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REMOVAL OF HEXAVALENT CHROMIUM
FROM AQUEOUS SOLUTION BY ADSORPTION
ON γ-ALUMINA NANOPARTICLES

The use of γ-alumina (γ-Al_2O_3) nanoparticles as adsorbent to remove Cr(VI) from aqueous solution was investigated using batch experiments. Adsorption experiments were carried out for various initial doses of Al_2O_3, initial concentrations of chromium(VI), contact times and pH. The structure and morphology of the sorbent was characterized by XRD, SEM, and TEM techniques. Results demonstrated that the removal efficiency of chromium(VI) was increased by increasing the contact time, initial concentration, and pH. The results of the study showed that adsorption of chromium by γ-alumina nanoparticles reached equilibrium after 60 min and after that a little change of chromium removal efficiency was observed. Furthermore, kinetics of chromium sorption was well fitted by pseudo-second order kinetic model, and well explained by the Freundlich isotherm ($R^2 > 0.992$). Overall, alumina nanoparticles recognized as an effective sorbent to remove chromium(VI) from aqueous solutions.

1. INTRODUCTION

Heavy metals including chromium, mercury, lead, cadmium, etc. are considered high risk for humans and animals. Generally, chromium makes its way into public sources of water by releasing from industrial effluents such as plating, tanning, metal-

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lurgical, pigment, electronic, chemical manufacturing plants, and so forth [1, 2]. Extensive use of chromium compounds by industries and discharging their effluents into the environment would have serious effects on the ecosystem and humans [3]. Under conventional oxidation states, chromium occurs in two forms: hexavalent Cr(VI) and trivalent Cr(III). Cr(VI) is toxic for most microorganisms, and can be carcinogenic for most creatures and responsible for damages of liver and kidneys in humans. However, Cr(III) is less toxic and can readily precipitate or adsorb on a variety of substances. Cr(VI) is very soluble in water and can form bivalent anions, such as chromates (CrO_4^{2-}), dichromates $(Cr_2O_7^{2-})$, and hydrogen chromates at various pH [1, 2, 4, 5].

According to the report of World Health Organization (WHO), chromium, mercury, and plumb have most health concerns. Thus in developed and some developing countries, a maximum acceptable concentrations (MAC) of these metals have been determined for treated wastewaters [6].

Some conventional techniques for removal of chromium are chemical treatment, extraction by solvents, ion exchange, adsorption, membrane filtration, electrochemical treatment technologies, biological processes [7, 8]. For instance, chemical precipitation has been used as a common method by industries [9]. However, on the one hand, most of the mentioned methods need high amounts of chemicals and energy, and on the other hand, they generate toxic sludge and wastes [2, 3]. To date, among various methods of removing heavy metals from aqueous solutions, adsorption process has been used as an efficient and cost-effective method, and as a result, varieties of different adsorbents were studied in recent years. Activated carbon is one of the most known and efficient adsorbents in the world, but its high cost has limited widespread use [4]. Some other used sorbents are clay minerals [10], organic polymers [11], metallic oxidants [12], and natural sorbents such as wheat bran [3], etc. Several inorganic materials have been examined as sorbents for the removal of Cr(VI). These materials have different specific surface areas and they are produced either in powdered and/or granulated form, depending upon their origin or preparation technique. The type of sorbents used ranged from specifically prepared materials, where manufacturing costs are high such as activated carbon, to relatively cheap, naturally occurring materials such as magnesite mineral fine particles [13]. Among modern sorbents, bilayer sorbents have attracted considerable attention due to their low cost, effectiveness, and high potential of ion exchange [4].

Metal oxides, especially iron and aluminium, are excellent sorbents for removal of anions from aqueous solutions. Negatively charged anions are sorbed on the positive charged surface of metal oxides by electrostatic attraction [14]. Alumina is a classical adsorbent and the form of γ-alumina is anticipated to be more adsorptive than α-alumina. γ-Al$_2$O$_3$ nanoparticles are a promising material as a solid phase adsorbent due to their high specific surface, reactivity, production in point of use, and potential of utilization in water remediation, mechanical strength and low temperature modification [15, 16]. However, only few reports are available in literature dealing with the

applications of nano-scale alumina for the removal of Cr(VI) from water. A number of methods such as co-precipitation, sol-gel, and thermal decomposition can be used to synthesize alumina (Al_2O_3) nanoparticles. In the present study, the sorption feasibility of nano alumina was investigated for removal of chromium from aqueous solution. The physical and chemical characterization of nano alumina was determined by scanning electron micrographs (SEM) and X-ray diffraction (XRD). Thereafter, the potential of the nano alumina for removal of chromium was evaluated.. The data from the experiments were fitted with different models to identify the adsorption mechanism.

2. EXPERIMENTAL

Instruments. Spectrometer apparatus (Perkin Elmer Lambda 25 UV/VIS spectrometer; Perkin Elmer, Norwalk, CT, USA) with 1 cm cell was used to determine Cr(VI) concentration in the solution. Jar-test apparatus was applied to agitate the solutions, and pH meter (Metrohom 827) was used to adjust pH of the samples.

Materials. Nano alumina (Al_2O_3 nano powder) was purchased from Mehregan-Sanat Ab Company (Tehran, Iran). Chromium(VI) stock solution was prepared by dissolving potassium dichromate ($K_2Cr_2O_7$) in single distilled water. Also, HCl and NaOH (1 M) were used to adjust pH. All reagent used were of GR grade.

Procedure. The study was performed in lab-scale, batch conditions, at room temperature. Sorbent morphology was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), and X-ray diffraction (XRD) techniques. Adsorption experiments were performed for various initial doses of Al_2O_3 (0.5–2 g/dm^3), initial Cr(VI) concentrations (5, 10, 15 mg/dm^3), pH (3, 5, 7, 9, 11), contact times (5–90 min). Chromium(VI) samples were prepared by dilution of the stock solution with double-distilled water at a required concentration range [6]. Then, a fixed amount of the adsorbent was added to chromium solution taken in 500 cm^3 beakers. Thereafter, the mixture was agitated with a jar-test apparatus at 160 rpm. Finally, the residual chromium concentration was determined by the diphenylcarbazide [6] method at the wavelength of 540 nm. All the experiments were performed based on standard methods.

Chromium adsorption studies. The amount of Cr(VI) adsorbed was calculated from:

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

where: q_e is the amount of adsorbed chromium (mg/g), C_0 – initial Cr(VI) concentration (mg/dm^3), C_e – equilibrium Cr(VI) concentration (mg/dm^3), V – volume of solution (dm^3), M – adsorbent weight (g).

After adjusting pHs of the chromium solutions, 0.05 g of alumina nanoparticles was added to 500 dm^3 of the solution, and after 1 h, the residual chromium was determined spectrophotometrically.

3. RESULTS AND DISCUSSION

3.1. ALUMINA NANO POWDER CHARACTERIZATION

According to the SEM analysis of nano alumina powder (Fig. 1a), it was revealed that the adsorbent does not possess porous structure. The BET surface area and apparent density of nano alumina powder were >160 m^2/g and 0.9 g/m^2, respectively.
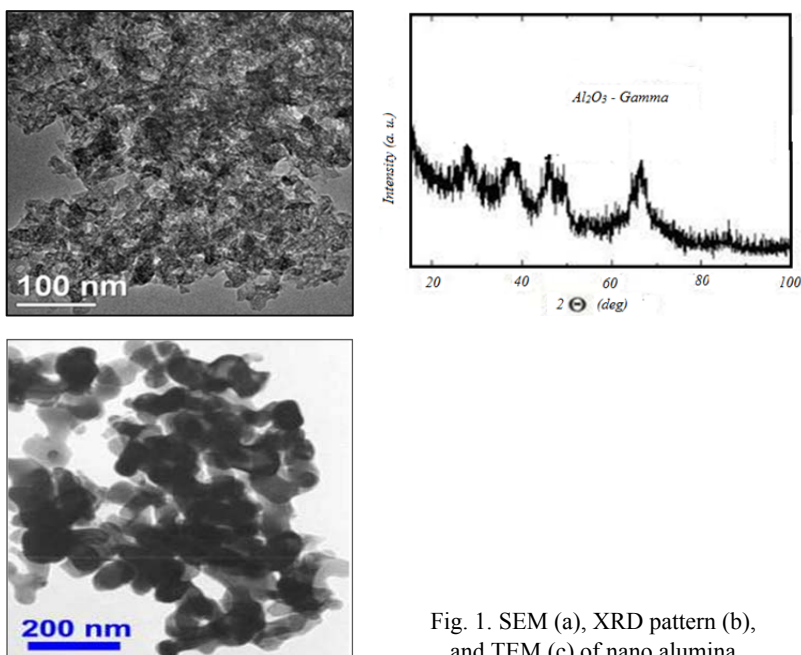
Fig. 1. SEM (a), XRD pattern (b),
and TEM (c) of nano alumina

Nano alumina phase was observed by XRD (Fig. 1b), and it confirmed the presence of γ-alumina phase. Based on the TEM images (Fig. 1c), it was revealed that alumina nanoparticles in the solution are in a spherical form and their mean diameter is 20 nm. These spherical particles have tendency to adhere together and form chains.

3.2. EFFECT OF CONTACT TIME

It was noticed that the efficiency of chromium removal increased upon the increasing contact time, and the highest removal efficiency was achieved at the beginning of the process (Fig. 2). The equilibrium was attained after 60 min.
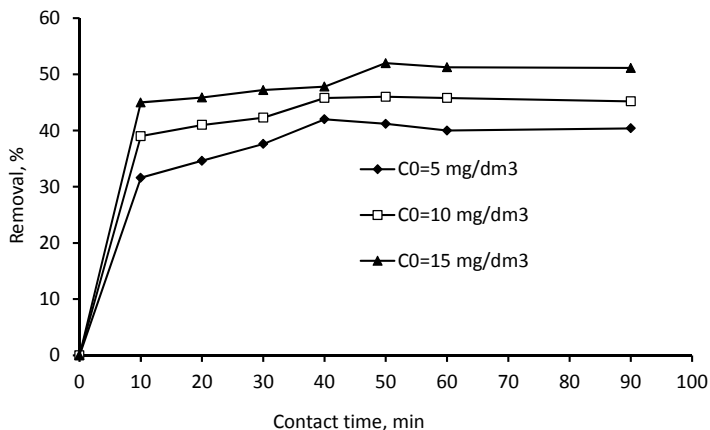
Fig. 2. Effect of contact time on removal efficiency of Cr(VI)
(adsorbent dose – 1g/dm^3, pH – 5)

The adsorption of Cr(VI) increased upon the increasing initial concentration, and adsorption equilibrium capacity (q_e) and equilibrium concentration of Cr(VI) increased as well. This phenomenon can be explained by the increase of the driving force with the increase of the initial Cr(VI) concentration. Likewise, in another study, the same results and optimum Cr(VI) removal of 87.6% by wheat bran was found for 1 h of contact time [3].

3.3. EFFECT OF INITIAL CHROMIUM CONCENTRATION AND pH

The removal efficiency of chromium in the initial concentrations of 2, 5, 10, 15, and 20 mg/dm^3 was determined as 45%, 58%, 65%, 67.4%, and 69.75%, respectively, after the contact time of 90 min, adsorbent dose 2 g/dm^3. Furthermore, the removal of chromium was increased by 24.75% after increase of the initial chromium concentration from 2 mg/dm^3 to 20 mg/dm^3 (Fig. 3) due to increase of the driving force [17]. The highest removal efficiency of chromium was attained at the initial time when the number of empty sites on the adsorbent surface is highest. Then, upon increasing time, the removal of chromium will decrease and reach a constant value [18].

The removal efficiency of chromium was increased with the increase of pH. Also, the optimum pH was 5 and after this point the removal efficiency was decreased (Fig. 4). The removal efficiencies of chromium were 36%, 48.4%, 42.4%, 33.8%, and 30.6% for pH of 3, 5, 7, 9, and 11, respectively (adsorbent dose, 1 g/dm^3, chromium concentration 5 mg/dm^3, time 90 min) This phenomenon can be explained by the increasing concentration of H$^+$ ions on the surface of the adsorbent [15].
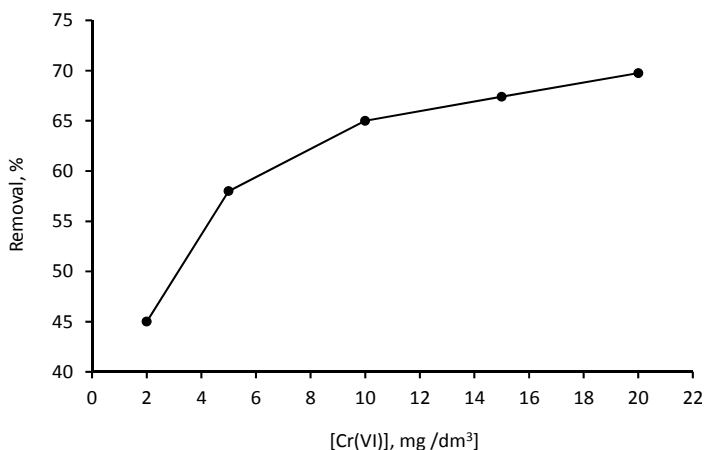
Fig. 3. Effect of initial concentration of chromium on removal efficiency;
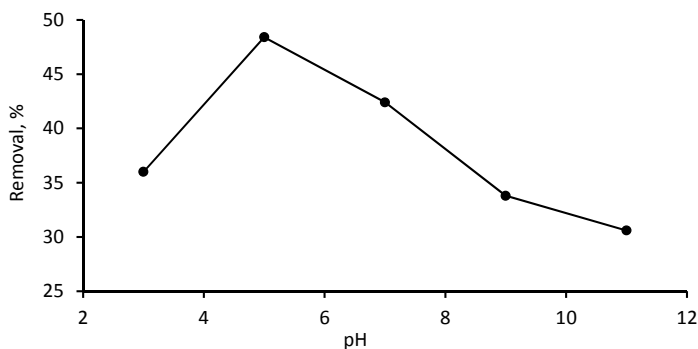adsorbent dose – 2 g/dm^3, pH – 5 and contact time – 90 min

Fig. 4. Effect of pH on removal efficiency of chromium;
adsorbent dose – 1 g/dm^3, chromium concentration – 5 mg/dm^3, contact time – 90 min

The distribution diagram of the different forms of Cr(VI) based on pH is shown in Fig. 5. As can be seen, neutral chromic acid (H$_2$CrO$_4$) molecules are dominant at pH below 2, while negatively charged ions such as CrO$_4^{2-}$, Cr$_2$O$_7^{2-}$ and HCrO$_4^{2-}$ prevail in solutions of pH above 2. Al$_2$O$_3$ particles can burden more positive charges under acidic conditions because pH of zero point of charge (pH$_{zpc}$) of Al$_2$O$_3$ particles is near 5.

It has been assumed that bimolecular reactions occur between neutral forms of H$_2$CrO$_4$ and positively charged surfaces of Al$_2$O$_3$. For solutions with pH higher than 6, it has been assumed that the neutral and negatively charged ions adsorb gradually on Al$_2$O$_3$ nanoparticle surface.
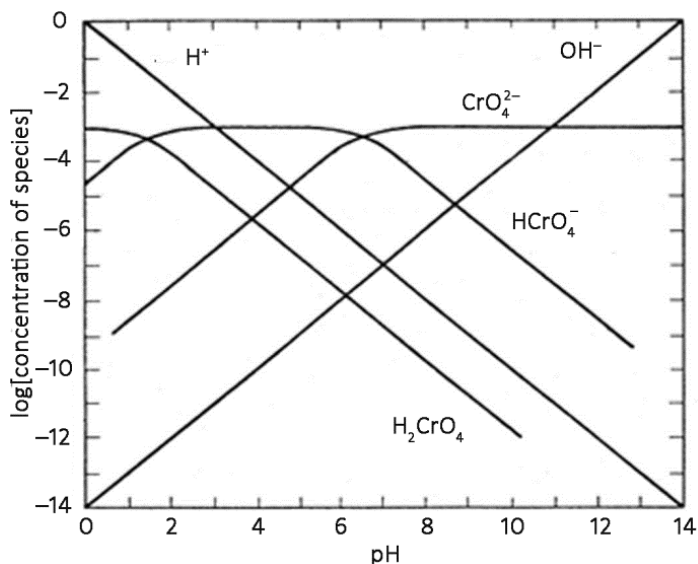
Fig. 5. pH dependent distribution of Cr(VI) ions in aqueous solution

Furthermore, from the electrostatic point of view, CrO_4^{2-}, $Cr_2O_7^{2-}$ and $HCrO_4^{2-}$ ions should be repelled from negatively charged surface groups and/or they should not have tendency to adsorb on neutrally charged surface [9]. Thus, the adsorption capacity of Cr(VI) would decrease at higher pH. Our results can be compared with the results of Li et al. [4]: 95.8–96.8% Cr(VI) adsorption was obtained on aluminum magnesium mixed hydroxide at pH of 2.5–5, and upon increasing pH over 5, the removal efficiency was decreased.

3.4. KINETIC MODELS

Adsorption kinetic studies enable determination of adsorption capacity in different times. By performing the kinetic experiments under various conditions, the influence of various factors on the adsorption rate can be determined and the rate-limiting step of adsorption as well [14]. Kinetics of the adsorption processes has been analyzed based on the following models:
- pseudo-first order kinetics:

$$\log\left(1 - \frac{q_t}{q_e}\right) = -\frac{K_1}{2.303}t$$

- pseudo-second order kinetics:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$

- modified pseudo-first order kinetics:

$$\ln\left(1 - \frac{q_t}{q_e}\right) + \frac{q_t}{q_e} = -K_m t$$
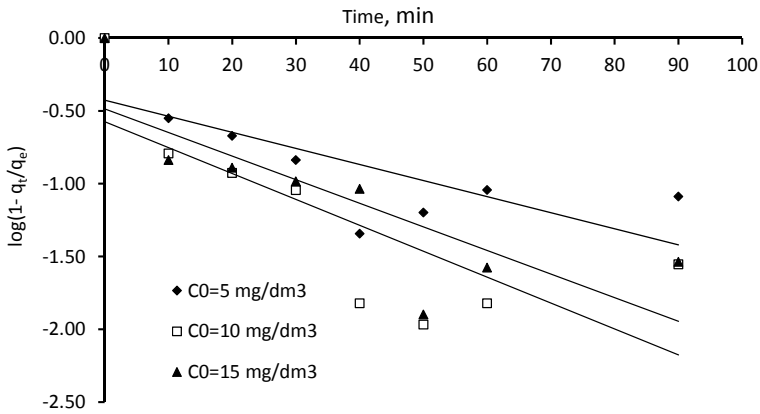

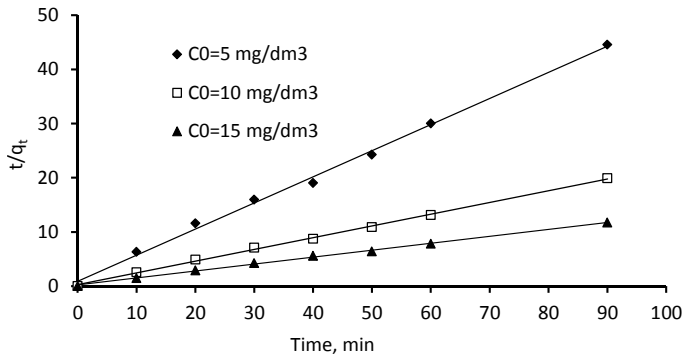Fig. 6. Fitting of experimental data to pseudo-first order equation

Fig. 7. Fitting of experimental data to pseudo-second order equation

Fitting of experimental data to pseudo-first and pseudo-second order kinetic equations is shown in Figs. 6 and 7. Parameters of the kinetic equations are given in Table 1. As seen in the table, calculations revealed that kinetics of sorption of chromium corre-

sponds to pseudo-second order kinetic model ($R^2 > 0.992$). Also, the calculated value of q_e was very close to that obtained experimentally. In contrast, for the pseudo-first order reaction, R^2 value was low and q_e differed markedly from the experimental value.

<div align="right">T a b l e 1</div>

<div align="center">Pseudo-first and pseudo-second order adsorption constants</div>

C_0 [mg/dm³]	Pseudo-first order				Pseudo-second order		
	q_e (ac)	q_e (cal)	k_1	R^2	K_2	q_e (cal)	R^2
5	2.07	2.00	0.041	0.17	0.232	2.74	0.096
10	4.46	4.69	0.062	0.305	0.046	4.63	0.998
15	7.81	8.05	0.055	0.379	0.016	7.812	0.997

3.5. ISOTHERM STUDIES

In order to investigate the effect of adsorbent mass on the removal of chromium to extract adsorption isotherms, it is necessary to perform kinetic experiments in order to find the equilibrium time. Usually, obtained data from the equilibrium experiments are known as adsorption isotherms. These data are the basic data to design adsorption systems. For this purpose, the Freundlich and Langmuir classic models were used. According to the Langmuir adsorption theory, first used to describe adsorption of gases on solid, adsorption would take place at specific homogenous sites on the surface of the adsorbent. Surface binding occurred due to physical forces, and equal affinity for the sorbate of all sites was assumed. However, the Langmuir adsorption isotherm can be used to describe equilibrium between a bulk liquid phase and a solid phase [19, 20]. Linear equation of Langmuir isotherm is expressed as

$$\frac{c_e}{q_e} = \frac{1}{q_m b} + \frac{1}{q_m} c_e \qquad (2)$$

where: q_e is the amount of adsorbed Cr(VI) on nano alumina at equilibrium (mg/g), C_e – equilibrium concentration of adsorbate in solution after adsorption (mg/g), q_m – the adsorption capacity corresponding to monolayer coverage (mg/g), b – Langmuir constant.

One of the parameters of the Langmuir equation is a non-dimensional parameter of R_L which is the coefficient of separation and can be calculated from

$$R_L = \frac{1}{\left(1 + bC_0\right)} \qquad (3)$$

By using this parameter, the type of the adsorption process can be specified. The values of R_L are given in Table 2.

Table 2

Type of adsorption depending on R_L

R_L	Adsorption process
$R_L > 1$	non-optimal
$R_L = 1$	linear
$0 < R_L < 1$	optimal
$R_L = 0$	non-reversible

The Freundlich isotherm is another used model for adsorption on amorphous surfaces. It is an empirical equation describing sorption to heterogeneous surfaces or surfaces supporting sites of varied affinities. It assumes the heterogeneity of the surface and exponential distribution of active sites and their energies. The linear form of Freundlich isotherm is expressed as [19, 20].

$$\log q_e = \log K_f + \frac{1}{n}\log C_e \qquad (4)$$

where: C_e is the equilibrium concentration of chromium in solution (mg/dm^3), q_e – adsorption capacity at the equilibrium state (mg/g), K_f and n – constants.

K_f demonstrates the adherence of adsorbate to the adsorbent, which should increase upon increasing K_f. The value of n should be 1–10 to obtain optimum adsorption [18].

In the present study, the adsorption capacity was 30.3 mg of adsorbate/g of adsorbent. Upon increasing equilibrium concentration of chromium solution, it gradually increased (Figs. 8 and 9). The main reason for this phenomenon is that the availability of adsorption sites was highest at the beginning of the process. Thus, with the increase of initial chromium concentration, the adsorption sites saturate, and no further adsorption sites for adsorption are available [14, 15]. Parameters of the both isotherm equations are given in Table 3.

Table 3

Parameters of the Freundlich and Langmuir isotherms and R^2 factors

Adsorbate	Freundlich isotherm			Langmuir isotherm			
	K_f	n	R^2	q_m [mg/g]	b [dm^3/mg]	R_L	R^2
Nano alumina	1.33	1.12	0.992	30.3	0.45	0.5	0.54

The R^2 for the Freundlich isotherm was higher than the R^2 for the Langmuir isotherm for adsorption of Cr(VI). The removal of chromium on alumina nanoparticles was better explained by the Freundlich isotherm ($R^2 > 0.992$). In addition, the value of $R_L = 0.5$ and $n = 1.2$ for the Freundlich equation (Table 3) was obtained that demonstrate the optimum adsorption of chromium on the adsorbent. As shown in Table 3, the maximum adsorption was 30.3 mg/g.
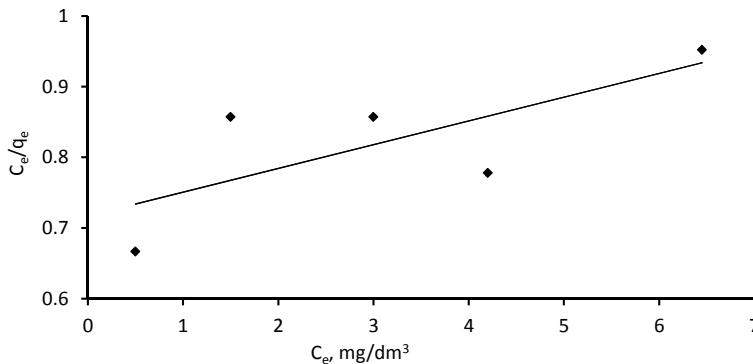

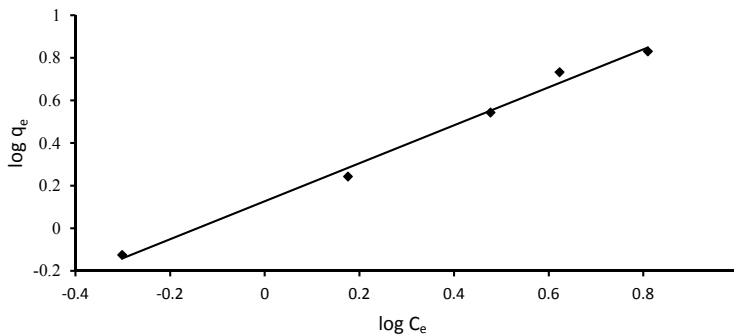Fig. 8. Langmuir isotherm model for the present study

Fig. 9. Freundlich isotherm model for the present study

Table 4

Adsorption capacities for Cr(VI) determined for various adsorbents

Adsorbent	q_m [mg/g]	Reference
Raw rice bran	0.07	[21]
Sodium hydroxide of N. crassa (ATCC 12526)	7.4	[23]
Activated carbon prepared from Terminalia arjuna nuts	28.4	[24]
Rice husks	0.6	[25]
Bagasse	0.0005	[22]

In the present study, adsorption capacity γ-Al$_2$O$_3$ has been compared with those for other adsorbents (Table 4). The q_m obtained from this study was relatively high, when compared to other studied materials, such as raw rice bran, sodium hydroxide of N. crassa (ATCC 12526), activated carbon prepared from Terminalia arjuna nuts, rice husks and bagasse. Removal of Cr by sodium hydroxide of N. crassa (ATCC 12526) has been studied and followed the Freundlich isotherm model [21]. The adsorption capacity of raw rice bran was 0.07 (mg/g), namely below that of γ-Al$_2$O$_3$ nanoparticles for Cr(VI) (30.3 mg/g). Cr removal was previously investigated using bagasse [22]. The maximum sorption capacity was 0.0005 (mg/g), namely significantly lower than those obtained in this work.

4. CONCLUSION

The removal efficiency of hexavalent chromium by γ-alumina nanoparticles was investigated. The results of this study demonstrated that the chromium removal efficiency increased with the increase of the contact time and initial concentration. In addition, the removal efficiency was improved upon the increasing pH up to 5, while in solutions with pH > 5, the removal efficiency decreased. The results of the adsorption studies revealed that the removal of chromium on the alumina nanoparticles adsorbent may be described by the Freundlich isotherm. The adsorption capacity was 30.3 mg/g. It was found that the γ-alumina nanoparticles were an effective adsorbent for removal of chromium from the aqueous solutions.

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