

Removal of Chromium from Real Tannery Effluent by Using Bioadsorbents

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Abstract: Several low cost biomaterials such as rice husk, saw dust and eucalyptus bark (EB) were tested for removal of chromium. All the experiments were carried out in batch process with real effluents collected from several industries. The adsorbent, which had highest chromium (VI) removal was EB. Influences of chromium concentration, contact time on removal of chromium from effluent was investigated. The adsorption data were fitted well by Langmuir isotherm. The results indicated that eucalyptus bark can be used for the removal of chromium.

Keywords: tannery effluent, eucalyptus bark, adsorption:

I. INTRODUCTION

Water pollution by chromium is of considerable concern, as this metal has found widespread use in electroplating, leather tanning, metal finishing, nuclear powerplant, textile industries, and chromate preparation. Chromium exists in two oxidation states as Cr(III) and Cr(VI). The hexavalent form is 500 times more toxic than the trivalent (Kowalski, 1994). It is toxic to microorganisms, plants, animals and humans. Human toxicity includes lung cancer, as well as kidney, liver, and gastric damage (US Department of Health and Human Services, 1991; Cieslak-Golonka, 1995). The tanning process is one of the largest polluters of chromium all over the world. Most of the tanneries in India adopt the chromium tanning process because of its processing speed, low costs, and light color of leather and greater stability of the resulting leather. In the chromium tanning process, the leather takes up only 60–80% of applied chromium, and the rest is usually discharged into the sewage system causing serious environmental impact. Chromium ion in liquid tanning wastes occurs mainly in trivalent form, which gets further oxidized to hexavalent Cr(VI) form, due to the presence of organics. The maximum levels permitted in wastewater are 5 mg/L for trivalent chromium and 0.05 mg/L for hexavalent chromium (Acar and Malkoc, 2004). With this limit, it is essential for industries to treat their effluents to reduce the Cr to acceptable levels. Due to more stringent environmental regulations, most of the mineral processing plants, metal-finishing industries are facing nowadays the difficult problem of disposal of wastewater produced in huge quantities, laden with Cr. Chromium metal ions are usually removed by precipitation (Patterson, 1977), although ion exchange (Tiravanti et al., 1997) and adsorption (Dahbi et al., 1999; Orhan and Buyukgangor, 1993) are also used for its removal. The hydroxides of heavy metals are usually insoluble, so lime is commonly used for precipitating them. The most important factor in precipitation of heavy metal is the valence state of metal in water. Cr whose hexavalent form, chromate, is considerably more soluble than trivalent form, Cr(III). In this case, the chromate, in which Cr is present as Cr(VI) must be reduced usually with SO₂ available from sodium metabisulphite at low pH for removal of chromium as Cr(III) by precipitation process. Another aspect of precipitation process is the zeta potential of the initial heavy metal colloidal precipitate.

In many plants where heavy metals are being removed, one of the principal problems in reaching the desired effluent limits is the colloidal state of precipitated materials. They have not been properly neutralized, coagulated and flocculated. A final aspect of heavy metals is the possible formation of complex ions, which is common when dealing with wastewaters containing ammonia, fluoride, or cyanide ions along with heavy metals. Because of these important aspects in the precipitation of heavy metals, there is no way to predict the best solution of a specific problem without undergoing a series of bench tests to evaluate the alternative available (Kemmer, 1988). The present study is aimed at selection of a low cost biosorbent, which can adsorb chromium from the wastewater. Detailed batch studies with the selected adsorbent, eucalyptus bark has been carried out in the present investigation. The effect of pH and temperature, contact time, adsorbent concentration were also investigated.

II. METHODS

2.1. Materials

The adsorbents selected for the preliminary study was Eucalyptus bark (EB). These were grounded and washed with deionized water. The adsorbents were dried at room temperature, (32 ± 1 °C) till a constant weight of the adsorbent was achieved. A uniform particle size of the adsorbent was maintained between 120 and 500 μm .

2.2. Preparation of eucalyptus bark adsorbent

Eucalyptus bark of Eucalyptus globulus tree species was collected from the local area. The bark was grounded to small particles of size $120 < d_p < 500$ μm . It was washed with deionized water and then dried. To avoid, the release of color by bark in to the aqueous solution during adsorption, it was treated with formaldehyde (Randall et al., 1976). For this 5 mL of aqueous formaldehyde was added to 100 mL of 0.1 M H_2SO_4 and then 10 g of grounded and washed bark was added to this solution. The final mixture was stirred and heated at 50 °C for 24–48 h till the mixture became thick slurry. The slurry (treated bark) was washed with deionized water until the pH of the filtrate was more than 4.5. Finally the bark was air-dried and sieved. Particles in the range of 120–500 μm size were collected as the final adsorbent.

2.3. Determination of chromium content

The chromium concentration in raw and treated effluent was determined by UV spectrophotometer. The wavelength of operation was kept at 540 nm. For this purpose, $\text{K}_2\text{Cr}_2\text{O}_7$ solutions of different concentrations were prepared and their absorbance recorded by using a UV-spectrophotometer. A calibration plots for Cr(VI) were drawn between % absorbance and time. Runs were made in triplicate. Cr(III) concentration was determined by measuring the difference between total chromium concentration and Cr(VI) concentration. Total Cr concentration was determined by oxidizing Cr(III) to Cr(VI) using KMnO_4 and then determining final Cr(VI) content in the sample.

2.4. Experimental

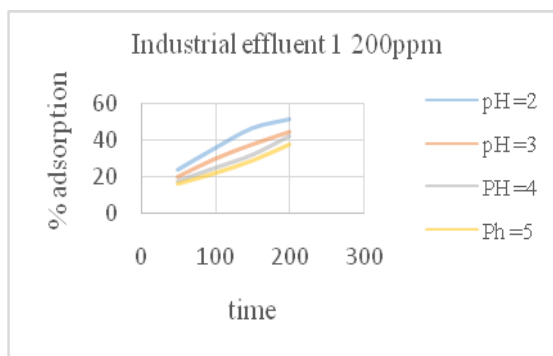
Stock solution of various concentration of Cr(VI) was prepared by dissolving $\text{K}_2\text{Cr}_2\text{O}_7$, in deionised, double-distilled water. All the batch adsorption studies were carried out using 100 mL of solution of appropriate concentration as desired by dilution of the stock solution. Requisite quantity of adsorbent was added to 250 mL plastic reagent bottles containing 100 mL of synthetic effluent of Cr(VI). The bottles were placed in a shaker at 32 ± 1 °C, for 24 h. The speed of shaker was kept at 100 rpm. After 24 h the bottles were removed and the content of the bottles was filtered through a filter paper. The filtrate was analyzed for p^{H} and final chromium concentration using UV spectrophotometer. The removal of Cr(VI) was studied by using eucalyptus bark. For all these runs the adsorbent dose was kept at 5 g/L of synthetic effluent of Cr(VI). Further studies which involved, varying initial Cr(VI) concentration ranging from 200 and 250 ppm. The pH was varied from 2 to 5 of with different initial concentrations. The temperature was varied from 30 °C to 45 °C of with different initial concentrations. The contact time in batch was varied from 50 s to 200 s. The studies were also carried with industrial effluent obtained from leather industry. The characteristics of industrial effluent is as follows: Cr(VI) concentration 200 mg/L, Cr(III) concentration 250 mg/L, total dissolved solids 780 mg/L, Ca concentration 135 mg/L and Mg concentration 92 mg/L.

III. RESULTS AND DISCUSSION

3.1. Effect of pH

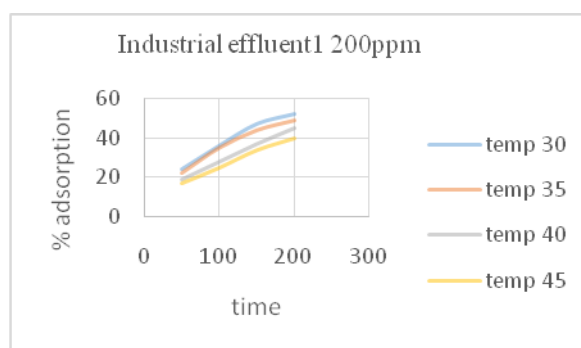
Effect of solution pH on removal of Cr was studied using EB as sorbent. As the pH of the solution was increased from 2 to 5 the adsorption of Cr(VI) decreased. Increasing p^{H} from 2 to 5, percent removal of Cr(VI) (200 ppm) decreased 92 to 52, whereas as the pH was increased from 2 to 5 the % removal of Cr(VI) (250 ppm) decreased significantly from 81 to 48. It was observed that the maximum percentage of removal of Cr(VI) was at p^{H} 2. Almost 100% of Cr(VI) removal was observed at this p^{H} at 200 ppm Cr(VI) concentration. Dominant form of Cr(VI) at initial p^{H} of 2 is HCrO_4^- (Namasivayam and Yamuna, 1995). Increase in p^{H} shifts concentration of HCrO_4^- to other forms, CrO_4 and $\text{Cr}_2\text{O}_7^{2-}$. It can be concluded that the active form of Cr(VI) that can be adsorbed by EB was HCrO_4^- . Further it was observed that there was an increase in pH during adsorption. The increase in p^{H} with contact time explained by hydrolysis of the adsorbent in water, which will create positively charged sites. Upon adsorption of HCrO_4^- , a net production of hydroxide ions will occur as shown below (Saliba et al., 2002). $\equiv \text{OH}_2^+ + \text{HCrO}_4^- \leftrightarrow \equiv \text{OH}_2^+(\text{HCrO}_4^-)$

Every mole of HCrO_4^- adsorbed results in the release of two moles of hydroxyl ions in the solution, which raises the solution p^{H} (Namasivayam and Yamuna, 1995). This change in p^{H} at lower initial p^{H} is very small since the solutions at lower p^{H} are well buffered by the acids used in this p^{H} range.



3.2. Effect of temperature:

The effect of temperature on the adsorption process were identified as follows The change in adsorption with respected to time and temperature were noted.this helped to study about the influence of temperature on adsorption



synthetic effluent concentration 200ppm temp 30 ⁰ C				
	P ^H =2	P ^H =3	P ^H =4	P ^H =5
Time	% adsorption	% adsorption	% adsorption	% adsorption
50	82	58	47	31
100	85	68	52	40
150	88	75	61	46
200	92	78	67	52
synthetic effluent concentration 200ppm,p ^H =2				
	temp 30 ⁰ C	temp 35 ⁰ C	temp 40 ⁰ C	temp 45 ⁰ C
Time	% adsorption	% adsorption	% adsorption	% adsorption
50	82	80	77	75
100	85	82	79	77
150	88	85	81	80
200	92	87	84	82
synthetic effluent concentration 250ppm,temp30 ⁰ C				
	P ^H =2	P ^H =3	P ^H =4	P ^H =5
Time	% adsorption	% adsorption	% adsorption	% adsorption
50	58	51	43	31
100	66	58	47	36
150	78	64	51	40
200	81	71	57	48
synthetic effluent concentration 250 ppm, p ^H =2				
	temp 30 ⁰ C	temp 35 ⁰ C	temp 40 ⁰ C	temp 45 ⁰ C
Time	% adsorption	% adsorption	% adsorption	% adsorption
50	58	55	51	48
100	66	59	54	52
150	78	65	58	55
200	81	75	67	59
real effluent 1 concentration 200ppm,temp 30 ⁰ C				
	P ^H =2	P ^H =3	P ^H =4	P ^H =5
Time	% adsorption	% adsorption	% adsorption	% adsorption

50	24	20	18	16
100	36	30	25	22
150	47	38	32	29
200	52	45	42	38
real effluent 1 concentration 200 ppm, p^H=2				
	temp 30 ^o C	temp 35 ^o C	temp 40 ^o C	temp 45 ^o C
Time	% adsorption	% adsorption	% adsorption	% adsorption
50	24	22	19	17
100	36	35	28	25
150	47	44	37	34
200	52	49	45	40
real effluent 1 concentration 250 ppm,temp30^oC				
	p ^H =2	p ^H =3	p ^H =4	p ^H =5
Time	% adsorption	% adsorption	% adsorption	% adsorption
50	20	14	12	9
100	28	24	18	16
150	38	32	26	22
200	44	38	34	28
real effluent 1 concentration 250 ppm,p^H=2				
	temp 30 ^o C	temp 35 ^o C	temp 40 ^o C	temp 45 ^o C
Time	% adsorption	% adsorption	% adsorption	% adsorption
50	20	18	17	15
100	28	25	21	19
150	38	33	29	24
200	44	40	36	32
real effluent 2 concentration 200 ppm,temp 30^oC				
	p ^H =2	p ^H =3	p ^H =4	p ^H =5
Time	% adsorption	% adsorption	% adsorption	% adsorption
50	25	21	19	17
100	35	32	28	22
150	47	41	37	32
200	54	47	43	37
real effluent 2 concentration 200 ppm,p^H=2				
	temp 30 ^o C	temp 35 ^o C	temp 40 ^o C	temp 45 ^o C
Time	% adsorption	% adsorption	% adsorption	% adsorption
50	25	22	20	18
100	35	31	27	23
150	47	40	35	31
200	54	49	45	42
real effluent 2 concentration 250,temp 30^oC				
	p ^H =2	p ^H =3	p ^H =4	p ^H =5
Time	% adsorption	% adsorption	% adsorption	% adsorption
50	19	16	15	12
100	24	20	18	14
150	33	28	24	21
200	46	39	30	27
real effluent 2 concentration 250ppm,p^H=2				
	temp 30 ^o C	temp 35 ^o C	temp 40 ^o C	temp 45 ^o C
Time	% adsorption	% adsorption	% adsorption	% adsorption
50	19	17	16	14
100	24	21	19	18
150	33	31	28	25
200	46	40	37	32

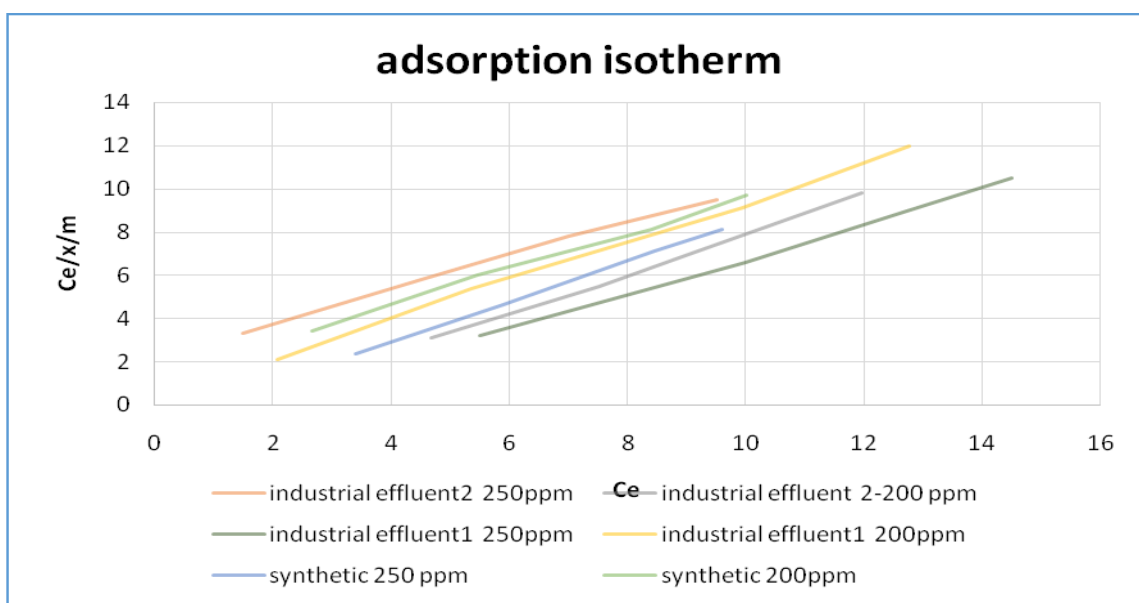
3.3. Effect of contact time

Fig. shows the effect of contact time. Increasing contact time from 0.25 h to 3 h increases % Cr removal. Maximum Cr removal was observed with in first 2 h. The kinetic data was fitted to the Lagergren equation (Singh and Pant, 2004).

$$\log(x_e - x) = \log x_e - K_{ads}t / 2.303$$

x = the amount of solute, Cr(VI), (mg/g of adsorbent) removed at time t, x_e = amount removed at equilibrium and K_{ads} = the rate constant of adsorption (1/min). The effect of contact time was studied for removal of Cr from effluent containing 200ppm of Cr(VI) at 32 ± 1 °C, p^H 2, p^H 3, p^H 4, p^H 5. Experiments were also carried out

industrial effluent containing Cr(VI) 200ppm and Cr(III) 250 ppm. For EB the contact time of 3 h was needed to establish equilibrium. The kinetic on different solution of Cr(VI) at different p^H with EB as adsorbent was found to follow the first order rate.



3.4. Adsorption isotherm

Adsorption isotherms, which are the presentation of the amount of solute adsorbed per unit of adsorbent, as a function of equilibrium concentration in bulk solution at constant temperature, were studied. The equilibrium data obtained were fitted to Langmuir isotherms.

Linear form of Langmuir equation,

$$1/X = 1/X_m + (1/C_e)(1/b \cdot X_m)$$

$X = x/m$, where 'x' is in mg the amount of solute adsorbed, 'm' is unit gram of adsorbent, C_e is the equilibrium concentration of solute (mg/L); X_m is the amount of solute adsorbed per unit weight of adsorbent required for monolayer coverage of the surface also called monolayer capacity and b is a constant related to the heat of adsorption.

IV. CONCLUSION

Removal of poisonous hexavalent form of chromium from solutions was possible using selected adsorbents. Eucalyptus bark (EB) was the most effective for which the removal reached 92% for Cr(VI) at concentration of 200ppm and at pH 2. Increase in the dose of adsorbent, initial concentration of Cr(VI) and increase in contact time up to 2 h are favorable for all increase the adsorption of Cr(VI). The kinetic of the Cr(VI) adsorption on EB was found to follow first order mechanism. The Gibbs free energy was obtained for each system. It was found to be -1.884 kJ/mol for Cr(VI) and -3.872 kJ/mol for Chromium(III) for removal from industrial effluent. The adsorption data can be satisfactorily explained by Langmuir isotherm. Higher sorption capacity of this sorbent indicates that eucalyptus bark can be used for the treatment of chromium effluent.

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