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ORIGINAL ARTICLE

Evaluation of Removal Efficiency of Cr (VI) Ions from Aqueous Solution Using Chitosan

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KEYWORDS

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ABSTRACT: In this research, chitosan was used for the removal of Cr (VI) ions from aqueous solution. The effect of parameters like solution pH, initial Cr (VI) concentration, agitation time, amount of adsorbent and agitation speed on the adsorption process was studied. The experimental equilibrium data were analyzed by using various models such as Langmuir and Freundlich. Freundlich isotherm model fitted well with data. In addition, the experimental data was fitted to kinetic models including the pseudo-first-order and pseudo-second-order and based on calculated respective parameters such as rate constants, equilibrium adsorption capacities and correlation coefficients. The removal process follows the pseudo-second-order kinetic model. The results suggest that chitosan could be employed as a low-cost material for the removal of Cr(VI) ions from aqueous solutions.

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

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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 [poly-ß(1,4)-2-amino-2-deoxy-D-glucose], 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 applications 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 [12, 13]. 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 [14, 15].

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. Finally, the isotherm and kinetics of adsorption were evaluated.

MATERIALS AND METHODS

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.

Reagents and materials

Chitosan with ash: 0.55%, moisture: 5.4%, deacetylation: 88% was purchased from Sigma–Aldrich

(South, Africa). Figure 1 shows the structure of chitosan. 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.

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 42 µm, 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 (qe, mg g^{-1}) was calculated using the following equation;

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

Where C0 and Ce 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:

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

(2)

Where: C0 and Ce (mg L^{-1}) were the initial and final Cr (VI) concentrations [16].

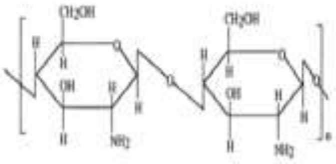

Figure 1. Chitosan structure

RESULTS AND DISCUSSION

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 Figure 2 shows 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 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].

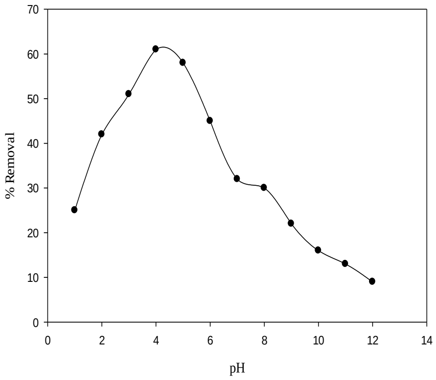

Figure 2. Effect of solution pH on the adsorption of Cr (VI) onto chitosan

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 Figure 3. 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, the highest adsorption percentage was observed and with increasing in concentration amount from 100 to 1000 mg L^{-1}, adsorption percentage decreased 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 et al. 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 [17].

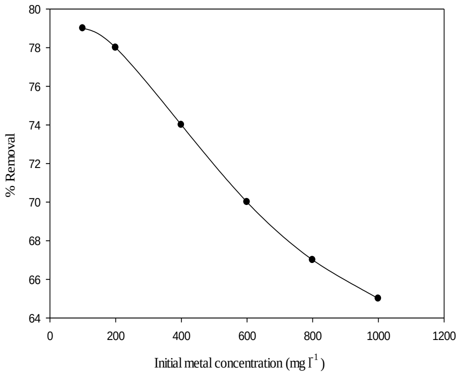

Figure 3. Effect of initial metal concentration on the adsorption of Cr (VI) onto chitosan

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. Figure 4 shows effect of contact time on removal percentage of Cr (VI) onto chitosan from solution. 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 200 min for the 100 mg L^{-1} concentration. Similar results have been found by Chen et al. [18].

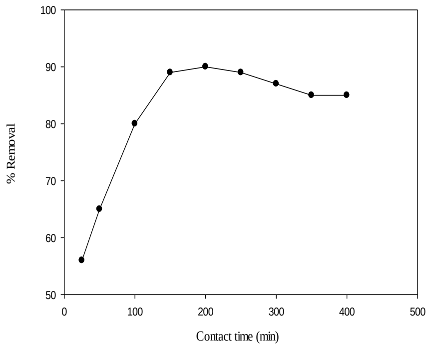

Figure 4. Effect of contact time on adsorption of Cr(VI) ions onto chitosan.

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 Figure 5. The removal percentage increased rapidly with the increase in the adsorbent dose until 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., 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 [19].

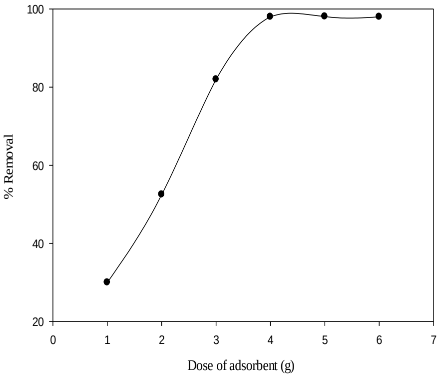

Figure 5. Effect of adsorbent dose on the adsorption of Cr(VI) ions onto chitosan.

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 Figure 6, 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. [20].

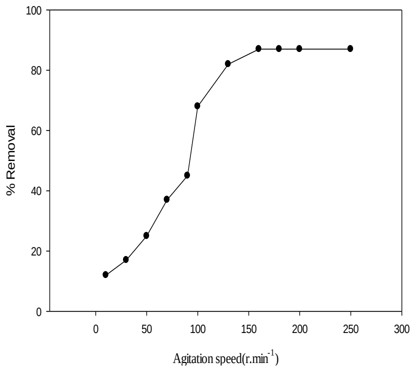

Figure 6. Effect of agitation speed on the adsorption of Cr(VI) ions onto chitosan.

Adsorption isotherm of Cr (VI) ions onto chitosan

The analysis of isotherm data is important for predicting the adsorption capacity of the adsorbent, which is one of the main parameters required for the design of an adsorption system. Adsorption of Cr (VI) ions onto chitosan were analyzed with the Langmuir and Freundlich models. The Langmuir isotherm Eq. (3) and Freundlich isotherm Eq.(4) can be written as follows [21, 22]:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m b_l} \qquad (3)$$

$$\ln q_e = \frac{1}{n}\ln C_e + \ln k_f \qquad (4)$$

where ce (mg L−1) is the equilibrium concentration of Cr (VI) ions in solution, qe (mg g^{-1}) is the equilibrium adsorption capacity of chitosan, qm (mg g^{-1}) is the maximum adsorption capacity of chitosan for monolayer coverage, b (L mg^{-1}) is a constant related to the adsorption free energy, Kf ($mg^{1-(1/n)}$ $L^{1/n\ g-1}$) is a constant related to adsorption capacity, and n is an empirical parameter related to adsorption. Table 1 showed the values of Langmuir and Freundlich constants, and the correlation coefficients R^2 obtained from the linear regression (Figure 7a, b). The higher correlation coefficient for Freundlich model indicate that the Freundlich model fitted the adsorption data better than the Langmuir model and demonstrates that a multilayer adsorption process has taken place on the surface of the chitosan. Value of n >1 for Cr (VI) ions indicates a heterogeneous nature of adsorption.

Finally, the maximum adsorption capacity, qm, of the prepared chitosan was compared with the corresponding values of other reported adsorbents. The results are presented in Table 2. The qm of chitosan was found to be 58.8 mg g^{-1} for Cr (VI).

Table 1. Isotherm parameters of adsorption of Cr (VI) ions onto chitosan

Model			
Langmuir	b (L mg^{-1})	q_m (mg g^{-1})	R^2
	0.002	58.8	0.984
Freundlich	K_f ($mg^{1-(1/n)}$ $L^{1/n}$ g^{-1})	n	R^2
	6.29	1.35	0.995

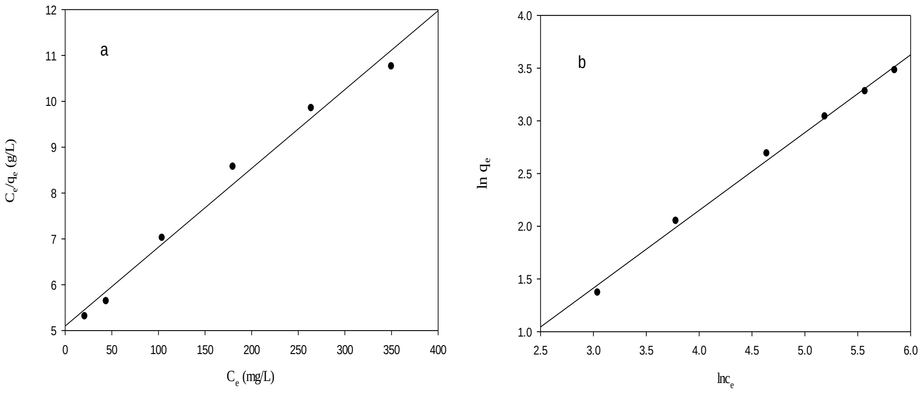

Figure 7. (a) Langmuir and (b) Freundlich isotherms for Cr (VI) ions adsorption onto chitosan.

Table 2. Comparison of adsorption capacities of Cr(VI) with other adsorbents.

Adsorbents	**pH**	**Adsorption capacity (mg g $^{-1}$)**	**Ref.**
Coconut tree sawdust	3	3.60	[23]
Magnetic Fe_3O_4@NiO	4	18.4	[24]
$Al(OH)CO_3$	7	60	[25]
Activated carbon	4.5	36	[26]
Sugarcane bagasse	2	13.4	[27]
Multiwalled carbon nanotubes	2	4.2	[28]
Chitosan	4	58.8	this study

Adsorption kinetics

In order to explain the adsorption mechanism and adsorption characteristics, two adsorption kinetics models, pseudo-first-order model (Eq. (5)) and pseudo-second-order model (Eq. (6)) were used to analyze the adsorption kinetic data. Their linear forms can be expressed as [29, 30]:

$$\ln(q_e - q_t) = \ln(q_e) - \frac{k_1 t}{2.303} \qquad (5)$$

$$\frac{t}{q_t} = \frac{1}{k^2 q_e^2} + \frac{t}{q_e} \qquad (6)$$

Where qe and qt are the amount of Cr (VI) ions adsorbed (mg/g) at equilibrium and time t (min); k_1 is the rate constant of pseudo-first-order (min^{-1}); k_2 is the rate constant of pseudo-second-order (g mg^{-1} min^{-1}) for adsorption. The kinetic parameters and the correlation coefficients (R^2) were determined by linear regression (Figure 8a, b), and the results are given in Table 3. The results indicated that experimental data better fits to pseudo-second-order kinetic model in terms of higher correlation coefficient values (R^2 = 0.995).

Table 3. Pseudo-first-order and pseudo-second-order kinetic model parameters for the adsorption of Cr (VI) ions onto chitosan

C_0 (mg L^{-1})	q_e exp(mg g^{-1})	Pseudo-first-order model			Pseudo-second-order model		
		q_{e1}(mg g^{-1})	k_1 (min^{-1})	R^2	q_{e2} (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2
100	4.5	0.07	0.002	0.551	4.44	0.02	0.995

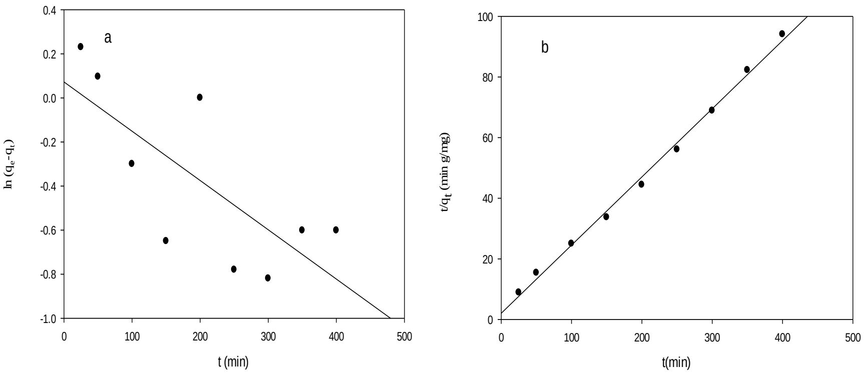

Figure 8. (a) Pseudo-first-order and (b) pseudo-second-order kinetics plots of Cr (VI) ions adsorption onto the chitosan.

CONCLUSIONS

The present study 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. Adsorption of Cr (VI) ions onto chitosan follows Freundlich model and kinetic of adsorption process follow pseudo-second-order model. The results revealed that chitosan could be used as an efficient adsorbent for the rapid removal of Cr (VI) ions from water samples.

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REFRENCES

1. Chen C., Hu J., Shao D., Li J., Wang X., 2009. Adsorption behavior of multiwall carbon nanotube/iron oxide magnetic composites for Ni (II) and Sr (II). J Hazard Mater. 164, 923–928.

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

3. Kaprara E., Seridou P., Tsiamili V., Mitrakas M., Vourlias G., Tsiaoussis I., Kaimakamis G., Pavlidou E., Andritsos N., Simeonidis K., 2013. Cu-Zn powders as potential Cr(VI) adsorbents for drinking water. J Hazard Mater. 262, 606–613.

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

5. Sobhanardakani S., Parvizimosaed H., Olyaie E., 2013. Heavy Metals Removal from Waste waters using

Organic Solid Waste-Rice Husk. Environ Sci Pollut Res. 20, 5265–5271.

6. Wang H., Yuan X., Wu Y., Huang H., Zeng G., Liu Y., Wang X., Lin N., Qi Y., 2013. Adsorption characteristics and behaviors of graphene oxide for Zn(II) removal from aqueous solution. Appl Surf Sci. 279, 432–440.

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

8. Kismir Y., Aroguz A.Z., 2011. Adsorption characteristics of the hazardous dye Brilliant Green on Saklıkent mud. Chem Eng J. 172, 199–206.

9.Celis R., Adelino M.A., Hermosin M.C., Cornejo J., 2012. Montmorillonite–chitosan bionanocomposites as adsorbents of the herbicide clopyralid in aqueous solution and soil/water suspensions. J Hazard Mater. 209, 67–76.

10. Wan Ngah W.S., Teong L.C., Hanafiah M.A.K.M., 2011. Adsorption of dyes and heavy metal ions by chitosan composites: A review. Carbohyd Polym. 83, 1446–1456.

11. Kołodynska D., 2011. Chitosan as an effective low-cost sorbent of heavy metal complexes with the polyaspartic acid. Chem Eng J. 173, 520–529.

12. Zhao F., Yu B., Yue Z., Wang T., Wen X., Liu Z., Zhao C., 2007. Preparation of chitosan gel beads for copper (II) ion adsorption. J Hazard Mater. 147, 67–73.

13. Deans J.R., Dixon B.G., 1992. Uptake of $Pb^{2+}$and Cu^{2+} by novel biopolymers. Water Res. 26, 469–472.

14. Popuri S.R., Vijaya V., Boddu V.M., Abburi K., 2009. Adsorptive removal of copper and nickel ions from water using chitosan coated PVC beads. Biores Technol. 100, 194–199.

15. Kaminski W., Modrzewska Z., 1997. Application of chitosan membranes in separation of heavy metal ions. Separ Sci Technol. 32, 2659–2668.

16. Deng C., Liu J., Zhou W., Zhang Y.K., Du K.F., Zhao Z.M., 2012. Fabrication of spherical cellulose/carbon tubes hybrid adsorbent anchored with welan gum polysaccharide and its potential in adsorbing methylene blue. Chem Eng J. 200-202, 452–458.

17. Lv G., Li Z., Jiang W., Ackley C., Fenske N., Demarco N., 2014. Removal of Cr(VI) from water using Fe(II)-modified naturalzeolite. Chem Eng J. 92, 384–390.

18. Chen C., Hu J., Shao D., Li J., Wang X., 2009. Adsorption behavior of multiwall carbon nanotube/iron oxide magnetic composites for Ni(II) and Sr(II). J Hazard Mater. 164, 923–928.

19. Sheela T., Arthoba Nayaka Y., Viswanatha R., Basavanna S., Venkatesha T.G., 2012. Kinetics and thermodynamics studies on the adsorption of Zn(II), Cd(II) and Hg(II) from aqueous solution using zinc oxide nanoparticles. Powder Technol. 217, 163–170.

20. Anbia M., Salehi S., 2012. Removal of acid dyes from aqueous media by adsorption onto amino functionalized nanoporous silica SBA-3, Dyes. Pigments. 94, 1–9.

21. Dotto G.L., Lima E.C., Pinto L.A.A., 2012. Biosorption of food dyes onto Spirulina platensis nanoparticles: Equilibrium isotherm and thermodynamic analysis. Biores Technol. 103, 123–130.

22. Konicki W., Pełech I., Mijowska E., Jasinska I., 2012. Adsorption of anionic dye Direct Red 23 onto magnetic multi-walled carbon nanotubes-Fe_3C nanocomposite: Kinetics, equilibrium and thermodynamics. Chem Eng J. 210, 87–95.

23. Selvi K., Pattabhi S., Kadirvelu K., 2001. Removal of Cr(VI) from aqueous solution by adsorption onto activated carbon. Biores Technol. 80, 87–89.

24. Li Y.L., Wang J., Li Z.S., Liu Q., Liu J.Y., Liu L.H., Zhang X.F., Yu J., 2013. Ultrasound assisted synthesis of Ca–Al hydrotalcite for U (VI) and Cr (VI) adsorption. Chem Eng J. 218, 295–302.

25. Zhong L.S., Hu J.S., Cao A.M., Liu Q., Song W.G., Wan L.J., 2007. 3D Flowerlike Ceria Micro/Nanocomposite Structure and Its Application for Water Treatment and CO Removal. Chem Mater. 19, 1648–1655.

26. Cao C.Y., Cui Z.M., Chen C.Q., Song W.G., Cai W., 2010. Ceria Hollow Nanospheres Produced by a Template-Free Microwave-Assisted Hydrothermal Method for Heavy Metal Ion Removal and Catalysis. J Phys Chem C. 114, 9865–9870.

27. Sharma D.C., Forster C.F., 1994. A preliminary examination into the adsorption of hexavalent chromium using low-cost adsorbents. Biores Technol. 47, 257–264.

28. Hu J., Chen C., Zhu X., Wang X., 2009. Removal of chromium from aqueous solution by using oxidized multiwalled carbon nanotubes. J Hazard Mater. 162, 1542–1550.

29. Azizian S., 2004. Kinetic models of sorption: a theoretical analysis. J Colloid Interface Sci. 276, 47–52.

30. Venkatesha T.G., Viswanatha R., Arthoba Nayaka Y., Chethana B.K., 2012. Kinetics and thermodynamics of reactive and vat dyes adsorption on MgO nanoparticles. Chem Eng J. 198, 1–10.