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Removal of Hexavalent Chromium (Cr (VI)) from Aqueous Solution Using Corncob and Pine Sawdust Biosorbents

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Abstract

Hexavalent chromium is a major pollutant released during several industrial operations. It is carcinogenic and has an adverse potential to modify the DNA transcription process. In this study removal of Cr (VI) from aqueous solution using corn cob and pine sawdust biosorbents has been studied by using batch adsorption techniques. Single beam UV-Visible spectrophotometer was used to monitor the concentration of Cr (VI) before and after adsorption. The influence of contact time, pH, initial chromium ion concentration, adsorbent dose and agitation speed on the efficiency of adsorption process were studied for both corn cob and pine saw dust. Among the studied parameters, agitation speed was found to be the most influential. At the optimum agitation speed, for corn cob (180 rpm, 94.64 %) and for pine sawdust (90 rpm, 93.1%) removal of Cr (VI) were achieved. The results indicate that these adsorbents can be employed as low cost alternatives to commercial adsorbents for the removal of Cr (VI) from effluents. Adsorption isotherms and kinetics were also studied. The results showed that the adsorption of Cr (VI) by these adsorbents follows Langmuir adsorption isotherm while the adsorption kinetics process follows the pseudo-second-order for both adsorbents.

Key words: hexavalent chromium, Isotherms, Kinetics, Bioadsorbents, Spectrophotometer

1. Introduction

The discharge of non-biodegradable heavy metals like copper, zinc, nickel, lead, cadmium and chromium into water stream is hazardous because the consumption of polluted water causes various health problems (Anjali et al., 2016).

Hexavalent Chromium is one of the heavy metals emitted from textile dye, tannery, nuclear power plants, and battery making steel and electroplating industries which cause chronic disorders in human. It is one of the most common metals present in the effluents. It is known to be carcinogenic and has an adverse potential to modify the DNA transcription process (Anjali et al., 2016, Rodgher and Espíndola, 2008). According to the Indian standards the permissible limit for chromium (VI) for potable drinking water is 0.05mg/l, for industrial effluent discharge into inland surface water is 0.10 mg/l and for public sewage is 2.00 mg/l (Venkateswarlu, 2007). But the industrial effluents contain much higher concentrations compared to the permissible limit. Cr(VI) can be removed from wastewater by various methods such as chemical precipitation, electrochemical reduction, sulphide precipitation, ion-exchange, reverse osmosis, electro dialysis, solvent extraction, evaporation, etc. These methods are very costly and are not affordable for large scale treatment of wastewater that is rich in hexavalent chromium. Therefore, there is currently a need for

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new innovation and cost effective methods for the removal of toxic substance from waste waters. Many researchers have studied various biosorbents which are relatively inexpensive and same time endowed with reasonable adsorption capacity including agricultural materials such as barks of Acacia albida, untreated coffee husks, saw dust and charcoal from sugarcane biogases (Gebrehawria, 2014). In this study it has been tried to remove Cr(VI) from artificially polluted water using corn cob and pine sawdust biosorbents.

2. Materials and Methods

Single beam UV–Visible spectrometer (XP -1000P, China, Number 2000708004) and Model 0.16 pH meter were mainly used to monitor the concentration of Cr(VI) before and after adsorption processes and to measure the pH of the solution, respectively. Digital electrical shaker was used to evaluate the adsorption efficiency with different agitation speeds. Potassium dichromate, $K_2Cr_2O_7$ (99.9 %, BDH) was used to prepare the required Cr(VI) solutions and distilled water was used throughout the experiment.

2.1 Adsorbent collection and preparation

Corncob and pine sawdust bio adsorbents were collected from nearby villages of Dilla town, Ethiopia. After the materials had been collected, they were cut in to small pieces and crushed manually by using mortar and pestle. These adsorbents were washed with tap water to remove any particulate matter and finally washed with distilled water. The adsorbents then dried in sun light for about 7 days. Then the adsorbents powder sieved using 0.5 mm sieve particle size analyzer and finally made ready prior to analysis.

2.2 Batch adsorption experiments

Five working standard Cr(VI) solutions with different concentrations 2, 4, 6, 8 and 10 ppm were prepared for calibration (Figure 1).

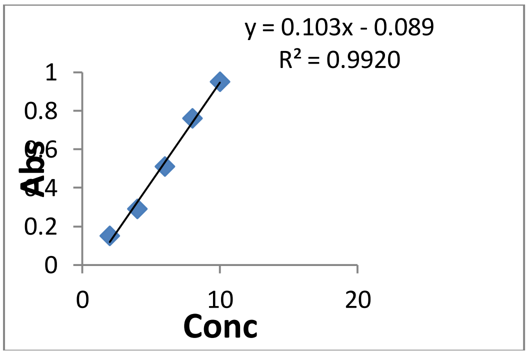

Fig. 1: Cr(VI) calibration curve

Batch experiments were carried out using a series of 100 ml volumetric flasks to investigate the effects of different parameters. Known amount of adsorbents were added to the solution. The mixture was shaken using electrical shaker. The suspensions were filtered using No.42 Watman filter paper and the concentration of the metal ion in the filtrate was analyzed using single beam UV- Visible spectrophotometer. The effects of various parameters on percentage of adsorption was observed by varying contact time (5,10,20,40,60,80,100 and 120 min) initial concentration of chromium (VI) ions, Co (5,8,11,14,17 and 20 mg/L), adsorbent dosage (0.5,1,1.5,2, 2.5 and 3 g), PH (2,3,5,7,9 and 11) and agitation speed (60,90,120,150,180 and 210). The Cr (VI) removal (%) at any instant of time was determined by the Eq. (1).

$$\textit{Chromium removal (\%)} = \frac{Co-Ct}{Co} X\ 100 \qquad (1)$$

Where C_o and C_t (mg /L) are the concentration of Cr (VI) ions initially and at a given instant of time, respectively. All experiments were carried out in triplicate measurements.

2.3 parameters Optimization

Five parameters, Contact time (5,10,20,40,60,80,100,120 minutes), pH (2, 3,5,7,9,and11), Initial (VI) concentrations (5,8,11,14,17,20 mg/L), adsorbent dosages (0.5,1.0,1.5,2.0,2.5,3 g) and agitation speeds (60, 90, 120, 150, 180, 210 rpm) have been studied for both corn cob and pine sawdust biosorbents (section 3).

3. Results and Discussion

3.1 Effect of contact time

In this experiment, all of the parameters include pH (natural pH, 5.62) initial chromium concentration(7 mg/L), adsorbent dose (1 g/100 mL), agitation speed (180 rpm) were kept constant while contact time was varied (5,10,20,40,60,80,100,120 minutes) for both adsorbents. The effect of contact time on Cr(VI) adsorption efficiency was monitored by directly measuring concentration of Cr(VI) ions before and after adsorption process using UV/Visible Spectrophotometer.

There is general increment in percent removal to a certain contact time. This is due to the unsaturation of the active sites in the adsorbents surfaces

(Abdullah and Devi, 2009, Singha and Das, 2010). The optimum contact time for corn cob is 60 mints (71.85 %) and 20 mints (74.89 %) for pine sawdust There is a decrement in the removal efficiency for both corn cob and pine sawdust after 60 and 20 mints contact time ,respectively. Therefore, 20 min for saw dust and 60 min for corn cab were selected as optimum contact time for both adsorbents and used in subsequent optimizations.

Table 1 Effect of contact on Cr(VI) removal

Time	Corncob		Pine Sawdust	
	Cf*	% removal (Sd,n=3)	cf*	% removal (Sd,n=3)
5	2.20	68.57(0.1227)	2.184	68.79(0.034)
10	2.28	67.4(0.701)	1.980	71.7(0.525)
20	2.23	67.4 (0.175)	1.757	74.89(0.525)
40	1.94	70.85(0.277)	2.039	70.59(0.069)
60	1.91	71.85(0.1402)	2.097	70.00(0.862)
80	2.08	70.18(0.1402)	2.165	69.00(0.702)
100	2.12	69.76(0.03501)	2.401	65.6(0.526)
120	2.36	66.297(0.0701)	2.600	62.69(0.053)

Where Cf* is final concentration (mg/L) remaining in the filtrate.

3.2 Effect of PH

pH is the main factor that affects the adsorbents uptake of Cr(VI) from the aqueous solution. The effect of pH for the two adsorbents was monitored and optimized by varying the solutions pH, (2, 3, 5, 7, 9, and 11) while keeping the other parameters constant (Table 2).

Table 2 Effect of pH on Cr(VI) removal

pH	Corncob		Pine Sawdust	
	Cf*	% removal (Sd,n=3)	cf*	% removal (Sd,n=3)
2	1.25	82.1(0.125)	1.407	79.88(0.038)
3	1.457	79.6(0.526)	1.59	77.025(0.044)
5	1.9	72.92(0.035)	1.805	74.12(0.208)
7	2.68	61.55(0.088)	2.828	59.59(0.070)
9	2.86	59.08(0.280)	3.19	54.42(0.035)
11	3.85	45.02(0.350)	4.72	32.50(0.350)

Where Cf* is final concentration (mg/L) remaining in the filtrate

At pH of 2, the average removal percentage value was found to be 82.1% for corn cab and 79.88% for saw dust. It is clear that the efficiency of adsorption is very high at low PH. The reason for this explained as follows. Chromium (VI) may be present in aqueous solutions mainly as chromate, dichromate, hydrogen chromate, chromic acid and hydrogen dichromate. Chromate ion (CrO_4^{2-}) is predominant at PH>7 while hydrogen chromate ($HCrO_4^-$) is predominant at PH < 6 (Cotton and Wilkinson, 1980; Greenwood,
and Earnshaw ,1984; Swietlik, 1998). In aqueous solution hydrolysis of **Cr_2O7^{2-} takes place $Cr2O_7^{2-}$ +H_2O $\longleftrightarrow$ 2$HCrO_4^-$** to from $HCrO_4^-$. Thus, although $Cr_2O_7^{2-}$ of $K_2Cr_2O_7$ was the source of Cr (VI) in the synthetic solution used in this study, at PH less than 6, the predominant form of Cr (VI) in aqueous solution ion is $HCrO_4^-$.Therefore, the $HCrO_4^-$form is inferred as the predominant species of Cr (VI) preferentially adsorbed by the adsorbents at pH 2 .At low pH, the surface of the bio sorbent is positively charged due to protonation with H^+ and this promotes the binding of the negatively charged $HCrO_4^-$ ions (Darko et al.,2011; Abdullah and Prasad ,2009).

3.3 Effect of Initial Cr(VI) concentration

The experiment was conducted by varying initial Cr(VI) concentration from 14 mg/L to 29 mg/L and keeping the other parameters constant for both corn cob and pine sawdust adsorbents. The experimental results of the effect of initial chromium concentration on removal efficiency were presented in Table3. Efficiency decreased with the increase in initial chromium concentration. In case of low chromium concentrations, the ratio of the initial chromium ions to surface sites of the adsorbent is small (large number of surface sites) so that the possibility to remove most ions is high (Pragathiswaran et al., 2013).

Table 3 Effect of Initial Cr(VI) concentration

Initial Cr(VI) (mg/L	Corncob		Pine Sawdust	
	Cf*	% removal (Sd,n=3)	cf*	% removal (Sd,n=3)
14	1.93	90.71(0.018)	1.18	91.59(0.140)
17	1.45	91.0(0.400)	1.74	89.97(0.111)
20	1.67	87.86(0.720)	1.60	85.44(0.053)
23	1.25	88.76(0.105)	1.57	80.35(0.070)
26	1.39	82.82(0.035)	1.50	70.18(0.088)
29	1.30	74.8(0.245)	6.00	69.88(0.070)

Where Cf* is final concentration (mg/L) remaining in the filtrate

3.4 Effects of adsorbents dosage on adsorption

This experiment was done by varying adsorbents dosage from 0.5 to 3 g with 0.5 g interval while keeping the other parameters constant (Table 4).

The result shows there is a general increment in percent removal of Cr (VI) ion with increasing in dose of pine sawdust and corncob from 0.5 to 3g. This is due to an increase in the active sites of adsorbents which are responsible for $HCrO_4^-$ and $Cr_2O_7^{2-}$ ions to be adsorbed on adsorption sites (Morshedzadeh et al, 2007).

Table 4 Effects of adsorbents dose on removal of Cr (VI)

Adsor bent dose (g)	Corncob		Pine Sawdust	
	Cr(VI adsorbed (mg/L)	% removal (Sd,n=3)	Cr(VI) adsorbe d (mg/L)	% removal (Sd,n=3)
0.5	1.360	80.01(0.052)	1.106	79.01(0.018
1.0	1.522	89.51(0.105)	1.227	87.62(0.035)
1.5	1.528	89.89(0.158)	1.260	89.99(0.105)
2.0	1.535	90.27(0.0526)))	1.262	90.15(0.053)
2.5	1.540	90.59(0.1578)	1.265	90.39(0.473)
3.0	1.542	90.68(0.0350)	1.266	90.41(0.018)

3.5 Effects of agitation speed

The agitation speeds were optimized for both corn cob and pine sawdust in such a way that all of the parameters in their optimal values kept constant and only agitation speed varied from 60-210 rpm (Table 5).

Table 5 Effect of agitation speed on removal of Cr (VI)

Speed(rpm)	Corncob		Pine Sawdust	
	Cf* (mg/L)	% removal (Sd,n=3)	Cf* mg/L	% removal (Sd,n=3)
60	2.26	86.69(±0.053)	2.54	81.83(±0.08)
90	1.90	88.8(±0.0526)	0.97	93.0(±0.121)
120	1.73	89.8(±0.070)	1.57	89.28(±0.052)
150	1.64	90.35(±0.876)	1.57	88.76(±0.070)
180	0.91	94.64(±0.035)	1.93	86.19(±0.035)
210	1.30	91.17(±0.035)	2.13	84.81(±0.018)

Where Cf* is final Cr(VI) concentration (mg/L) remaining in the filtrate

As can be seen in table 5, at 180 rpm agitation speed for corn cob removes Cr(VI) to the maximum (94.64%). In the case of saw dust, 93.1% removal was recorded at 90 rpm. After the optimum agitation speed, the percent removal decreases. This may be due to desorption of the adsorbate from the adsorbent surface as the speed increases.

3.6 Adsorption isotherms

Adsorption isotherms were studied by fixing adsorbent dosage at 1 g and varying adsorbate concentration. The Langmuir and Freudlich adsorption models were applied for the experimental data at room temperature and the Langmuir parameters q_{max} and k_L were calculated from the intercept and slopes of the linear plots of $1/q_e$ versus $1/C_e$ Eq. (2) .Where q_{max} and k_L (L/mg) are the Langmuir constants related to maximum sorption capacity (mg/g) and energy of adsorption, respectively.

$$1/q_e=1/q_{max}+1/k_L\,q_{max}*\ 1/C_e \qquad (2)$$

Similarly the Freudlich parameters (n, k_f) were calculated from the slope and intercepts of linear plot of logqe versus $\log C_e$, Eq. (3). Where 1/n is adsorption intensity and k_f is related to biosorption capacity.

$$\mathrm{Log}\ q_e= \log k_f+1/n\ \log c_e \qquad (3)$$

In both equations, 2 and 3, q_e and C_e are amount adsorbed per amount of adsorbent (mg/g) and equilibrium concentration mg/L, respectively.

From the value of correlation coefficients (Appendix 1, Table 6) the equilibrium data are better fitted to the Langmuir isotherm model than the Freudlich adsorption model for both adsorbents. This implies that all the adsorption site are equivalent and each site can only accommodate one molecule i.e. only a monolayer adsorption is formed (Dereje et al., 2014).

3.7 Adsorption Kinetics

The kinetics parameters for the adsorption process were studied from variation in constant interval of time and analyzed using two simple kinetics models: the pseudo-first -order and pseudo-second-order. The pseudo-first-order rate expression of lagergren was used to calculate the kinetics parameters for both corn cob and pine sawdust, Eq. (4).

$$\mathrm{Log}\ (q_e-q_t) = \log q_e-0.4342k_1t \qquad (4)$$

Straight line was obtained by plotting $\log(q_e-q_t)$ versus t. The slope and intercept of this plot were used to obtain the pseudo-first-order rate constant k1 and equilibrium adsorption capacity qe, respectively. The pseudo-second-order kinetics parameters were calculated from the linear plot of t/qt versus t in for both Corn cob and pine sawdust, Eq. (5).

$$t/q_t= t/k_2(q_e)^2+t/q_e \quad (5)$$

The values of pseudo-second-order rate constant k_2 and equilibrium adsorption capacity qe were calculated from the intercept and slope of the plot of respectively. From the parameter values, it can be concluded that the adsorption kinetics better fitted to pseudo-second-order rate (Appendix 1, Table 7).

4. Conclusions

Corn cob and pine sawdust biosorbents have comparable removal efficiencies and above 93 % efficiency is obtained for removal of Cr(VI) using each adsorbent.
Among these parameters, agitation speed was found to be the most important parameter that influences the adsorption process. Based on the parameter values, the data are better fitted to Langmuir adsorption isotherm model than Freudlich for both adsorbents indicating monolayer homogenous surface conditions.
Based on the values of calculated and experimental adsorption capacities and correlation coefficients, the kinetics better fitted to Pseudo- second- order for both adsorbents , suggesting that chemisorptions is the rate-determining step in the adsorption process. The corn cob and pine sawdust biosorbents are very effective in removing Cr(VI) from aqueous solution. In addition, these biosorbents in Ethiopia are easily accessible and less costly so that they are promising and can be Substitute of the commercially available adsorbents which are being used in industries.

Appendix 1

Table 6: Langmuir and Freudlich parameters for Cr(VI) sorption using corn cob and spine sawdust biosorbents

Adsorbents	Langmuir parameters			Freudlich parameters		
	qmax	KL	R^2	n	Kf	R^2
Corn cob	2.429	1.651	0.9969	1.142	0.055	0.9301
pine sawdust	4.646	2.028	0.9963	1.234	0.434	0.9286

Table 7: Parameter values of kinetic models for removal of Cr(VI)

	Bioadsorbents	
Kinetic model	Corn cob	pine sawdust
qe experimental	1.221	1.049
Pseudo-first-order		
k1	0.0418	0.0371
qe	0.571	0.601
R^2	0.9821	0.9571
Pseudo-second-order		
k2	0.0801	0.07933
qe	0.7984	0.8062
R^2	0.9988	0.99701

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