REMOVAL OF CHROMIUM FROM TANNERY WASTEWATER USING NON AGRICULTURAL WASTES

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Abstract:
The adsorption of chromium Cr (III) from tannery wastewater at room temperature by batch adsorption technique using different low-cost adsorbents has been investigated.The main objective of the study was to find out a suitable low-cost, available,environmentally friendly and highly effective adsorbent. In the present study different low cost adsorbents (non-agricultural wastes) such as animal hair, newspaper, rubber, packaging box, plastic, brick powder, bone, concrete etc.have been studied. Among of them, the highest removal efficiencies of newspaper and packaging box were 63% and 69% respectively. Batch adsorption studies were carried out under varying experimentalconditions of adsorption dose, contact time, pH, particle size, operational temperature and initial adsorbateconcentration.

Keywords: Non-agricultural wastes, Tannery wastewater, Adsorption, Chromium, Batch, Isotherms
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INTRODUCTION

Leather processing is an important economic activity around the world and uncontrolled release oftannery effluents to natural water bodies causes environmental degradation and increases health risks tohuman beings. The treatment of tannery effluent is a complex technological challenge because of thepresence of high concentrations of organic and inorganic pollutants of both conservative and non-conservative nature[1].However, the leather-making process, in turn,generates by-products and wastes. It is known that only 20% of wet salted hides and skinsare converted into commercial leather, while 25% becomes chromium containing leatherwaste (CCLW), and the remainder becomes non-tanned waste or is lost in wastewater asfat, soluble protein and solid suspended pollutants [2]. Environmental pollution is a difficult problem for world leather industry [3-4]. The real problem, however, that the leather industrypresently faces the environmental challenge [5].Due to increased pollution from point andnon-point sources quality of the water become a crucial problem, particularly for the third-worldcountries [6].All industrial works create waste and pollute the environment. Among all the industrial wastes tanneryeffluents are ranked as the highest pollutants. This industry is an important industrial sector inBangladesh which has a massive impact on our economy. The industry has become an area of exportthrust with footwear having been identified as an area of extreme focus [7].

Due to increasingly strict requirements for leather and with regard to recycling of leather wastes, the manufacture chromium-free leather becomes very important [8]. Chromium tanning uses chromium III salts which are not considered to be harmful when in leather. On the other hand, Chromium VI is a hazardous form of chromium. A chronic effect from chromium VI skin exposure is the formation of ulcers, but the greatest danger is an increased risk of lung cancer and lung tumours through the inhalation of chromium VI. Also, as chromium VI is a skin sensitizer, future reactions can be caused when only a very small amount is in contact with the skin. Inhalation is obviously not a significant risk with leather in consumer goods, but there are dangers from ingestion [9].The main sources ofCr pollution are mining, leather tanning, the cement industry, uses in dyes, electroplating,production of steel, photographic material, and corrosive paints. The principal techniques for recovering or removing Cr from wastewater are chemical reduction and precipitation, adsorption by several types of adsorbents such as activated carbon, pinusSylvester's bark,fly ash and wollastonite, sphagnum moss peat and bone charcoal, ion exchange andmembrane technologies.

Most of these methods suffer from some drawback such as highcapital and operational costs. Therefore there is a need for the development of low cost,easily available materials which can adsorb Cr economically.The physicochemical properties of the adsorbents have been studied using different characterization techniques. The de-sorption process was also studied on saturatedadsorbents using different chemicals such as KOH, NaOH, HNO_3, HCl, H_2SO_4 solution.Among the five chemicals, one was selected as the most efficient de-sorbent.Finally, the adsorbents were applied to the effluents coming from tanneries and it is found effective for the removal of the Cr (III) from the effluent. Thus the study concluded thatthe selected adsorbents serve as an inexpensive and easy to operate as the adsorbent toremove Cr (III) from tannery wastewater discharges.

MATERIALS AND METHODS

Adsorbents collection

Adsorbents which are available in our country are collected from the following points:

Table 1: Collection site of adsorbents

Sl No.	Adsorbents	Collection Site
01.	Plastic	Plastic industry wastes, Household
02.	Rubber	Rubber industry wastes, Factory, Household
03.	Hen hair	Local raw market, Household, Communitycentre
04.	Sheep wool	Tannery industry
05.	Newspaper	Household, Office, Company, Newspaperindustry wastes, Wastage paper market
06.	Activated bone carbon	Hazaribagh dumping sites, Butcher housesites
07.	Goat skin trimmings	Tannery industry
08.	Brick powder	Construction sites
09.	Concrete	Construction sites
10.	Packaging box (Corrugated box)	Household, Office, Company, Corrugatedboxes industry wastes, Wastage paper market

Adsorbents digestion

The selected adsorbents available in our country were first collected and dried in anoven at a temperature of 100 - 105°C for an hour. Then the adsorbents were ground topowder form. From them, 0.5 g of each of the adsorbents was mixed with 6 ml of HNO_3(in case of hair and wool both Nitric acid and Perchloric acid used). The solution wasthen digested in a digester. Finally, the digested solution was made to 10ml with the addition of the required amount of distilled water. The solution was furtherdiluted if required for analysis. The solution was then analyzed by using an AtomicAdsorption Spectrometerto determine the chromium content in the adsorbents before absorptionexperiment. From this analysis, we get the following contents of chromium in differentadsorbents.

Table 2: Chromium content in different adsorbents

Name of the adsorbent	**Chromium content (ppm)**
Plastic	7.15
Rubber	7.48
Hen hair	11.67
Sheep wool	10.67
Newspaper	2.15
Activated bone carbon	0.05
Goatskin trimmings	12.58
Brick powder	0.49
Concrete	7.45
Packaging box (Corrugated box)	2.25

Adsorption experiment

Adsorption experiments were carried out in conical flasks using standard chromiumsolution with the required amount of adsorbent. The flasks were continuously shaken forthe required time period by a shaker at 60 rpm rotation speed till equilibrium reached. Themixtures were filtered through filter paper and the residual Cr (III) concentration afterfiltration was determined using Atomic AbsorptionSpectrophotometer (AA-7000, Shimadzu, Japan, detection limit 0.03 ppm). Volume (V)of the solution was kept constant (100 ml).The effects of various parameters on the rate of adsorptionprocess were observed by varying contact time, t (30,60, 120, 180, 240, 300, 360, 420,480 and 540 min), the initial concentration of chromium ion, Conc. (100, 200, 400, 800,1600and 3200 ug/L), adsorbent concentration, W (1, 2, 3, 4, 5, 6, 7, 8, 9, and 10 g/100 ml) andinitial pH of solution (1.5, 2, 3, 4, 6, 8, 10 and 12). Adsorption isotherm studies werecarried out with different adsorbent doses ranging from 1 to 10 g/100 mL at the same time as maintaining the initial chromium concentration at 200 µg /L. The pH of the solutionwas maintained at the desired value by adding H_2SO_4 or NaOH before adsorption.

Standard solution preparation

Chromium having concentration 1000 ppm was taken as the standard solution at the volumetricflask. Experimental solutions of the desired concentrations were obtained by successivedilutions using dilution theory. The diluted solution was taken 10 ppm and then to required concentration 100ppb, 200 ppb, 400 ppb, 800 ppb, 1600 ppb, 3200 ppb taken for the experiment.

RESULTS AND DISCUSSION

Chromium(III) removal process

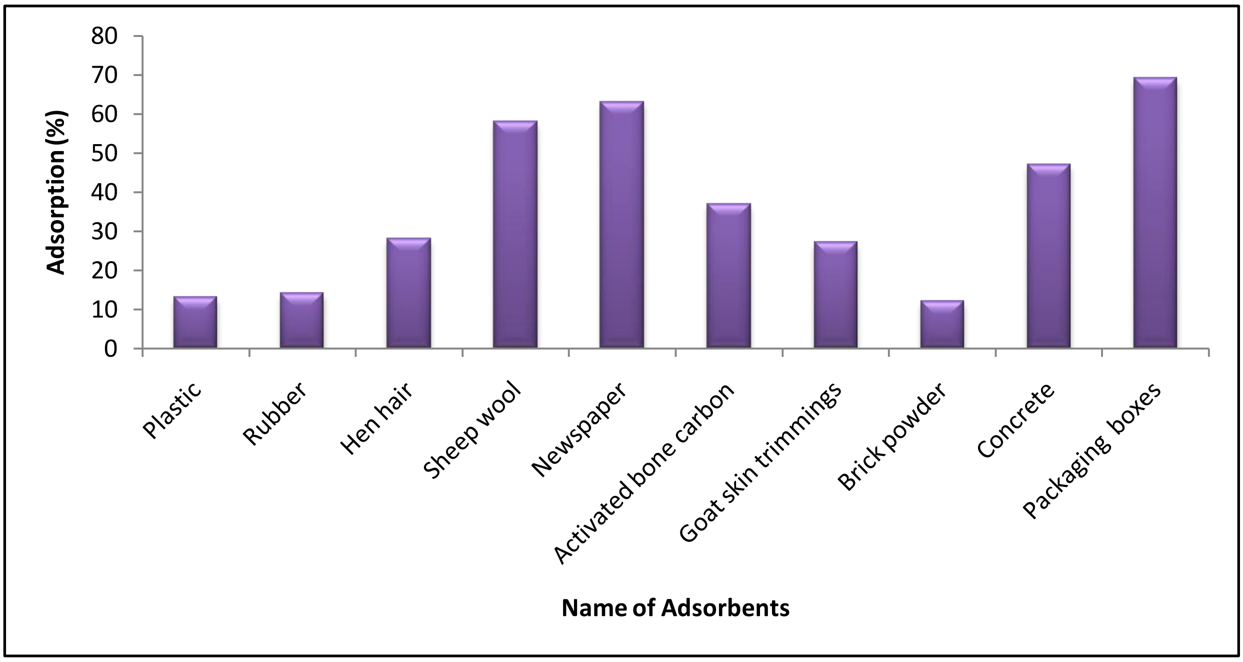

Figure 1: Amount of chromium adsorbed in different adsorbents (contact time 180 min,initial cone 200 µg/L, adsorbent 1 g, initial pH 1.5, agitation speed 60 rpm)

The performances often adsorbents such as Plastic, Rubber, Hen hair, Sheep wool,Newspaper, Activated bone carbon, Goat skin trimmings, Brick powder, Concrete andPackaging (Corrugated box) boxes were evaluated for the removal of Chromium (III)from aqueous solutions. The removal efficiencies with Plastic, Rubber, Hen hair, Sheepwool, Newspaper, Activated bone carbon, Goat skin trimmings, Brick powder, Concreteand Packaging (Corrugated box) boxes were 13%, 14%, 28%, 58%, 63% ,37%, 27%,12%, 47% and

69% respectively. These adsorbents had lower removal efficiencies thanNewspaper and Packaging (Corrugated box) box. Therefore, they were not considered forfurther investigation.

Effect of adsorbent dose on chromium (III) adsorption

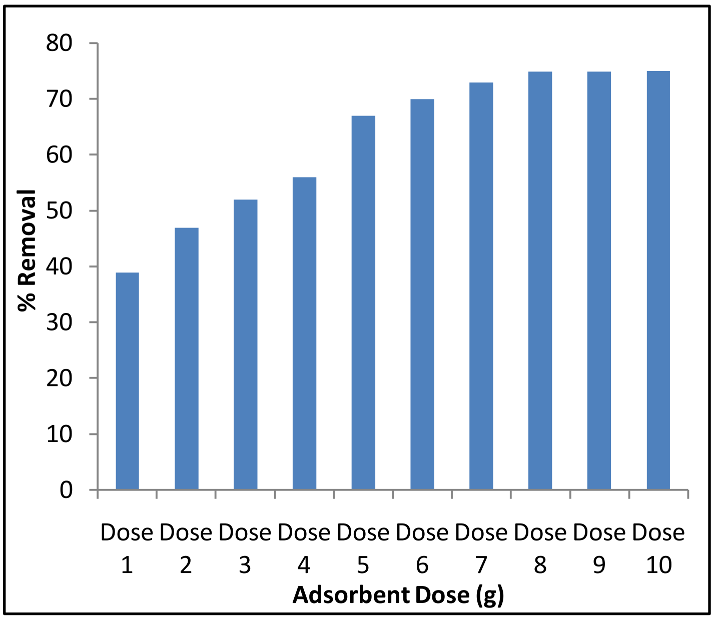

Figure 2: Effect of adsorbent dosage on Cr (III) adsorption (contact time 120 min, initial concentration 200 µg/L, initial pH 1.5 of Cr (III) solution in the case of newspaper

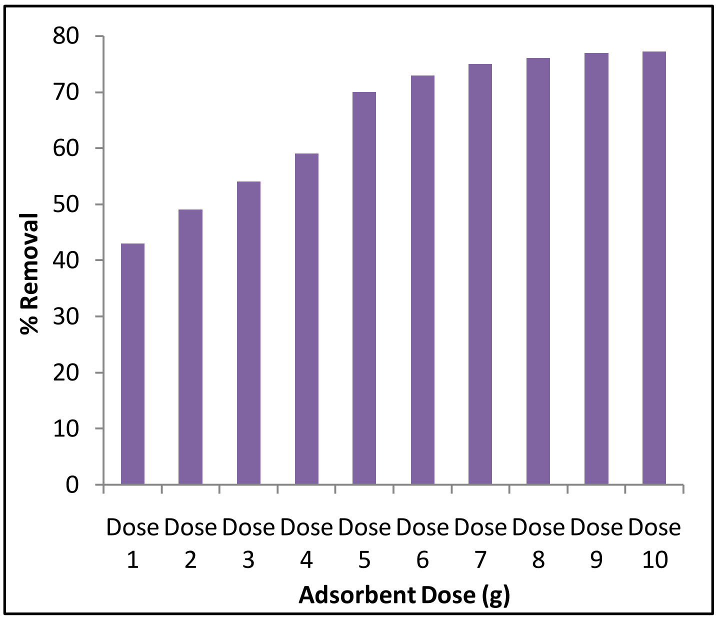

Figure 3: Effect of adsorbent dosage on % removal of Cr(III) ions for aqueous solutions (contact time 120 min, initial concentration 200 µg/L, initial pH 1.5 of Cr(III) solution in the case of packaging box

The experiments were done under the conditions with pH of 1.5 and variableadsorbent doses (1, 2, 3, 4, 5, 6, 7, 8, 9 and 10 g/100 mL). The effect of adsorbent doseson the adsorption of chromium by newspaper and packaging boxwereshowed in Figure 2 and 3. As illustrated inFigure 2 and 3, the increase in percentage adsorption with the increase in adsorbent dose mightbe due to the increased number of free surface available, which caused the increased numberof adsorbate molecules to adsorb. The decrease in uptake might be due to the largersurface area at the higher dose which remained free for adsorption at equilibrium.Chromium removal efficiency increased with increase in adsorbent dose,since contact surface of adsorbent particles increased and then the availability of morebinding sites for adsorption [10].

Effect of contact time on chromium adsorption:

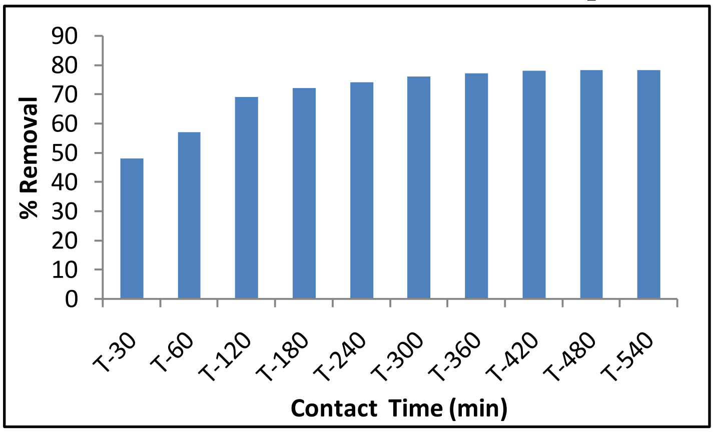

Figure 4:Effect of contact time on Cr(III) removal in the case of Newspaper (initial concentration 200 µg/L, adsorbent dose 5g/100ml, pH 1.5)

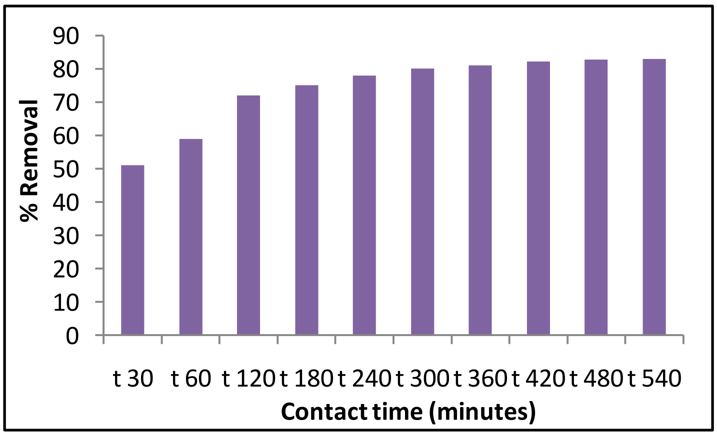

Figure 5:Effect of contact time on Cr(III) removal in the case of Packaging box (initial concentration 200 µg/L, adsorbent dose 5g/100ml, pH 1.5)

In order to find out the equilibrium contact time, experiments were carried out for 9 h.From the experimental data it was observed that, percentage adsorption increased withincrease in contact time up to 6h & 7h and after that it attained a stationary phase respectively. Fromfigure 4&5, it is observed that initially the adsorption rate was fast followed by a slowerrate.

Further, the plots between times vs. percentage adsorption were smooth and continuoussuggesting the possible monolayer adsorption of Cr (III) on the surface of the adsorbent. Asoptimum adsorption was achieved in 2 h, rests of the experiments were carried out for 2 htime.In figure 4, there was no significant change inequilibrium concentration after 360 min up to 420 min and after 360 min, whereas, in figure 5, there was no significant change inequilibrium concentration after 420 min up to 480 min and after 420 min, the adsorptionphase reached to equilibrium. During the initial stage of sorption, a large number ofvacant surface sites are available for adsorption. After a lapse of time, the remainingvacant surface sites are difficult to be occupied due to repulsive forces between theadsorbate molecules on the solid surface and in the bulk phase. Besides, the metal ionsare absorbed into the mesopores that get almost saturated during the initial stage ofadsorption. Thus the driving force for the mass transfer between the bulk liquid phase andthe solid phase decreases with the passage of time. Further, the metal ions have totransverse further and deeper into the pores encountering much larger resistance[11-12]. This results in the slowing down of the adsorption during thelater phase.

Effect of pH on chromium adsorption:

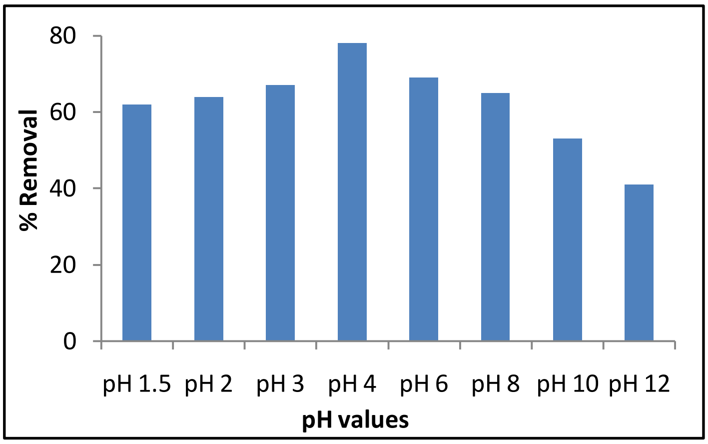

Figure 6:Effect of pH on Cr(III) removal in the case of Newspaper (contact time 120 min, initial concentration 200 µg/L, adsorbent dose 5g/100ml) in the case of Newspaper

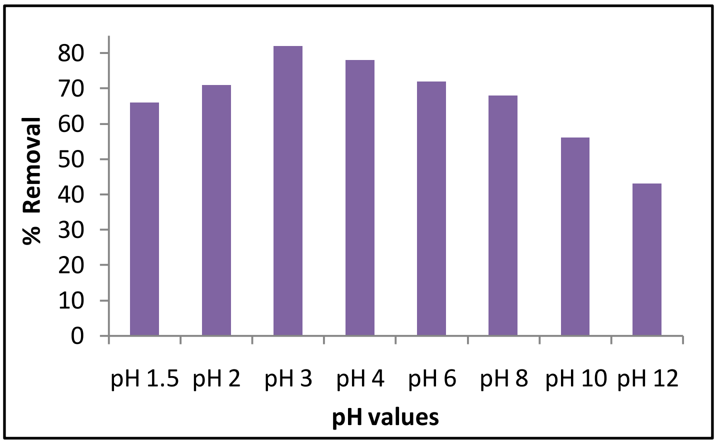

Figure 7:Effect of pH on Cr(III) removal in the case of packaging box contact time 120 min, initial concentration 200 µg/L, adsorbent dose 5g/100ml)

Adsorption experiments were performed at different pH values (1.5, 2.0, 3.0, 4.0, 6.0, 8.0, 10.0, and 12.0). From figure 6, it is observed that the percentage of adsorption increased from 62 to 78 percent at a pH from 1.5 to 4 then decrease the percent adsorption with theincrease of pH up to 12. On the other hand, from figure 7, it is observed that the percentage of adsorption increasedfrom 66 to 82 percent at a pH from 1.5 to 3 then decrease the percent adsorption with theincrease of pH up to 12.The increase in percentage adsorption, as well as uptake at lowerpH, could be well explained by protonation properties of the adsorbent. At low pH values,i.e., higher hydrogen ion concentration, the negative charge at the surface of internal pore were neutralized and some more new adsorption sites were developed which provided a positive charge for anionic Cr (III) complex to get adsorbed on the surface. Again it isobserved that the final pH of the solution was always greater than the initial pH of thesolution, which confirmed the neutralization of H^+ions with the negative charge at thesurface and envelopment of more H^+ions in the formation of the positively charged surface. As aresult, the concentration of H^+ions decreased in the solution and hence the pH of the solution increased. Many authors also reported similar results [13]. From the adsorption uptake at both higher and lower pH (12 and 1.5), it is concluded that theadsorbent can be used for the treatment of Cr (III) contaminated Tannery water at lowerpH.

Effect of initial chromium concentration on adsorption Process

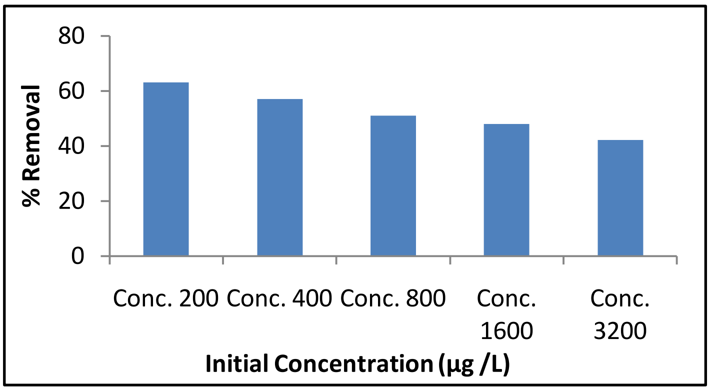

Figure 8:Effect of initial concentration on Cr(III) removal in the case of Newspaper (contact time 120 min, adsorbent dose 5g/100ml, pH 1.5)

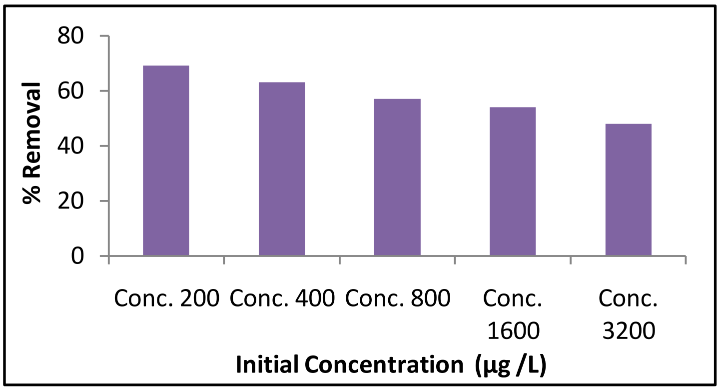

Figure 9:Effect of initial concentration on Cr(III) removal in the case of Packaging box (contact time 120 min, adsorbent dose 5g/100ml, pH 1.5)

The percentage adsorption with different adsorbate concentrations was studied by varyingCr (III) concentration from 200 ppb to 3200 ppb keeping the adsorbent dose at (5g/100 ml),stirring speed (60 rpm), pH (1.5) and temperature (25^{0}C) constant. Figure8 & 9shows theeffect of initialadsobate concentration. It was observed that the percentage of adsorptiondecreased with the increase of adsorbate concentration.This may be due to the fact that at a fixed adsorbent dose, the number of active adsorptionsites toaccommodate the adsorbate ions remained unchanged while with higher adsorbateconcentrations, the adsorbate ions to be accommodated increased. Thus, the loading wasfaster with higher initial concentrations of adsorbate.

Effect of particle size chromium adsorption

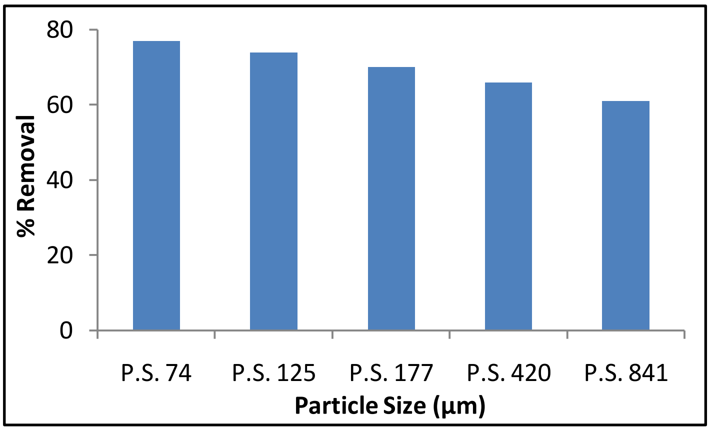

Figure 10:Effect of particle size on Cr(III) removal in the case of Newspaper (contact time 120 min, initial concentration 200 µg/L, adsorbent dose 5g/100ml, pH 1.5)

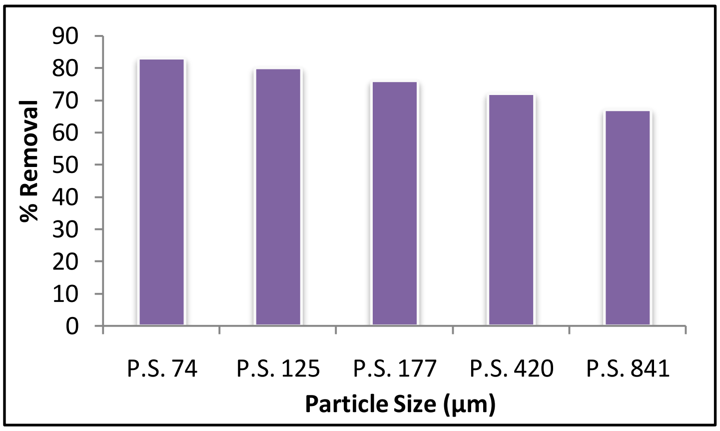

Figure 11:Effect of particle size on Cr(III) removal in the case of packaging box (contact time 120 min, initial concentration 200 µg/L, adsorbent dose 5g/100ml, pH 1.5)

Batch adsorption experiments were carried out for the removal of chromium from aqueous solution using five different particle sizes (0.074, 0.125, 0.177, 0.42, 0.841 mm).The results are shown in figure 10 & 11, with decreasing particle size, the removalincreased from 61 to 77% and 67 to 83% respectively.When the size of theadsorbent particles increased, the adsorption of metal ions decreased [14-15]. These phenomena might be due to the fact that thesmaller particles offer comparatively larger surface areas and greater numbers ofadsorption sites compare to larger particles.

DESORPTION

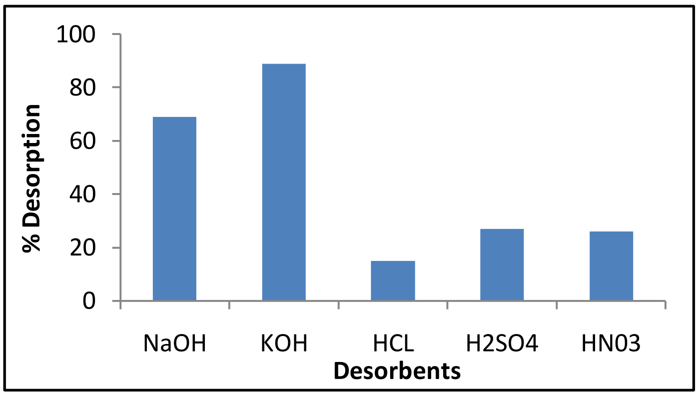

Figure 12:Desorption in case of Newspaper using different desorbents (shaking time 2 hours, conc. 0.5M)

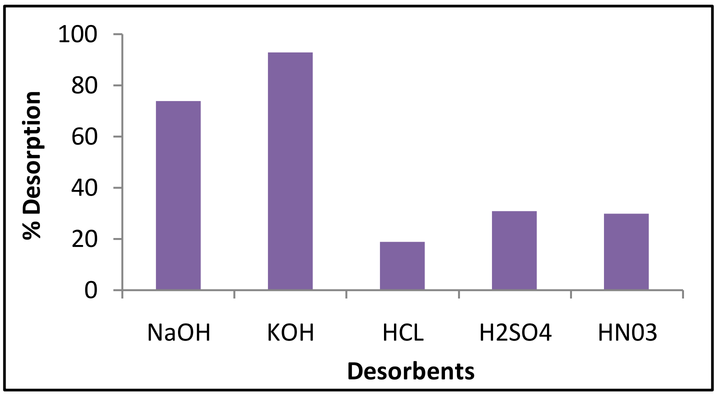

Figure 13: Desorption in case of Packaging using different desorbents (shaking time 2 hours, conc. 0.5M)

Recovery of the adsorbed material and regeneration of the adsorbent are also important aspects of wastewater treatment. Attempts were made to desorb chromium (III) from the ground newspaper surface with various eluents, such as hydrochloric, sulfuric and nitricacid solutions and base solutions containing sodium hydroxide and potassium hydroxide.For each experiment, after adsorption, 100mL of desorption solution was added to theadsorbent and was shaking for two hours. The results are shown in figure 12 & 13. Thepresent work showed that effective desorption was obtained with alkaline solutions. These phenomena are consistent with the results observed for the effect of pH. Potassium hydroxide solution was used for desorptionof chromium from the surface ofnewspaper and the desorption efficiencies with 0.5M of KOH were89% and 93% respectively.

Adsorption Isotherms

Freundlich isotherm

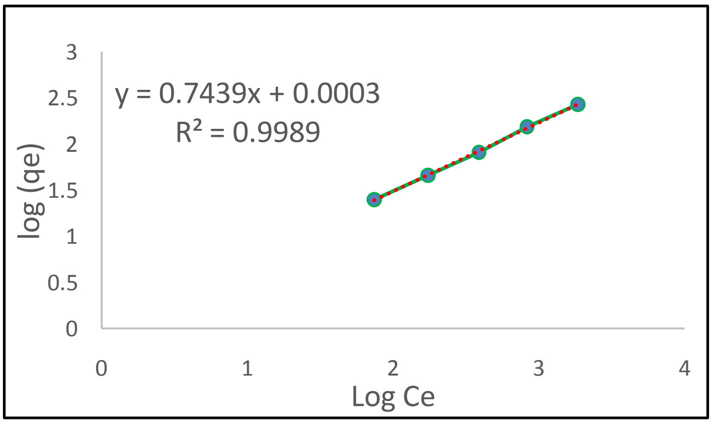

Figure 14: Freundlich isotherm (newspaper)

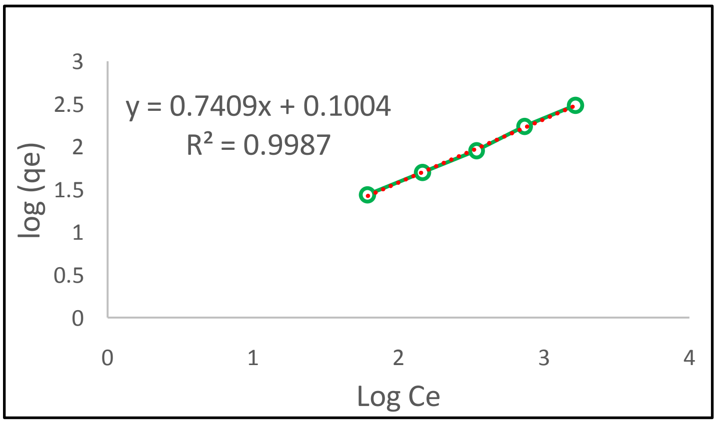

Figure 15: Freundlich isotherm (packaging box)

Langmuir isotherm

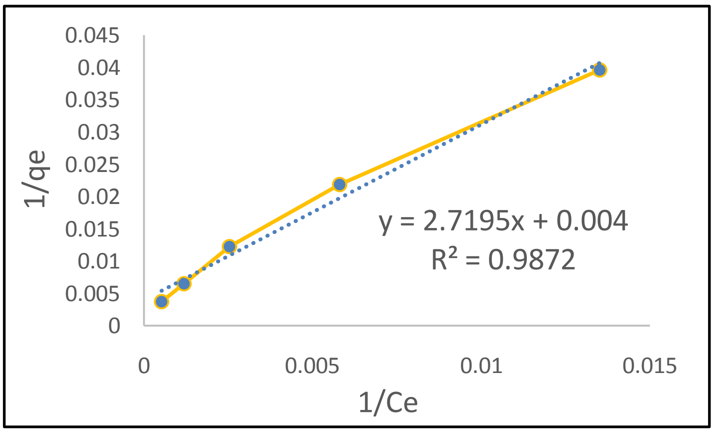

Figure 16: Langmuir isotherm (newspaper)

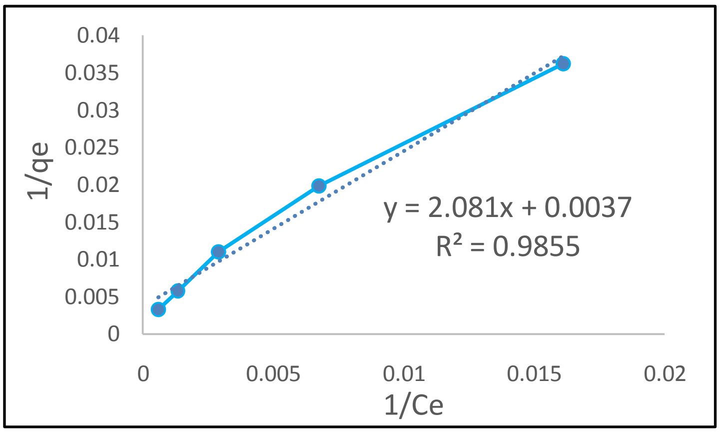

Figure 17: Langmuir isotherm (packaging box)

Pseudo first order kinetics

In order to find the adsorption kinetic of heavy metal ions, the kinetic parameters for the adsorption process were studied for contact times ranging from 30 to 540 min bymonitoring the removal percentage of the Cr (III). The data were then regressed againstthe Lagergren equation, which represents a first-order kinetics equation [16].

$$\log (q_e - q_t) = \log q_e - (K_1/2.303)t$$

where, q_t is the metal uptake per unit weight of adsorbent (ug/g) at time t, q_e is the metal uptake per unit weight of adsorbent (ug /g) at equilibrium, and $k_1(min^{-1})$ is the rateconstant of the pseudo-first-order [17]. The slopes and intercepts of thesecurves were used to determine the values of K_1, as well as the equilibrium capacity (q_e).

The correlation coefficient and rate constants of kinetic variables in case of newspaper and packaging boxwere presented. The correlation coefficients are in good agreementwith the pseudo first-order kinetics in this studied.

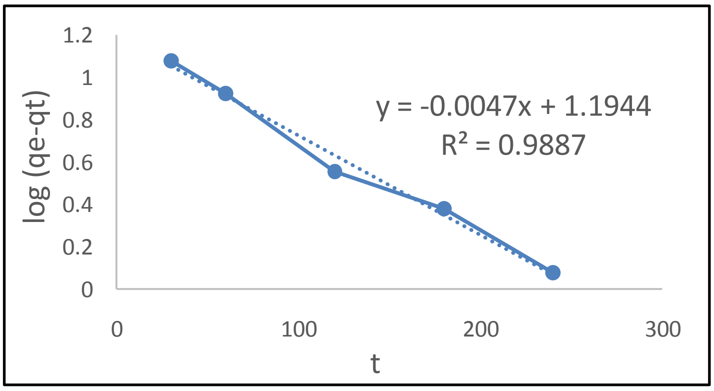

Figure 18: Kinetic variables in case ofnewspaper

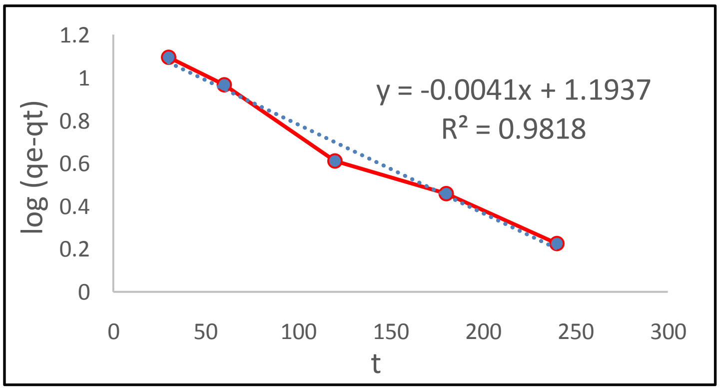

Figure 19: Kinetic variables in case of packagingbox

FT-IR Analysis

FT-IR analysis for newspaper

Apart from the electrostatic force of attraction, the adsorption might be due to the formation ofthe complex in the ligands available in the adsorbents. The adsorbent as such showed peaks at 893.06, 1029.04, 1344.41, 1422.53, 1501.61 and 1664.60 cm^{-1}. The results are shownin table 3.

Table 3: FT-IR peaks and group assignment of Newspaper

Peak wavelength(cm^{-1})	Assign to
893.06	=C-H bending usually strong
1029.04	C-F stretching, strong
1344.41	C-N stretching, medium weak
1422.53	-C-H bending, variable
1501.61	C=C stretch, medium weak, multiple bands
1664.60	C=C stretch usually variable

FT-IR analysis for packaging box

Apart from the electrostatic force of attraction, the adsorption might be due to the formation ofthe complex in the ligands available in the adsorbents. The adsorbent as such showed peaks at 896.91, 1030.97, 1421.56, 1675.21, 2881.70 and 3618.52 cm^{-1}. The results are shownin table 4.

Table 4: FT-IR peaks and group assignment of Packaging Box

Peak wavelength (cm^{-1})	Assign to
896.91	=C-H bending usually strong
1030.97	C-F stretching usually strong
1421.56	-C-H bending, variable
1675.21	C=C stretch, variable
2881.70	C-H stretch, usually strong
3618.52	0-H (Stretch, free), usually strong, sharp

Conclusion

The experimental results show that newspaper and packaging box (corrugated box) arethe excellent alternative for the removal of Cr (III) from aqueous solution. The adsorption ofCr (III) was dependent on pH, particle sizes, contact time, adsorbent dose and initialchromium concentration. It was observed that the best efficiency of absorption of Cr (III)by newspaper is at a condition of pH 4, adsorption time 2 hours, adsorbent amount 5g/100 ml solution of 200 ppm Cr (III) solution and that for packaging box is at acondition of pH 3, adsorption time 2 hours, adsorbent amount 5g/100 ml solution of 200 ppm Cr (III) solution.Both Langmuir and Freundlich isotherms were followed by theadsorption of Cr (III). The kinetic analysis of the study showed that the adsorption of Cr(III) ions onto powdered newspaper and packaging box could be well described with thepseudo-first-order kinetic model. The de-sorption experiments show that the metal can bedesorbed after adsorption and Cr (III) can be recovered. Based on the results of this research, Newspaper and Packaging box can be considered as available, low-cost, environmental friendly and effective adsorbent for removal of chromium from tannerywastewater.

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