ASSESSMENT OF THE EFFECT OF SOME PARAMETERS ON REMOVAL OF CHROMIUM (VI) IONS FROM AQUEOUS SOLUTION USING CHITOSAN

[1]SOHEIL SOBHANARDAKANI, [2]RAZIYEH ZANDIPAK, [3]SEYED VALI HOSSEINI, [4]LIMA TAYEBI, [5]MEHRDAD CHERAGHI, [6]BAHAREH LORESTANI

[1,5,6]Department of the Environment, College of Basic Sciences, Hamedan Branch, Islamic Azad University, Hamedan, Iran,
[2]Young Researchers & Elite Club, Hamedan Branch, Islamic Azad University, Hamedan, Iran,
[3]Department of Fisheries, College of Agriculture & Natural Resources, University of Tehran, Karaj, Iran, [4]Department of the Environment, Malayer University, Malayer, Iran.
E-mail: [1]s_sobhan@iauh.ac.ir, [2]raziyeh.zandi@yahoo.com, [3]hosseinisv@ut.ac.ir, [4]lima_tayebi@yahoo.com, [5]cheraghi@iauh.ac.ir, [6]lorestani@iauh.ac.ir

Abstract- In this study Cr(VI) concentration, agitation time, amount of adsorbent and agitation speed on the adsorption process was studied. The results showed that chitosan could be employed as a low-cost material for the removal of Cr(VI) ions from aqueous solutions.

Keywords- Cr(VI) ions, Chitosan, Adsorption, Removal efficiency.

I. INTRODUCTION

The presence of heavy metals in waste and surface waters is becoming a severe environmental problem and because of their non-biodegradability, they can accumulate in the food chain posing a significant danger to human health (1). Fertilizer, fungicides, paints, pigments, batteries and metals used in manufacturing are important sources of pollution of heavy metals (2). The use of chromate and dichromate in metal plating and as corrosion control agents in cooling waters is quite extensive. Chromium occurs in two stable oxidation states, depending on the local redox conditions, Cr(III) and Cr(VI), exhibiting very different toxicological and transport characteristics. Hexavalent chromium is much more soluble and mobile in water having the ability to enter easily into living tissues or cells and thus become more toxic (3). Removal of heavy metals from waters has been a major preoccupation for many years (4,5). A number of methods have been studied for the removal of Cr(VI) ions from water, such as precipitation, coagulation, adsorption, ultrafiltration, reverse osmosis, and membrane separation (6). The disadvantage of precipitation method is production of sludge that needs further processing after precipitation. Reverse osmosis is an expensive method. Adsorption is one of the best methods reported for removing of pollutant (7).
Activated carbon is an effective and widely used adsorbent. However, its high initial cost and the need for a regeneration system make it less economically viable as an adsorbent. Recently, there is an increasing interest in the use of low-cost adsorbents, which are able to remove metallic ions from aqueous solutions (8). Chitosan is a polysaccharide obtained by deacetylation of chitin (9). Chitin is the second most abundant natural biopolymer after cellulose and the most abundant amino polysaccharide. It is found in the shells of crustaceans, shells and skeletons of mollusks and krill, on the exoskeletons of some arthropods and in the cell walls of some fungi. Both chitin and chitosan have numerous application in many fields, including biomedical, pharmaceutical, microbiological, food preservatives and environmental protection (10,11).

Chitosan is well known as an excellent adsorbent for pollutants removal because the large number of NH_2 groups. The excellent adsorption characteristics of chitosan for heavy metals can be attributed to: high hydrophilicity due to large number of hydroxyl groups of glucose units, presence of a large number of functional groups (acetamido, primary amino and/or hydroxyl groups), high chemical reactivity of these groups and flexible structure of the polymer chain (4,12). Chitosan are used in the different form of powder, flakes, beads, membranes, sponge, fibers and hollow fibers. From the literature it is clear that chitosan can be used to remove numerous trace metals (Cu(II), Pb(II), U(VI), Cr(III), Cr(VI), Ni(II), Cd(II), Zn(II), Co(II), Fe(II), Mn(II), Pt(IV), Ir(III), Pd(II), V(V) and V(IV)) from wastewater (13,14).
In the present study, chitosan was used for removal of Cr(VI) from aqueous solution. The effect of pH, initial metal concentration, contact time, agitation speed and adsorbent dose were investigated.

II. DETAILS EXPERIMENTAL

2.1. Instrumentation

A pH meter (780, Metrohm, Herisau, Switzerland), equipped with a combined Ag/AgCl glass electrode was used for pH measurements. All concentrations were measured using an inductively coupled plasma spectrometry (ICP) (Verian710-Es Australia). All the operating parameters were those recommended by the manufacturer. The optimum operating conditions and

measurement parameters for ICP are including: RF power: 1.5 kW, Carrier gas flow rate: 0.9 L min^{-1}, Makeup gas flow rate: 0.15 L min^{-1}, Integration time: 0.1 s.

2.2. Reagents and materials

Chitosan with ash: 0.55%, moisture: 5.4%, deacetylation: 88% was purchased from Sigma–Aldrich (South, Africa). All chemicals and reagents were purchased from Merck (Darmstadt, Germany). Double-distilled water was used throughout the study. Stock solution (1000 mg L^{-1}) of Cr(VI) was prepared by dissolving 2.829 g $K_2Cr_2O_7$ in 1000 ml double-distilled water. The solutions of different initial concentrations were prepared by diluting the stock solution in appropriate proportions.

2.3. Batch adsorption experiments

For batch adsorption experiments, 100 mL of Cr(VI) solution in the concentration range of 100–1000 mg L^{-1} was transferred into a 200 mL volumetric flask. After adjustment of the initial pH of the Cr(VI) solution using 0.1 mol L^{-1} HCl and/or 0.1 mol L^{-1} NaOH solutions, 4.0 g of Chitosan was added to the solution, and then the mixture was agitated using a magnetic stirrer with a the stirring speed 160 rpm for 200 min. After reaching the equilibrium the Chitosan was separated using Whatman filter paper with a diameter of 42µm, and the concentrations of the Cr(VI) which remained in the solution were determined by inductively coupled plasma spectrometry (Verian710-Es Australia).

The Cr(VI) concentrations remained in the adsorbent phase (q_e, mg g^{-1}) were calculated using the following equation;

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e are the initial and final Cr(VI) concentrations, respectively (mg L^{-1}), V the volume of the solution (L) and W is the weight (g) of the adsorbent used.

To study the effect of solution pH on Cr(VI) adsorption, experiments were examined over the pH ranges 1.0 to 12. Effect of adsorbent mass for the removal of Cr(VI) from aqueous solution was carried out using from 1.0 to 6.0 g of Chitosan for the initial Cr(VI) concentration of 100 mL of 100 mg L^{-1}.

Effect of contact time on adsorption Cr(VI) by Chitosan was investigated in contact times 25, 50, 100, 150, 200, 250, 300, 350 and 400 min. For the effect of agitation speed on adsorption process used from stirring speeds of 10, 30, 50, 70, 90, 100, 130, 160, 180, 200 and 250 rpm. Finally, the Cr(VI) ions removal efficiency (R%) was calculated by the following equation:

$$R\,(\%) = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

where: C_0 and C_e (mg L^{-1}) were the initial and final Cr(VI) concentrations (15).

III. RESULTS AND DISCUSSION

3.1. Effect of solution pH on the adsorption of Cr(VI) ions

The initial pH of Cr(VI) solution is an important factor in the adsorption process and particularly on the adsorption capacity by controlling the surface charge of the adsorbent and the degree of ionization /dissociation of the adsorbate molecule. It is well known that surface charge of adsorbent can be modified by charging the pH of the solution and the chemical species in the solution depends on this parameter. The Fig. 1 show the effect of pH on the adsorption of Cr(VI) by chitosan. The adsorption efficiency increases with an increase in the pH of the solution until an optimum pH point was reached at about pH 4.0. A decrease in the adsorption was observed with an increase in the pH after pH 4.0. At pH low, the chromium ions exists in the form of H_2CrO_4, while in the pH range of 1–6, different forms of chromium such as $Cr_2O_7^{-2}$, $HCrO_4^-$, and $Cr_3O_{10}^{-2}$ coexist while $HCrO_4^-$ predominates. As the pH increases, those form shifts to $Cr_2O_4^{-2}$ and $Cr_2O_7^{-2}$. Cr(VI) exists predominantly as $HCrO_4^-$ in aqueous solution below pH 5 and the amino groups ($–NH_2$) of chitosan would be in protonated cationic form ($–NH_3^+$) to a higher extent in acidic solution. This results in the stronger attraction for negatively charged ions. Electrostatic interaction between the adsorbent and $HCrO_4^-$ ions also contributes to the high chromium removal. However, at the pH lower than 4, decrease in uptake capacity is observed as the predomination of H_2CrO_4 and the strong competition for adsorption sites between H_2CrO_4 and protons. The decreasing of the adsorption capacity at higher pH values may be explained by the dual competition of CrO_4^{-2} and OH^- for adsorption. Thus, pH 4 was selected as the optimum pH value for the following adsorption experiment. Similar phenomenon also has been shown in the adsorption of Cr(VI) ion from water with Cu-Zn powders (3).

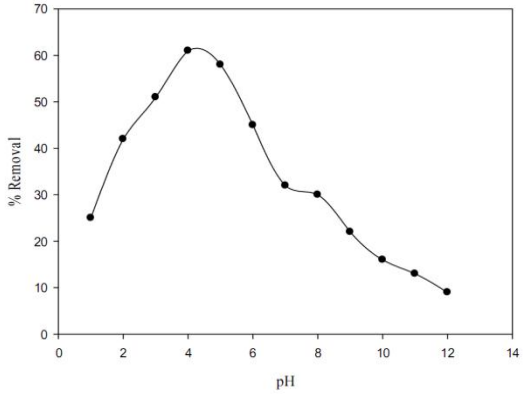


Fig. 1. Effect of solution pH on the adsorption of Cr (VI) onto chitosan.

3.2. Effect of initial metal concentration on the adsorption of Cr(VI) ions

The removal of Cr(VI) onto Chitosan as a function of their concentrations was investigated at constant

temperature (25±0.1˚C) by different the Cr(VI) concentration from 100 to 1000 mg L^{-1} while keeping all other parameters constant. The adsorption results of Cr(VI) by the Chitosan are shown in Fig. 2. As in Fig. 2 was seen, by increasing the initial concentration of Cr(VI) ions in aqueous solution, removal percentage was decreased, so that in the concentration of 100 mg L^{-1} and constant contact time, observed highest adsorption percentage and with increasing in concentration amount from 100 to 1000 mg L^{-1}, decreased adsorption percentage from 79% to 65%.

At a constant Chitosan concentration, the decrease in the adsorption percentage is probably due to the saturation of the active sites on the Chitosan surface at higher Cr(VI) concentrations. On the other hand, by increasing the initial Cr(VI) concentration the actual amount of Cr(VI) adsorbed per unit mass of the Chitosan increased. The higher initial concentration of Cr(VI) provides an important driving force to overcome the mass transfer resistance for Cr(VI) transfer between the solution and the surface of the Chitosan. Similar results were observed by Lv (2014) who investigated the effect of initial concentration of metal ions on removal of Cr(VI) from aqueous solution by Fe(II)-modified naturalzeolite and indicated that adsorption efficiency decreases with increasing initial concentration of metal (16).

3.3. Effect of contact time on adsorption of Cr(VI) ions

Equilibrium time between adsorbate and adsorbent is one of the most important parameters in the design of economical wastewater treatment systems. Fig. 4 shows effect of contact time on removal percentage of Cr(VI) onto Chitosan from solution. As can be seen that Cr(VI) removal efficiency onto Chitosan increased from 56% to 90% when contact time was increased from 25 to 200 min.

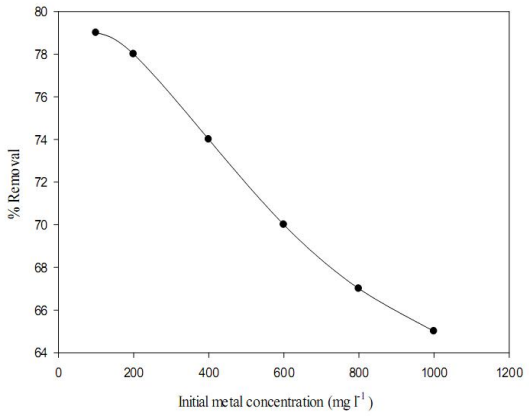


Fig. 2. Effect of initial metal concentration on the adsorption of Cr (VI) onto chitosan.

3.4. Effect of contact time on adsorption of Cr(VI) ions

Equilibrium time between adsorbate and adsorbent is one of the most important parameters in the design of economical wastewater treatment systems. Fig. 3 shows effect of contact time on removal percentage of Cr(VI) onto chitosan from solution. As can be seen that Cr(VI) removal efficiency onto chitosan increased from 56% to 90% when contact time was increased from 25 to 200 min.

A equilibrium adsorption is observed within 200 min for Cr(VI) ions, that due to the availability of large number of vacant sites. Subsequently, the less availability of the remained active sites and the decrease in the driving force lead to the slow adsorption process. Therefore optimum contact time for chitosan adsorbent was found to be 200 min for the 100 mg L^{-1} concentration. Similar results have been found by Chen et al (17).

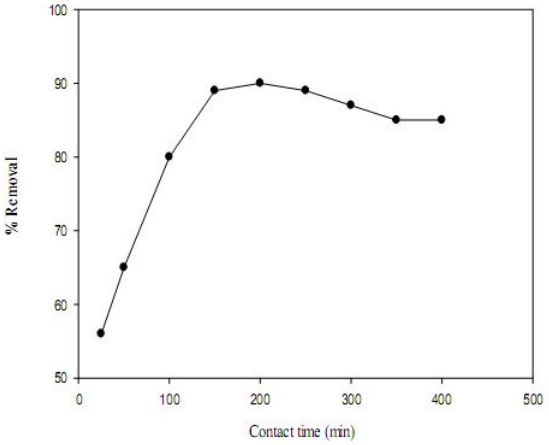


Fig. 3. Effect of contact time on adsorption of Cr(VI) ions onto chitosan.

3.5. Effect of adsorbent dose on the adsorption of Cr(VI) ions

One of the factors that strongly affect the adsorption capacity is the quantity of adsorbent dose. The dependence of the adsorption of Cr(VI) to the amount of chitosan was studied at constant temperature (25±1 ˚C) and at pH 4.0 by addition of various amount of adsorbent in the range of 1.0 to 6.0 g in contact with 100 mL solution of 100 mg L^{-1} of Cr(VI). The effect of adsorbent dose on Cr(VI) removal percentage is shown in Fig. 4.

It was observed that the removal percentage increased rapidly with the increase in the adsorbent dose till 4.0 g, and afterwards 4.0 g, the removal percentage reached almost a constant value. This can be attributed to the increase in the adsorbent vacant surface area and availability of more active adsorption sites on the chitosan surface with increasing the dose of the adsorbent. Therefore, 4.0 g adsorbent was selected for subsequent work. This results was also observed by Sheela et al. (2012), who studied the adsorption efficiency of Zn(II), Cd(II) and Hg(II) on zinc oxide nanoparticles and indicated that adsorption percentage increases with increasing adsorbent dose (18).

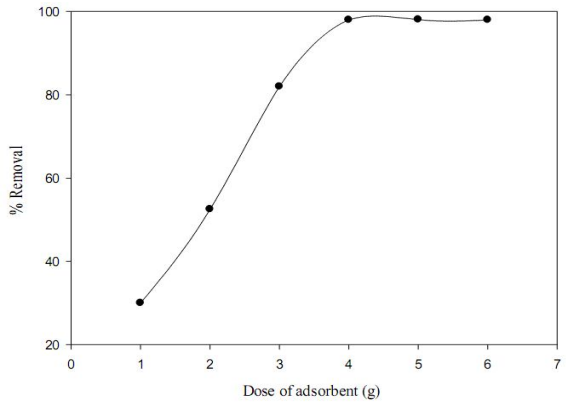


Fig. 4. Effect of adsorbent dose on the adsorption of Cr(VI) ions onto chitosan.

3.6. Effect of agitation speed on the adsorption of Cr(VI) ions

The effect of agitation speed on removal efficiency of Cr(VI) was studied by varying the speed of agitation from 10 to 250 rpm while keeping the optimum dose of adsorbents and optimum pH as constant. As can be seen from Fig. 5, the Cr(VI) removal efficient generally increased with increasing agitation speed. The Cr(VI) removal efficiency onto chitosan adsorbent increased from 12% to 87% when agitation speed increased from 10 rpm to 160 rpm and the adsorption capacity remained constant for agitation rates greater than 160 rpm. These results can be associated to the fact that the increase of the agitation speed, improves the diffusion of Cr(VI) ions towards the surface of the adsorbents. This also indicates that a shaking rate in the range 160-250 rpm is sufficient to assure that all the surface binding sites are made readily available for Cr(VI) uptake. The agitation speed of 160 rpm was selected as optimum speed. Similar results have been found by Anbia et al. 2012 (19).

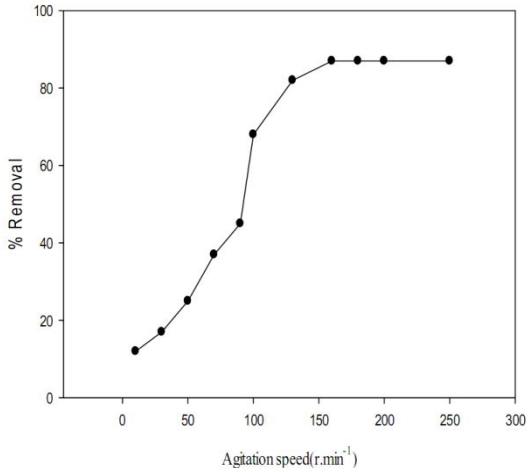


Fig. 5. Effect of agitation speed on the adsorption of Cr(VI) ions onto chitosan.

CONCLUSIONS

The present research focuses on adsorption of Cr(VI) from aqueous solution using the chitosan as an effectively adsorbent. Results of adsorption experiments revealed that removal efficiency of the Cr(VI) is strongly affected by the initial solution pH. The optimum pH for the maximum removal of Cr(VI) by chitosan was found at pH 4.0. Moreover, increasing in the initial concentration of Cr(VI) ions in aqueous solution from 100 to 1000 mg L^{-1}, lead to reduction in adsorption percentage of Cr(VI) ions from 79% to 65% by chitosan. The Cr(VI) adsorption equilibrium was attained after 200 min and by increasing agitation speed, and adsorbent dose the amount removed was increased. The results revealed that chitosan can be used as an efficient adsorbent for the rapid removal of Cr (VI) ions from water samples.

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REFRENCES

[1]. C. Chen, J. Hu, D. Shao, J. Li, and X. Wang, "Adsorption behavior of multiwall carbon nanotube/iron oxide magnetic composites for Ni (II) and Sr (II)", Journal of Hazardous Materials,vol.164, pp.923-928,2009.

[2]. S.Y. Quek, D.A.J. Wase, and C.F. Forster, "The use of sago waste for the sorption of lead and copper", Water SA,vol.24(3).pp.251-256,1998.

[3]. E. Kaprara, P. Seridou, V. Tsiamili, M. Mitrakas, G. Vourlias, I. Tsiaoussis, G. Kaimakamis, E. Pavlidou, N. Andritsos, and K. Simeonidis, "Cu-Zn powders as potential Cr(VI) adsorbents for drinking water", Journal of Hazardous Materials, vol.262, pp.606-613,2013.

[4]. J.R. Deans, and B.G. Dixon, "Uptake of Pb^{2+} and Cu^{2+} by novel biopolymers", Water Research, vol.26(4), pp.469-472,1992.

[5]. S. Sobhanardakani, H. Parvizimosaed, and E. Olyaie, "Heavy Metals Removal from Waste waters using Organic Solid Waste-Rice Husk", Environmental Science and Pollution Research, vol20,pp.5265-5271,2013.

[6]. H. Wang, X. Yuan, Y. Wu, H. Huang, G. Zeng, Y. Liu, X. Wang, N. Lin, and Y. Qi, "Adsorption characteristics and behaviors of graphene oxide for Zn(II) removal from aqueous solution", Applied Surface Science, vol.279,pp.432-440,2013.

[7]. X.S. Wang, L. Zhu, and H.J. Lu, "Surface chemical properties and adsorption of Cu (II) on nanoscale magnetite in aqueous solutions", Desalination,vol.276,pp.154-160, 2011.

[8]. Y. Kismir, and A.Z. Aroguz, "Adsorption characteristics of the hazardous dye Brilliant Green on Saklıkent mud", Chemical Engineering Journal,vol.172, pp.199-206,2011.

[9]. 9. R. Celis, M.A. Adelino, M.C. Hermosin, and J. Cornejo, "Montmorillonite–chitosan bionanocomposites as adsorbents of the herbicide clopyralid in aqueous solution and soil/water suspensions", Journal of Hazardous Materials,vol.209,pp.67-76,2012.

[10]. W.S. Wan Ngah, L.C. Teong, and M.A.K.M. Hanafiah, "Adsorption of dyes and heavy metal ions by chitosan composites: A review", Carbohydrate Polymers,vol.83,pp.1446-1456,2011.

[11]. D. Kołodynska, "Chitosan as an effective low-cost sorbent of heavy metal complexes with the polyaspartic acid", Chemical Engineering Journal,vol.173,pp.520-529, 2011.

[12]. F. Zhao, B. Yu, Z. Yue, T. Wang, X. Wen, Z. Liu, C. Zhao, "Preparation of chitosan gel beads for copper (II) ion adsorption", Journal of Hazardous Materials,vol.147,pp.67-73,2007.

[13]. S.R. Popuri, V. Vijaya, V.M. Boddu, and K. Abburi, "Adsorptive removal of copper and nickel ions from water using chitosan coated PVC beads", Bioresource Technology,vol.100,pp.194-199,2009.

[14]. W. Kaminski, and Z. Modrzewska, "Application of chitosan membranes in separation of heavy metal ions", Separation Science and Technology,vol.32,pp.2659-2668, 1997.

[15]. C. Deng, J. Liu, W. Zhou, Y.K. Zhang, K.F. Du, and Z.M. Zhao, "Fabrication of spherical cellulose/carbon tubes hybrid adsorbent anchored with welan gum polysaccharide and its potential in adsorbing methylene blue", Chemical Engineering Journal,vol.200-202,pp.452-458,2012.

[16]. G. Lv, Z. Li, W. Jiang, C. Ackley, N. Fenske, and N. Demarco, "Removal of Cr(VI) from water using Fe(II)-modified naturalzeolite", Chemical Engineering Journal,vol.92,pp.384-390,2014.

[17]. C. Chen, J. Hu, D. Shao, J. Li, and X. Wang, "Adsorption behavior of multiwall carbon nanotube/iron oxide magnetic composites for Ni(II) and Sr(II)", Journal of Hazardous Materials,vol.164,pp.923-928,2009.

[18]. T. Sheela, Y. Arthoba Nayaka, R. Viswanatha, S. Basavanna, and T.G. Venkatesha, "Kinetics and thermodynamics studies on the adsorption of Zn(II), Cd(II) and Hg(II) from aqueous solution using zinc oxide nanoparticles", Powder Technology,vol.217,pp.163-170, 2012.

[19]. M. Anbia, S. and Salehi, "Removal of acid dyes from aqueous media by adsorption onto amino functionalized nanoporous silica SBA-3, Dyes", Pigments,vol.94,pp.1-9, 2012.

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