

RESEARCH ARTICLE

REMOVAL OF HEXAVALENT CHROMIUM USING ACTIVATED COCONUT SHELL AND ACTIVATED COCONUT COIR AS LOW COST ADSORBENT

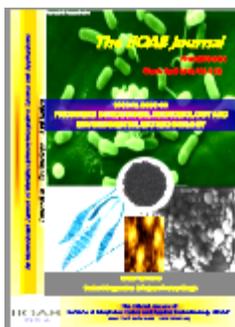
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ABSTRACT



Studies were conducted to assess the comparative efficiency of activated coconut shell and activated coconut coir in removing toxic hexavalent chromium from its synthetic solution and tannery industrial effluent in batch mode. The parameters studied include- pH, adsorbent dose, contact time & initial metal ion concentration and the applicability of adsorption isotherms. Activated coconut shell exhibited more adsorption potential as compared to Activated coconut coir and maximum removal exhibited by ACS was 88% and 83.0 % for 0.3 mm and 1.0 mm in case of synthetic solution & 76%(0.3mm) and 66%(1.0mm) in case of tannery effluent at optimized conditions (pH =2, dose=1.0g/100ml, contact time=60 minutes & initial metal ion concentration=10 ppm). In general ACS was observed to be better adsorbent than ACC while adsorbents of particle size 0.3 mm have greater efficiency than 1.0 mm. On application of adsorption kinetics, Adsorption of Cr (VI) by ACS and ACC followed the pseudo first order and pseudo second order model. The results showed that the activated coconut coir is an efficient adsorbent for hexavalent chromium removal.

Key Words: dose; removal efficiency; effluent; activated carbon; sorption

[I] INTRODUCTION

Heavy metal contamination of industrial effluents is one of the significant environmental problems due to their toxic nature and accumulation throughout the food chain as non-biodegradable pollutants [1]. Tannery is the one of the oldest and fastest growing industry in India. There are about 2161 tanneries in India; however sustenance of tanneries is becoming increasingly difficult because of alarming level of environmental pollution caused by various tannery operations and practices. The main pollutants of concern in tanneries are BOD/COD, suspended solids and heavy metals. Heavy metals like mercury, lead, cadmium, copper, chromium and nickel are extremely toxic even at minute quantities [2]. Chromium is more abundant in earth's crust and is widely used in electroplating, leather tanning, metal finishing & chromate preparation. It exists in two stable oxidation states Cr (III) & Cr (VI). Cr (VI) is of particular concern as because of its high toxicity, it may cause many adverse effects on human health such as epigastric pain, hemorrhage, severe diarrhea, vomiting, nausea, dermatitis by skin contact, ulcer, lung cancer and tissue necrosis. Thus it becomes essential to remove

Cr (VI) from industrial waste water before discharging it into water body or on to land.

Widespread concern over the cumulative toxicity and environmental impact of heavy metals has led to extensive research into developing effective alternative technologies for the removal of these potentially damaging substances from effluent and industrial wastewater [3]. Conventional technology for the removal of metal ions from aqueous solution includes chemical precipitation, ion exchange, chemical oxidation/reduction, reverse osmosis, electro dialysis, ultra filtration, etc. which have their own inherent limitations such as less efficiency, sensitive operating condition, production of secondary sludge and further the disposal is costly affair [4]. The search for alternate and innovative treatment techniques has focused attention on the use of biological materials for heavy metals removal & has gained important credibility during recent years because of the good performance and low cost of these materials [5]. So the efforts are being directed towards the use of natural low cost adsorbents for removal of heavy metals. Use of natural materials which are available in large quantities [6] or certain waste products from industries or agriculture may have potential as inexpensive

adsorbents. Recently some of these low cost adsorbent (natural or processed) have been tested as adsorbents for heavy metal removal [7-10]. Conversion of this waste to a useful adsorbent contributes not only for the treatment of heavy metals contaminated environment but also to minimize the solid wastes. These research activities indicated promising results but further efforts are still required in order to maximize metal removal efficiency and minimize preparation costs.

Coconut shell and coconut coir are agricultural based waste materials and these materials have the potential to sequester metals from solutions. Abundant availability, high biosorption capacity, cost-effectiveness and renewability are the important factors making these materials as economical alternatives for water treatment and waste remediation [11]. The activated carbon prepared from coconut shell and coconut coir is highly porous, amorphous solid consisting of microcrystallites with a graphite lattice. They are non-polar and cheap. Keeping this in view, in the present study the potential of agro-waste-Activated coconut shell and Activated coconut coir was investigated for removal of hexavalent chromium from its synthetic solution and industrial effluent.

[II] MATERIALS AND METHODS

2.1. Preparation of adsorbents

Coconut shell and coir was collected from local market of Hisar, Haryana. Then properly washed with water, sun dried and finally kept in muffle furnace for 60 minutes at 270 °C temperature for carbonization. Then they were washed with distilled water to make the pH near neutral and kept the material in oven at 120°C for 18 hours. Dried material was ground and sieved through standard sieve to obtain particles of size 0.3mm and 1.0 mm. These adsorbents were treated as ACS and ACC.

2.2. Preparation of Cr (VI) solution

A stock solution of Cr (VI) of concentration 1000 mg/l was prepared using an accurately weighed quantity of the $K_2Cr_2O_7$ in double-distilled water. Experimental solutions of the desired concentrations were obtained by successive dilutions. pH values of metal solutions were adjusted using 1 N NaOH and HNO_3 .

2.3. Batch adsorption experiments

Batch adsorption experiments were conducted in triplicates to evaluate the effects of adsorbent dose, contact time, pH and initial metal ion concentration on removal of Cr (VI) ions by ACS and ACC (0.3 mm and 1.0 mm). All the adsorption experiments were conducted in 250 ml round bottomed flask on rotatory shaker at 150 rpm. After desired contact period, flasks were removed and allowed to stand for two minutes. The solution was filtered through What man filter paper 41 and filtrate was analyzed for Cr (VI) concentration spectrophotometrically at wavelength 540 nm using the complexing agent 1,5-diphenyl-carbazide in acid medium according to the standard methods [12]. Finally all the adsorbents were applied on the tannery industrial effluent under the optimized conditions (Obtained from experiment on synthetic solution) for removal of Cr (VI).

2.4. Adsorption isotherms and kinetics

The adsorption data obtained for the Cr (VI) was analyzed using Langmuir and Freundlich isotherm and the kinetics for adsorptions of Cr (VI) on activated coconut shell and coir were studied for their utilization in the treatment of industrial effluents.

Langmuir's isotherm model is valid for monolayer adsorption onto a surface containing a finite number of identical sites, which is represented as equation:

$$\frac{C_e}{q_e} = \frac{1}{Q_{ob}} + \frac{C_e}{Q_o}$$

Where q_e is the amount adsorbed at equilibrium (mg/g); C_e is the equilibrium concentration (mg/l); Q_o and b are the Langmuir constants.

The Freundlich equation [13] proposes an empirical model that is based on the sorption on heterogeneous surface and has the form:

$$\log x/m = \log k + 1/n \log C_e$$

Where k (mg/g) and n are Freundlich isotherms constants; C_e is the equilibrium concentration (mg/l); x/m is the amount adsorbed (mg/g) and m is the adsorbent dose (g/l).

The kinetics for adsorption of Cr (VI) on coconut shell and coir were studied for their utilization in the treatment of industrial effluents. The first order rate constant for adsorption of Cr (VI) has been studied with the help of Lagergran's equation.

$$\log (q_e - q) = \log q - Kt/2.303$$

Where q_e = The amount of metal adsorbed at equilibrium (mg/g)

q = Amount of metal adsorbed at time t (mg/g)

k = rate constant of adsorption (per minute)

t = Time (minute)

Pseudo-second order rate equation

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

Where,

k_2 = Second order rate constant for adsorption ($g\ mg^{-1}\ min^{-1}$)

q_e = Amount of metal adsorption at equilibrium ($mg\ g^{-1}$)

q_t = Amount of metal adsorption in time t (min^{-1})

In order to obtain the rate constant graph was plotted between t/q_t vs t .

Line obtained after plotting $\log (q_e - q_t)$ vs t and t/q_t vs t shows degree of fitness of metal sorption to first and second order rate kinetic models respectively. Straight line indicates best fitness of experimental data to corresponding models. This is based on the assumption that the adsorption capacity for metal on the adsorbent is proportional to the number of active sites occupied on the sorbent and metal uptake is due to chemisorption [14].

[III] RESULTS AND DISCUSSION

3.1. Effect of Adsorbent dose

Adsorbent dose had a very profound effect on Cr (VI) removal. Adsorption experiments were carried out at varying adsorbent dose (0.2-1.2gm/100ml), while other parameters like contact time (1 hr.), pH (2.0) and initial metal ion concentration (10 mg/l), were kept constant. The removal of Cr (VI) by ACS (0.3 mm & 1.0 mm) and ACC (0.3 mm & 1.0 mm) as a function of adsorbent

dose is shown in [Figure-1]. As evident from the results increase in Cr (VI) removal was observed with increase in adsorbent dose and ACS showed greater removal than ACC. Both the adsorbents showed maximum removal at 0.3 mm particle size as compared to 1.0 mm. The reason may be the higher porosity of 0.3 mm size as compared to 1.0 mm due to which it provides greater adsorption sites to the adsorbate molecules. It was observed from

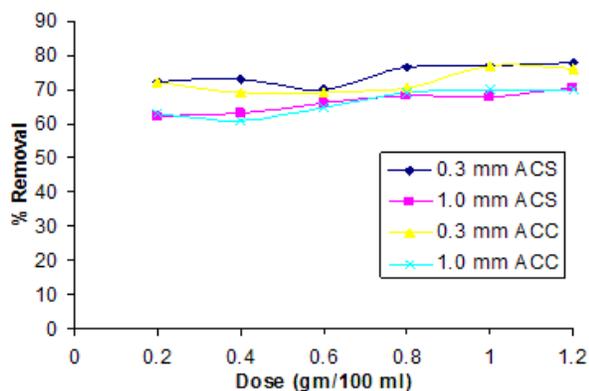


Fig. 1. Effect of adsorbent dose on Cr (VI) removal using activated coconut shell and activated coconut coir

the results that the percentage removal of Cr (VI) increases with increase in adsorbent dose up to some extent, thereafter with further increase in adsorbent dose; there was no appreciable increase in percentage removal. The optimum dose for removal of Cr (VI) was found to be 0.8 gm/100 ml for ACS with 76.5% (0.3mm) and 68.1% (1.0 mm) removal respectively, while for ACC it was 1.0 gm/100 ml with 76.8% and 70.1% for 0.3 mm and 1.0 mm respectively. The phenomenon of increase in percentage removal of Cr (VI) with increase in adsorbent dose up to certain level and beyond that more or less constant removal may be explained as with increase in adsorbent dose, more and more binding sites becomes available for the complexation of Cr (VI) ions and this increased the rate of adsorption. However very slow increase in removal beyond an optimum dose may be attributed to attainment of equilibrium between adsorbate and adsorbent at the existing operating conditions [15]. Higher adsorbent dose cause screening effect of dense outer layer of cells, blocking the binding sites from metal ions, resulting in lower metal removal per unit adsorbent [16].

3.2. Effect of contact time

The effect of contact time on Cr (VI) removal was investigated at optimized adsorbent dose by varying the contact time (20-80 min.), while other parameters were kept constant [Figure-2]. Increase in percentage removal was observed with increase in contact time for all type of adsorbents.

Optimum time observed was 60 min. for all adsorbents at which % removal of Cr (VI) was 77.8% (0.3 mm) and 76.4% (1.0mm) for ACS while in case of ACC, % removal was 72.3% and 66.3%

for 0.3 mm and 1.0 mm respectively. There was no appreciable increase in percent Cr (VI) removal after these optimum times. As shown in Figure-2, the adsorption process took place in two stages. The first stage was rapid, where about 60% adsorption was completed within first 20 min. The second stage represented a slower progressive adsorption. The rapid initial biosorption may be attributed to the accumulation of metals on to the surface of adsorbent, due to its large surface area. With the progressive occupation of these sites, process became slower in the second stage. Moreover the initially deposited metal ions penetrate to the interior of the biosorbent through intra-particle diffusion which was slower process. This is in accordance with the observations of other similar studies [17]. The adsorption process attained equilibrium in 1 hr. Based on the results of kinetics experiments, a time of 1 hr was considered to be adequate for remaining experimentations. It may be explained as initially adsorbent showed the fast adsorption which gets slowed down later on, because initially large number of vacant surface site may be available for adsorption and after some time the remaining vacant surface sites may be exhausted due to repulsive forces between the solute molecules of solid and bulk phase [18].

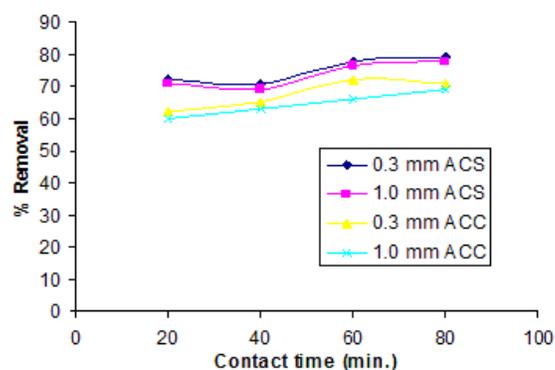


Fig. 2. Effect of contact time on Cr (VI) removal using activated coconut shell and activated coconut coir

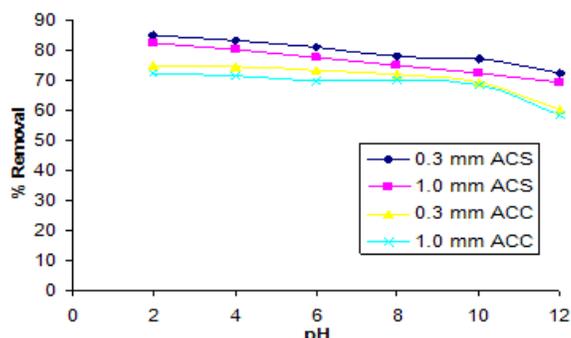


Fig. 3. Effect of pH on Cr (VI) removal using activated coconut shell and activated coconut coir

3.3. Effect of pH on Cr (VI) removal

The effect of pH on Cr (VI) removal by Activated coconut shell (ACS) and Activated coconut coir (ACC) was investigated at

optimized adsorbent dose and contact time by varying pH from 2.0-12.0 [Figure-3]. Progressive decrease in Cr (VI) adsorption was observed with increase in pH from 2 to 12 and maximum adsorption was observed at pH 2. ACS showed maximum removal i.e. 85 % and 82 % (0.3 mm and 0.1 mm) while ACC showed 75% and 72% (0.3 mm and 1.0 mm) respectively at pH 2. The effect of pH on adsorption of Cr (VI) onto the adsorbent can be interpreted on the basis of the structure of the sorbent and the speciation of chromium. Chromium solution contains a larger number of $\text{Cr}_2\text{O}_2^{7-}$ ions and a smaller number of HCrO_4^- ions in the regions of lower pH and only CrO_2^{-4} ions above pH 8.0. In the pH range 3 to 6, the equilibrium shifts to dichromate according to the overall equilibrium, $2\text{CrO}_2^{-4} + 2\text{H}^+ = \text{Cr}_2\text{O}_2^{7-} + \text{H}_2\text{O}$. A major fraction of negative sites are occupied by H^+ ions via electrostatic attraction in the regions of lower pH and these positively charged sites of the adsorbent are occupied by $\text{Cr}_2\text{O}_2^{7-}$ ions [19]. Hence the maximum chromium removal was observed at lower pH i.e. 2. Higher removal of chromium at low pH may also be due to reduction of chromium (VI) to chromium (III) [20, 21], which was then adsorbed by the adsorbent.

3.4. Effect of initial metal ion concentration

Effect of initial Cr (VI) ion concentration on its removal was carried out at optimized adsorbent dose, contact time and pH by varying the metal ion concentration from 10-50 ppm [Figure-4] Adsorption of Cr (VI) was found to decrease with increase in metal ion concentration from 10-50 ppm. This is due to increase in number of metal ions competing for available binding sites and due to lack of binding sites for complexation at higher metal ion concentration. At lower concentration almost all the metal ions could interact with binding sites facilitating maximum adsorption [22] at 10 ppm concentration i.e. 88% and 83 % for ACS (0.3 mm and 1.0 mm) while 79% and 75% for ACC (0.3 mm and 1.0 mm). Maximum Cr (VI) removal was observed at 10 ppm concentration using low cost adsorbents [23]. At higher concentration more chromium ions are left unadsorbed in the solution due to saturation of adsorption sites [24].

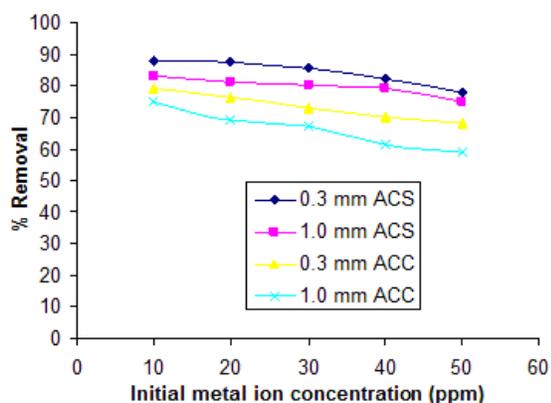


Fig. 4: Effect of initial Cr (VI) ion concentration on removal using activated coconut shell and activated coconut coir

3.5. Industrial feasibility of adsorbent

The industrial feasibility of ACS and ACC was studied for the removal of hexavalent chromium from tannery effluent at optimized conditions obtained from experiments on synthetic solution in batch mode. The adsorption efficiency of the adsorbent was reduced from 85 % to 76% and 80.2% to 66% in case of ACS for 0.3 mm and 1.0 mm respectively. Similarly, in case of ACC, adsorption efficiency decreased from 75% to 67% for 0.3 mm and 72 % to 59 % for 1.0 mm adsorbent particle size. This reduction in percent removal may be due to presence of co-metal ions present in industrial effluents [25].

3.6. Adsorption isotherms and kinetics

The Langmuir and Freundlich adsorption models were used for mathematical description of adsorption of Cr (VI) ions and isotherms constants were determined to find out the adsorption capacity of adsorbent. As shown in Table-1 and -2, the value of correlation coefficients $R^2 \geq 0.8$ indicated that the adsorption data are well fitted in Langmuir and Freundlich models. The values of n more than 1 for all the adsorbents indicated that significant adsorption takes place at low concentration of the adsorbent.

Table: 1. sotherm model constant and correlation coefficient for adsorption of hexavalent chromium

Adsorbents	Langmuir constant (mg/g)			Freundlich Constant (mg/g)		
	Qo (mg/g)	B	R ²	K	n	R ²
ACS (0.3 mm)	2.337	0.761	0.9256	14.09	6.067	0.8962
ACS (1.0 mm)	5.319	0.1332	0.3622	25.61	3.577	0.4958
ACC (0.3 mm)	3.409	0.387	0.690	194.5	4.466	0.6955
ACC (1.0 mm)	7.849	0.0778	0.1508	11.24	2.33	0.216

Table: 2. Kinetics model constant and correlation coefficient for adsorption of hexavalent chromium

Adsorbents	Pseudo first order		Pseudo second order		
	K _d	R ²	q _e	K ₂	R ²
ACS (0.3 mm)	0.0495	0.8291	10.384	0.2239	0.9961
ACS (1.0 mm)	0.0479	0.945	10.2459	0.04488	0.9951
ACC (0.3 mm)	0.0439	0.9717	7.5988	0.0855	0.9966
ACC (1.0 mm)	0.0231	0.9737	7.2727	0.9705	0.9986

The pseudo-first order and second order kinetics models were successfully employed for explaining the kinetics data of adsorption process. Straight line obtained after plotting $\text{Log}(q_e - q_t)$ vs t and t/q_t vs t shows degree of fitness of metal sorption to first and second order rate kinetics model. This is based on the assumption that the adsorption capacity for metal on the adsorbent is proportional to the number of active sites occupied on the sorbent and metal uptake is due to chemisorption [14]. The values of constants K_d and R^2 were calculated from the plots. The pseudo-first order equation was able to describe the adsorption of Cr (VI) onto both forms of adsorbents as evidenced from the coefficient of determination values ($R^2 > 0.90$).

[V] CONCLUSION

The adsorption of hexavalent chromium was observed to pH, adsorbent dose, contact time and initial metal ion concentration dependent. ACS can remove more Cr (VI) as compared to ACC from its synthetic solution and tannery effluent at optimized conditions. Both activated coconut shell and Activated coconut coir were found suitable adsorbents for the removal of Cr (VI) from its synthetic solution and tannery effluent and may also have wide applicability. The adsorption efficiency of both forms of adsorbents of particles size 0.3mm for Cr (VI) is also well evident from the coefficient of determination values ($R^2 > 0.90$). The coconut shell and coconut coir are abundantly available as an agro waste which makes this technology industrially feasible and economically cheaper.

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