Research Article

OPEN ACCESS

Removal of Hexavalent Chromium from Tannery Industry by Adsorption Using Chitosan

Nibret Mekonen Ayele

Food Science and Nutrition Research, Ethiopian Institute of Agricultural Research (EIAR), P.O. Box 2003, Addis Ababa, Ethiopia.
Corresponding author e-mail: anibretmekonen@gmail.com

ABSTRACT

Chromium (Cr) is one of the most toxic heavy metals to living organisms, with different adverse health effects on humans, animals, plants, and microorganisms, and it must be reduced or removed from the body of water. The objective of this study was to remove hexavalent chromium from the tannery industry using chitosan. The batch adsorption experiments were conducted using a UV-Vis spectrophotometer. Equilibrium adsorption isotherms and the kinetic behavior of the process were also studied. The optimum conditions of the study were 120 min of contact time, 0.5 g adsorbent dose, and a solution pH of 3.0, which resulted in maximum Cr (VI) uptake. The maximum removal percentage of Cr (VI) was 86.00. The experimental data better fitted the Langmuir isotherm with a monolayer adsorption capacity of 20.82. The kinetic analysis revealed that the pseudo-second-order model fitted well to the acquired experimental data.
Keywords: Adsorbent, hexavalent chromium, and chitosan.

INTRODUCTION

Environmental pollution is one of the major concerns in the world due to urbanization, industrialization, high population density, *improved living conditions,* and economic development (Ali *et al*., 2017). A large number of environmental pollutants, primarily toxic heavy metals, are directly or indirectly discharged into the environment as a result of natural or anthropogenic activity and are extremely harmful to the human body and other life forms, even at low concentrations due to the lack of an effective removal mechanism (Ali *et al*., 2017) and (Ghosh *et al*., 2012). *Natural sources of heavy metals in the environment include natural weathering of rocks, soil erosion, and volcanic eruptions, and anthropogenic activities such as* metallurgical processes, industry, agriculture, printing, photographic materials, combustion of fossil fuel, forest fires, mining activity, automobile emissions, and sewage (Ghosh *et al*., 2012) and (Wongrod *et al*., 2018). *From the eco-toxicological point of view,* Chromium (Cr) is one of the most toxic heavy metals to living organisms, with different adverse health effects on humans, animals, plants, and microorganisms (Vasylkiv *et al*.,2010). Chromium (Cr) is widely present in industrial wastewater from electroplating, petroleum refining, alloy manufacturing, and battery production, which contaminates the soil and water resources (Sawalha *et al*., 2020)**.** Chromium exists primarily in the natural environment as Cr (III) and Cr (VI), with Cr (VI) being far more poisonous or lethal, soluble, and mobile than Cr (III) (Rambabu *et al*., 2021).

Hexavalent chromium could cause poisonous and harmful effects on humans and animals. Water and food consumption are the most common ways for Cr (VI) ions to enter plant and animal metabolisms.

Urban agriculture is developing at a rapid rate to contribute to food and nutrition security in most parts of the world, and they use wastewater. Farmers in urban areas of developing countries, including Ethiopia, depend on wastewater sources to irrigate high-value edible crops for urban markets. Vegetables or high-valued edible crops accumulate heavy metals depending on plant species and the efficiency of different parts of the plants by either plant uptake or soil-to-plant transfer factors of the metals and type of plant species with their stage of maturity. In this way, toxic heavy metals enter the food chain of animals and humans. According to the United States Environmental Protection Agency (EPA) and WHO, the permissible limit of hexavalent chromium in drinking water is 0.1 mg/L and 0.05 mg/L, respectively (WHO, 2020 and WHO, 2011). Several reports have revealed that the accumulation of chromium metal in humans is above the WHO permissible limit (Zewdu *et al*., 2018). Hexavalent chromium affects various components of the immune system and can cause several health effects such as lung cancer, kidney failure, DNA damage, and reproductive and respiratory problems (Costa *et al*., 2006, Alvarez *et al*., 2021, Aruldhas *et al*., 2004 and Kimbrough *et al*., 1999).

Therefore, toxic waste must be reduced or removed from the environment using different technologies or

methods. Some of these methods are chemical precipitation (Djedidi *et al*., 2009), ion-exchange (Hubicki *et al*., 2012), reverse osmosis (Thaçi *et al*., 2019), coagulation, membrane separation, and adsorption (Di Natale *et al*., 2015). Among these conventional techniques, adsorption is one of the most promising and frequently used due to its selectivity, low cost, ease of use, high efficiency (even when these metals are in low concentration) and the possibility of reusing the materials involved (Xu *et al*., 2018). The aim of this study focuses on the removal of hexavalent chromium from tannery wastewater by adsorption using chitosan, a low-cost adsorbent.

MATERIALS AND METHODS

Study area

This study was conducted in Ethiopian Institute of Agricultural Research, Ethiopia. In food science and nutrition research directorate.

Apparatus and instruments

Electrical balance (ae ADAM), chopper (mechanical grinder), mortar and pestle, Oscillator, centrifugation, beakers, conical flask, measuring cylinder, filter paper, water bath, oven, muffle furnace, pH meter (Jenway, UK) and Agilent Cary 60 UV-Vis spectrophotometer were used.

Chemicals and reagents

Potassium dichromate ($K_2Cr_2O_7$) (Carelabmed, India), sulfuric acid (H_2SO_4) (95-97%, (Fluka, Germany), hydro chloric acid (HCl) 37% (Fluka, Germany), nitric acid (HNO_3) 69% (Fluka), sodium hydro oxide (NaOH) assay > 97% (RPE, ACS-ISO for analysis), ammonium persulfate (($NH_4)_2S_2O_8$) assay =99% (BDH, England), ethanol, 1,5- diphenylcarbazide ($C_{13}H_{14}N_4O$ assay > 99% (Sigma Aldrich, India), acetone > 99% (Fisher chemical) and hydrogen peroxide (30%), sodium azide (NaN_3), methyl red indicator and ammonium hydroxide (NH_4OH) (BDH, China) were used.

Analytical method

Real sample digestion

The diphenylcarbazide method was used to determine hexavalent chromium from tannery wastewater. The real sample that was collected from Bahir Dar tannery and filtered through a Whatman No. 45 filter paper. The samples were analyzed for Cr(VI) by the a UV-Vis spectrophotometer method using 1,5-diphenylcarbazide reagent (63 mg 1,5-diphenylcarbazide in 25 mL of acetone), which reacts with Cr(VI), forming a colored complex that absorbs at 540 nm (Dhungana *et al*., 2009).

Standard solution preparation

A stock solutions of hexavalent chromium concentration (1000 mg/L) was prepared by dissolving 2.829 g $K_2Cr_2O_7$ in 0.2 M H_2SO_4 then diluted to 1000 mL, and 0.2 M H_2SO_4 was also prepared by adding 11.22 mL of concentrate H_2SO_4 (95-97) % to 600 mL distilled water and leveled it to 1000 mL. After preparation of 1000 mg/L hexavalent chromium then use serial dilution formula for further concentration level of chromium. Low range standards were (0.025, 0.05, 0.1, 0.2, 0.4, 0.8,

1.2, 1.6, 2.4, 3.2, 4.0 and 4.8) mg/L. The absorbance of the standard solutions was measured at 540 nm by UV-Vis spectrophotometer.

Adsorption study

Adsorption isotherms and kinetics study

All batch adsorption studies were carried out at room temperature (25 $\pm$ 2 °C) using 10 mL of a Cr(VI) ion solution and shack at constant speed using KS oscillator. The pH (1, 2, 3, 4, 5 and 6) of the experimental solutions was adjusted to the desired pH by drop wise addition of 0.1 M H_2SO_4 and 0.1 M NaOH to the ion solution with stirring and monitoring by a Benchtop pH meter which was calibrated using pH 4.0 and 7.0 buffer solutions.

For the equilibrium isotherm study, 5 mg of chitosan adsorbent was mixed with 10 mL of (0.5, 1, 2, 4, 5, 6, 8, 10, 12, 14 and 16) mg/L initial concentration of hexavalent chromium solutions at pH 3 and shack for 120 min. For the adsorption kinetics study, 5 mg of chitosan was added to the adsorbate solution with initial concentration of 5 mg/L in the time intervals (5, 10, 15, 20, 30, 60, 90, 120,150, 180,210, and 240 min). The concentration of Cr(VI) was measured using UV-Vis spectroscopy at 540 nm wavelength for low range initial concentrations. For each measurement, three replicates were performed and averaged.

The equilibrium adsorption capacity and the percent removal (% R) of Cr(VI) was calculated using Equations (1) and (2).

$$q_e = \frac{(C_o - C_e)V}{m} \tag{1}$$

$$\% R = \frac{(C_o - C_e)100}{C_o} \tag{2}$$

Where q_e (mg/g) is the adsorption capacity of adsorbent for Cr(VI), C_0 and C_e (mg/L) are the liquid phase concentrations of Cr(VI) before and after adsorption respectively. V (L) and m (g) are the volume of the adsorption solution and the mass of the dry adsorbent used respectively. An adsorption isotherm is a function of the metal ion concentrations or materials in (mol m^{-2} or mg m^{-2}) adsorbed on a substrate (solid, liquid, or gas) at room temperature. The obtained results was tested with the two well-known models that are Langmuir and Freundlich models. In Langmuir isotherm model, adsorption occurs at specific sites on the adsorbent and adsorption energy has been homogeneously distributed on the absorbent surface (Langmuir 1918). The fundamental characteristics of Langmuir isotherm can be expressed by the following equations:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{C_e}{q_m} \tag{3}$$

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \tag{4}$$

$$R_L = \frac{1}{1 + K_L C_o} \tag{5}$$

Where C_e and q_e equilibrium concentration and adsorption capacity respectively q_m (mg/g) is the maximum monolayer adsorption capacity of the adsorbent, K_L (L/mg) is the Langmuir constant describing adsorption affinity for the adsorbent. The value of R_L indicates the type of the isotherm to be either; unfavorable ($R_L> 1$), linear ($R_L =1$), favorable ($0<R_L<1$) and irreversible ($R_L=0$). The Freundlich isotherm model is suitable for adsorption processes occurring on heterogeneous surfaces. Heterogeneous distribution of active sites and also multilayer adsorption are assumptions of Freundlich isotherm. Freundlich isotherm is a mathematical expression for the adsorption equilibrium between a fluid (liquid or gas) and a solid material and the equation is represented by Eq. (6) and Eq. (7) for nonlinear and linear, respectively.

$$q_e = K_F C_e^{\frac{1}{n}}$$

(6)

The equation can be linearized and temperature dependent constants K_F and $1/n$ are obtained by linear regression:

$$ln q_e = ln K_F + \frac{1}{n} ln C_e$$

(7)

K_F (mg/g) (L/mg)$^{1/n}$ is the Freundlich constant related to the multilayer adsorption capacity and n is the heterogeneity factor, which represents the extent to which the adsorption depends on the equilibrium concentration. If $1/n = 0$, it means irreversibility; if $0 < 1/n < 1$, it means desirability; and if $1/n > 1$, it means undesirable isotherm.

Adsorption kinetics is a curve (or line) that describes the rate of retention or release of a solute from an aqueous environment to solid-phase interface at a given adsorbents dose, flow rate and pH. In batch adsorption systems, several models describing the adsorption kinetics. However, PFO and PSO models have been widely used to describe the rate of adsorption in liquid - solid interactions. The data obtained from the kinetic tests are fitted to the pseudo-first-order and pseudo-second-order models respectively. The kinetic model that fits to Pseudo-first-order reaction plot by giving R^2 value close to 1, it indicates that the reaction is more inclined towards Physisorption. Similarly, if the reaction fits well to Pseudo-second-order model it indicates an inclination towards chemisorption. Pseudo-first-order Equation (8) and pseudo-second-order model, Equation (9) assumes that the adsorption rate is based on the adsorption capacity.

$$ln\,(q_e - q_t) = ln q_e - K_1 t$$

(8)

Where q_t and q_e (mg/g) are the amount of hexavalent chromium adsorbed per mass of adsorbent (g) at time t (min) and at equilibrium, respectively, and k_1 (1/min) the rate constants of the pseudo-first-order.

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

(9)

Where q_e (mg/g) and q_t (mg/g) are the adsorption capacity at equilibrium and at any time t (min), respectively and K_2 (g/mg min) is the PSO equation rate constant.

$$\frac{t}{q_t} = \frac{1}{h} + \frac{t}{q_e}$$

(10)

The adsorption kinetics reflect the evolution of the adsorption process versus time and the adsorption process is depends on the experimental parameters, such as pH, ionic strength, temperature, concentration of solute, adsorbent dose, the texture of adsorbents. Therefore, the contact time where the adsorption process approaches a true equilibrium must be determined according to these parameters.

RESULTS AND DISCUSSION
Low and high range standards were measured using UV-Vis spectroscopy at 540 wavelengths. The calibration curve and correlation coefficient of hexavalent chromium was determined by plotting absorbance versus working standard concentrations. The correlation coefficient of hexavalent chromium for low range standards was 0.99667.
Analysis of hexavalent chromium standard calibrations
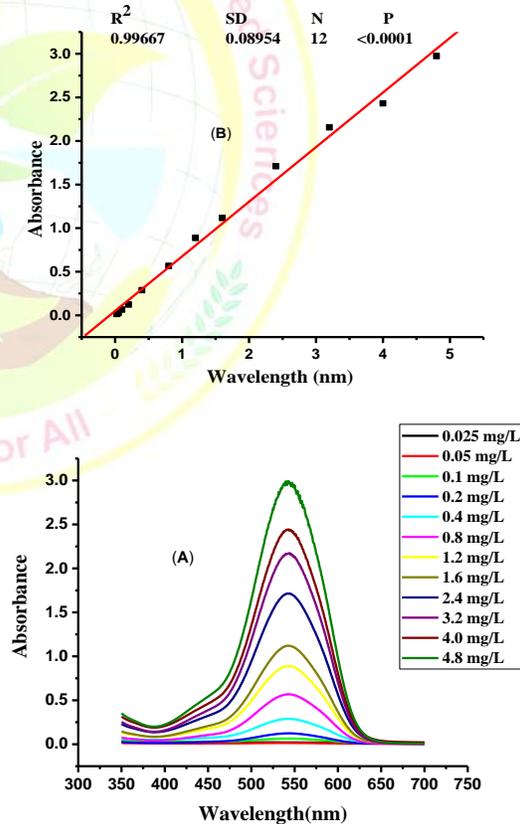
**Figure 1**. (A) Represents the voltammogram and (B) the standard calibration curve of low concentrations.

Optimization of the adsorption studies
Effect of pH

The effect of pH on the adsorption of hexavalent chromium was studied at different pH (1.0-6.0). Because the pH of the solution affects the adsorbent properties such as surface charge, adsorbate speciation and degree of ionization in aqueous solutions. In aqueous solutions, Cr (VI) exist in several stable forms such as, $HCrO_4^-$, $HCr_2O_7^-$, H_2CrO_4 (pH < 1), $Cr_2O_7^{2-}$ and CrO_4^{2-} (pH 2–6) depending upon the pH of the solution (Yusuff 2019). $HCrO_4^-$ which is the predominantly acidic solution, and has better removal efficiency due to the increase in H $^+$ ions on the adsorbent surface which makes surface positive and electrostatic attractions with negatively charged Cr (VI) ions. Figure 2 summarizes the effect of pH on Cr (VI) removal by chitosan. The optimum pH for the maximum removal percentage of Cr (VI) was found to be pH 3. The removal percentage of Cr (VI) was 65 % on the chitosan adsorbent.
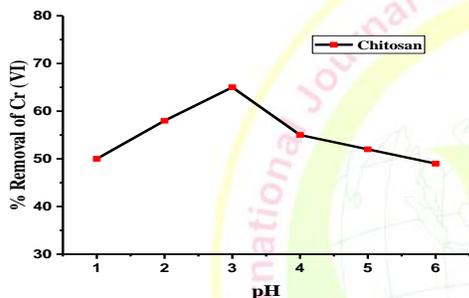
Figure 2. Graphical illustration of the effect of pH on the percent removal of hexavalent chromium by chitosan. Experimental conditions: adsorbent dose 5 mg, volume 10 mL, contact time 120 min and temperature 25 ± 2 °C.
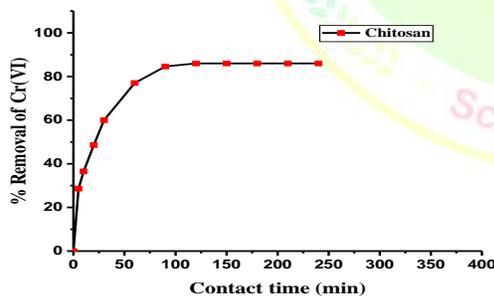
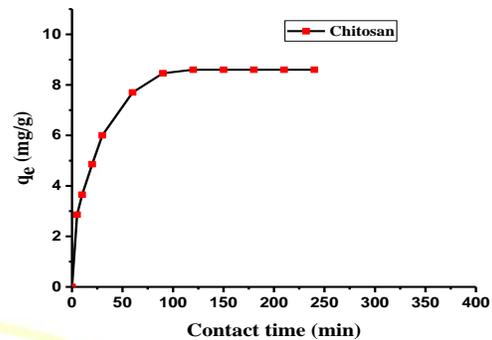**Figure 3.** Removal percentage of hexavalent chromium by chitosan. Experimental conditions: adsorbent dose 5 mg/ 10 mL, PH 1 and temperature 25 ± 2 °C.

Effect of contact time

The effect of contact time (5-240 min) on the batch adsorption process at temperature of 25 ± 2 °C, adsorbent dose (5 mg), 10 mL of volume and pH (3) was studied. Figure 3 and figure 4 shows the effect of contact time on the removal percentage of Cr (VI) and the adsorption capacity respectively. The adsorption of capacity and the removal percentage of Cr (VI) was increase with time in the first stage of adsorption process and reached maximum removal percentage, (86 %) at equilibrium

time of 120 min. Because there is high availability of vacant adsorption sites in the first stage adsorption. As time increase removal percentage and adsorption capacity becoming constant due to the repulsive forces of the adsorbed ions and it is difficult to access the active sites (Sattar *et al*., 2019).
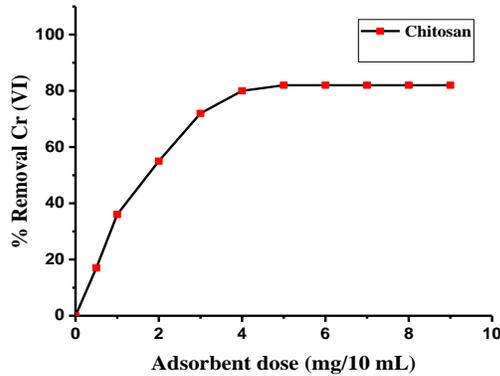

Figure 4. Adsorption capacity of hexavalent chromium by chitosan. Experimental conditions: adsorbent dose 5 mg/ 10 mL, PH 1 and temperature 25 ± 2 °C.

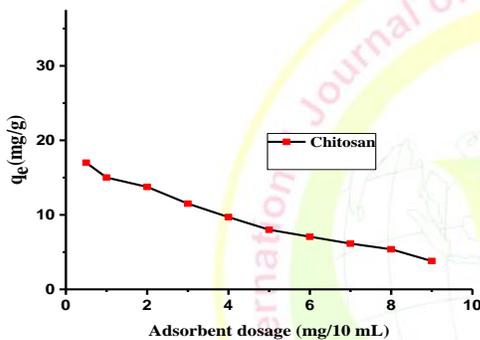## Effect of initial concentration

The Cr(VI) solutions of different concentrations (0.5, 1, 2, 4, 5, 6, 8, 10, 12, 14 and 16) mg/L were studied at pH 3, constant agitation speed, contact time 120 min for chitosan, and the adsorbent dose 0.5 g/L as shown in Figure 5 and 6. The removal percentage of Cr(VI) was slightly reduced, and the adsorption capacity of Cr(VI) was increased for chitosan adsorbent with an increase in initial concentration of Cr(VI) and becomes constant after equilibrium time. This behavior could be ascribed to the presence of a higher concentration of adsorbate per unit mass of adsorbent and which may restrict adsorption because, initial concentration provides a significant driving force to overcome all mass transfer resistance of metal ions between aqueous and solid phases (Gokila *et al*., 2017). Therefore, at low concentration, the binding sites took up the available ions quickly, but at higher concentration, the adsorption species needed to diffuse to the internal sites by intra-particle diffusion, resulting in reduced adsorption rate.
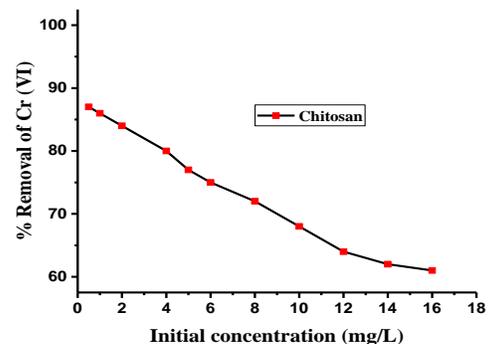
Figure 5. Effect of initial concentration on the removal percentage of hexavalent chromium by chitosan.

Figure 7. Removal percentage of hexavalent chromium by chitosan. Experimental conditions: at different dose, initial concentration 5 mg/L, PH 1 and temperature 25 ± 2 °C.

Figure 8. Adsorption capacity of hexavalent chromium by chitosan. Experimental conditions: at different dose, initial concentration 5 mg/L, PH 1 and temperature 25 ± 2 °C.

Adsorption isotherm

The adsorption isotherms describe the distribution of adsorbed molecules between the solid and liquid phase when the adsorption reaches at equilibrium. Langmuir and Freundlich models are well-known adsorption isotherm models. The adsorption isotherm model of the experiment was followed Langmuir model, which indicates that the adsorption process was onto homogeneous surfaces and that exhibit one type of adsorption site (Langmuir 1918). The adsorption capacity corresponding to the monolayer adsorption (q_m) was 20.82 for chitosan adsorbent.

Adsorption kinetics

Pseudo-first and pseudo-second-order kinetics model parameters; the higher correlation coefficient (R^2) values obtained from the pseudo-second-order (0.999) compared to those of the pseudo-first-order (0.975) kinetic model for the chitosan adsorbent. The adsorption more closely followed the pseudo-second-order kinetics which is chemisorption.

Analysis of real sample

The wastewater was collected from Bahir Dar tannery in Amhara region, Ethiopia. Table 1 show, the obtained results in tannery wastewater were 0.170 mg/L, 0.001 and 0.59 for mean, standard deviation and percent of relative standard deviation respectively, that is above permissible limits of EPA and WHO. The data was analyzed using **Minitab 17** software. Minitab is the statistical software that helps in taking out the complexities of statistical calculations because it is easy to use, to calculate and draw various graphs.

Table 1. Summary of the mean total chromium concentration in wastewater samples collected from Bahir Dar tannery.

Sample	Total Chromium in (mg/L)	SD	% RSD	SE Mean	SS	MS	F_{expt}	F_{crit}	P
WWS1	0.170	0.001	0.59	5.8×10^{-4}	5×10^{-7}	5×10^{-7}	0.33	6.61	0.67
WWS2	0.169	0.001	0.59	5.8×10^{-4}	1.5×10^{-6}	1.5×10^{-6}			

N indicates the number of triplicate trials.

The obtained P–value (0.67) is greater than 0.05 within 95% confidence level, which doesn't show statistically significant difference between wastewater samples (WWS1 and WWS2), and indicates strong evidence for the null hypothesis. This means retain the null hypothesis and reject the alternative hypothesis. The value of F_{expt} (0.33) is less than F_{crit} (6.61) which also indicates that there is no significant difference between the two wastewater samples, but the values of the two samples are not exactly the same due to random error.

Removal of hexavalent chromium from wastewater

Chitosan was used as an adsorbent material for the removal of Cr(VI) from the wastewater. Figure 9 shows that, the removal of Cr(VI) ions from the collected wastewater sample by using chitosan adsorbent material. The removal of Cr(VI) ions from real sample achieve WHO permissible limit at a time of 20 min. These results indicated that, chitosan was efficient for the removal of Cr(VI) ions from wastewater.
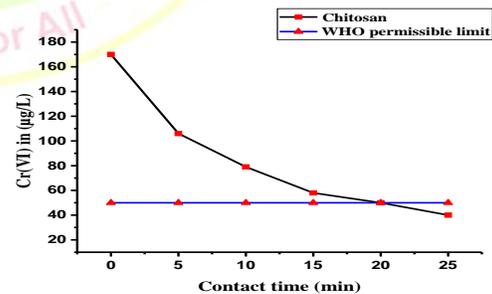
Figure 9. Concentration-time profile for the removal of 170 µg/L of Cr(VI) ions from the collected tannery wastewater sample by using chitosan adsorbent.

CONCLUSION

The adsorption capacity q_e (mg/L) and removal percentage of hexavalent chromium were influenced by the concentration, contact time, and pH of the solution as well as the adsorbent dosage. The maximum removal percentage of Cr (VI) is 86.00% for chitosan. The

adsorption kinetics followed the pseudo-second-order kinetics more closely, and it was discovered that the pseudo-second-order rate constant (K_2) was inversely proportional to the initial concentration of Cr(VI), indicating that surface saturation was dependent on the initial ion concentration, which is chemisorption. The maximum adsorption (q_m) calculated from the Langmuir equation was 20.82.

ACKNOWLEDGEMENTS

REFERENCES

Ali, H. and Khan, E. 2017. Environmental chemistry in the twenty first century. *Environmental chemistry letters*, **15**(2): 329–346.

Alvarez, C.C., Gómez, M.E.B. and Zavala, A.H. 2021. Hexavalent chromium: Regulation and health effects. *Journal of trace elements in medicine and biology*, **65**:126729.

Aruldhas, M.M., Subramanian, S., Sekhar, P., Hasan, G.C., Govindarajulu, P. and Akbarsha, M.A. 2004. Microcanalization in the epididymis to overcome ductal obstruction caused by chronic exposure to chromium–a study in the mature bonnet monkey (Macaca radiata Geoffroy). *Reproduction*, **128**(1):127-137.

Costa, M. and Klein, C.B. 2006. Toxicity and carcinogenicity of chromium compounds in humans. *Critical reviews in toxicology*, **36**(2):155-163.

Dhungana, T.P. and Yadav, P.N. 2009. Determination of chromium in tannery effluent and study of adsorption of Cr (VI) on saw dust and charcoal from sugarcane bagasses. *Journal of Nepal chemical society*, **23**:93-101.

Di Natale, F., Erto, A., Lancia, A. and Musmarra, D. 2015. Equilibrium and dynamic study on hexavalent chromium adsorption onto activated carbon. *Journal of hazardous materials*, **281**:47-55.

Djedidi, Z., Bouda, M., Souissi, M.A., Cheikh, R.B., Mercier, G., Tyagi, R.D. and Blais, J.F. 2009. Metals removal from soil, fly ash and sewage sludge leachates by precipitation and dewatering properties of the generated sludge. *Journal of hazardous materials*, **172**(2-3):1372-1382.

Dönmez, G. and Aksu, Z. 2002. Removal of chromium (VI) from saline wastewaters by Dunaliella species. *Process biochemistry*, **38**(5):751-762.

Ghosh, A.K., Bhatt, M.A. and Agrawal, H.P. 2012. Effect of long-term application of treated sewage water on heavy metal accumulation in vegetables grown in Northern India. *Environmental monitoring and assessment*, **184**(2): 1025-1036.

Gokila, S., Gomathi, T., Sudha, P.N. and Anil, S. 2017. Removal of the heavy metal ion chromiuim (VI) using chitosan and alginate nanocomposites. *International journal of biological macromolecules*, **104**:1459-1468.

Hubicki, Z. and Kołodyńska, D. 2012. Selective removal of heavy metal ions from waters and waste waters using ion exchange methods. *Ion exchange technologies*, **7**:193-240.

Khalil, U., Shakoor, M.B., Ali, S. and Rizwan, M. 2018. Tea waste as a potential biowaste for removal of hexavalent chromium from wastewater: equilibrium and kinetic studies. *Arabian journal of geosciences*, **11**(19):1-9.

Kimbrough, D.E., Cohen, Y., Winer, A.M., Creelman, L. and Mabuni, C. 1999. A critical assessment of chromium in the environment. *Critical reviews in environmental science and technology*, **29**(1):1-46.

Langmuir, I. 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of the American chemical society*, **40**(9):1361-1403.

Rambabu, K., Thanigaivelan, A., Bharath, G., Sivarajasekar, N., Banat, F. and Shaw, P.L. 2021. Biosorption potential of phoenix dactylifera coir wastes for toxic hexavalent chromium sequestration. *Chemosphere,* 268, p.128809.

Sattar, M.S., Shakoor, M.B., Ali, S., Rizwan, M., Niazi, N.K. and Jilani, A. 2019. Comparative efficiency of peanut shell and peanut shell biochar for removal of arsenic from water. *Environmental science and pollution research*, **26**(18):18624-18635.

Sawalha, H., Al-Jabari, M., Elhamouz, A., Abusafa, A. and Rene, E.R. 2020. Tannery wastewater treatment and resource recovery options. In *waste biorefinery* (pp. 679-705). Elsevier.

Thaçi, B.S. and Gashi, S.T. 2019. Reverse osmosis removal of heavy metals from wastewater effluents using biowaste materials pretreatment. *Polish journal of environmental Studies*, **28**(1):337-341.

Vasylkiv, O. Y., Kubrak, O. I., Storey, K. B. and Lushchak, V. I. 2010. Cytotoxicity of chromium ions may be connected with induction of oxidative stress. *Chemosphere,* **80** (9), pp.1044–1049.

Wongrod, S., Simon, S., Guibaud, G., Lens, P.N., Pechaud, Y., Huguenot, D. and van Hullebusch, E.D. 2018. Lead sorption by biochar produced from digestates: Consequences of chemical modification and washing. *Journal of environmental management,* 219, pp. 277-284.

World Health Organization, 2011. Drinking water standards and health advisories office of water US Environmental Protection Agency Washington.

World Health Organization,2020. *Chromium in drinking-water* (No.

WHO/HEP/ECH/WSH/2020.3). World Health Organization.

Xu, J., Cao, Z., Zhang, Y., Yuan, Z., Lou, Z., Xu, X. and Wang, X. 2018. A review of functionalized carbon nanotubes and graphene for heavy metal adsorption from water: Preparation, application, and mechanism. *Chemosphere*, **195**, pp.351-364.

Yusuff, A.S. 2019. Adsorption of hexavalent chromium from aqueous solution by leucaena leucocephala seed pod activated carbon: equilibrium, kinetic and thermodynamic studies. *Arab journal of basic and applied sciences*, **26**(1), pp.89-102.

Zewdu, F. and Amare, M. 2018. Determination of the level of hexavalent, trivalent, and total chromium in the discharged effluent of Bahir Dar tannery using ICP-OES and UV–Visible spectrometry. *Cogent chemistry*, **4**(1), p.1534566.