. Ikram, M. A. Rauf, and N. Rauf. (2002). Trace level removal studies of Cr(III) from aqueous solution. *Instrumentation Science Technology*. 20: 119 - 125.
- [12] S. Dahbi, M. Azzi, N. Saib, M. Guardia, R. Faure and R. Durand. (2002). Removal of trivalent chromium from tannery wastewaters using bone charcoal. *Analytical and Bioanalytical Chemistry*. 374: 540 - 546.
- [13] B.H. Hintermeyer, N.A. Lacour, A. Pérez Padilla and E.L. Tavani. (2008). Separation of the chromium(iii) present in a tanning wastewater by means of precipitation, reverse osmosis and adsorption, *Latin American Applied Research*. 38: 63-71.
- [14] S. Debnath, U.C. Ghosh. (2008). Kinetics, isotherm and thermodynamics for Cr(III) and Cr(VI) adsorption from aqueous solutions by crystalline hydrous titanium oxide, *Journal of Chemical Thermodynamics*. 40: 67-77.
- [15] M. Aloy, and B. Vulliermet. (1998). Membrane technologies for the treatment of tannery residual floats, *Journal of Society of Leather Technologists and Chemists*. 82: 140-142
- [16] Y. S. Yun, D. Park, J. M. Park, and B. Volesky. (2001). Biosorption of trivalent chromium on the brown seaweed biomass, *Environmental Science Technology*. 35: 4353-4358.
- [17] B. J. Lafferty and R. H. Loeppert. (2005). Methyl Arsenic Adsorption and Desorption Behavior on Iron Oxides. *Environmental Science Technology*. 39: 2120.
- [18] M. Ozmen, K. Can, G. Arslan, A. Tor, Y. Cengeloglu and M. Ersoz. (2010). Adsorption of Cu(II) from aqueous solution by using modified Fe₃O₄ magnetic nanoparticles. *Desalination*. 254: 162.
- [19] Y. T. Liu, M. K. Wang, T. Y. Chen, P. N. Chiang, P. M. Huang and J. F. Lee. (2006). Arsenate Sorption on Lithium/Aluminum Layered Double Hydroxide Intercalated by Chloride and on Gibbsite: Sorption Isotherms, Envelopes, and Spectroscopic Studies. *Environment Science Technology*. 40:7784.
- [20] A. K. Bhattacharya, T. K. Naiya, S. N. Mandal, S. K. Das. (2008). Adsorption, kinetics and studies on removal of Cr(VI) from aqueous solutions using different low-cost adsorbents. *Chemical Engineering Journal*. 137: 529-541
- [21] F. Granados-Correa, J. Jime' nez-Becerril. (2009). Chromium (VI) adsorption on boehmite. *Journal of Hazardous Materials*. 162: 1178-1184.
- [22] P. Alphonse, M. Courty. (2005). Structure and thermal behavior of nanocrystalline boehmite. *Thermochimica Acta*. 425: 75-89.
- [23] F. Granados-Correa, N. G. Corral-Capulin, M. T. Olguín, C. E. Acosta-León. (2011). Comparison of the Cd(II) adsorption processes between boehmite (γ -AlOOH) and goethite (α -FeOOH). *Chemical Engineering Journal*. 171: 1027.
- [24] U. Forstner and G. T. W. Wittman. (1981). *Metal pollution in the aquatic environment*, Springer Verlag, Berlin-Heidelberg, New York. pp. 21.
- [25] A. Saied, I. Muhammed and M. Waheed Akhtar. (2005). Removal and recovery of lead(II) from single and multimetal (Cd, Cu, Ni, Zn) solutions by crop milling waste (black gram husk). *Journal of Hazardous Materials*. 117: 65-73.
- [26] S. M. Nomanbhay and K. Palanisamy. (2004) Removal of heavy metal from industrial wastewater using chitosan coated oil palm shell charcoal. *Electronic Journal of Biotechnology*. 8: 43-53.
- [27] T. C. Wang, J. C. Weissman, G. Ramesla, R. Varadarajan, and J. R. Benemann. (1998). Heavy metal binding and removal by *Phormidiu*. *Environmental Contamination Toxicology*. 60: 739-744.