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Modification of coconut shell charcoal for metal removal from aqueous solutions

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ABSTRACT

Treatment of the contaminated aqueous solutions to improve their quality is indispensible for their reuse resulting in an emergent challenge to develop facile, nontoxic and less energy consuming techniques to purify water. Present study is therefore aimed at the synthesis of an adsorbent using agricultural waste i.e. coconut shell. The charcoal obtained from coconut shell was modified by acid activation and manganese doping following a simple chemical route. The products were characterized by scanning electron microscopy, energy dispersive X-ray analysis and infrared spectroscopy. Preliminary studies were carried out to compare the adsorption potential of acid modified coconut shell charcoal (AMCSC) and manganese doped coconut shell charcoal (MDCSC) for the removal of chromium (VI) and iron (III) from aqueous solutions. Various physicochemical parameters such as adsorbent dosage, initial metal ions concentration and pH were studied. MDCSC was found to be a better adsorbent for metals as compared to AMCSC and removed chromium more efficiently than iron from synthetic solutions i.e. 56.10% at optimum conditions i.e. 0.6 g/L adsorbent dosage, 10 mg/L initial metal ions concentration and pH = 3. The effect of adsorbents on color and conductivity of the aqueous solutions was also noted; slight variation in color of all the aqueous solutions with a maximum of 91.67% removal was observed.

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1. Introduction

Over the past decades, charcoal is being extensively used as a raw material for producing a variety of activated carbons. These activated carbons have been employed as physical adsorbents for the removal of dissolved or dispersed organic and inorganic pollutants such as dyestuff, insecticides, herbicides, hydrocarbons, polychlorinated aromatic compounds and heavy metal ions from aqueous solutions [1]. Surface chemistry of activated carbons is of primary importance for the removal of organic as well as inorganic contaminants since large surface area and high porosity from macro to microporous structures induce outstanding adsorption properties that enable activated carbons to capture chemicals of even lower molecular weights [2]. Powdered activated carbon is more efficient as compared to granular carbon owing to its extremely high surface area and hence the availability of more adsorption sites. In addition, an assortment of oxygen-containing surface functional groups also enhances the adsorption capacity [1,3].

Surface area of activated carbons can be further improved by physical, chemical or biological activation processes that lead to an increase in surface oxygen groups and produce activated carbons having surface area equivalent to that of commercial activated carbons [2,4]. Among these methods, chemical activation is believed to enhance the adsorption capacity and selectivity of activated carbons by modifying surface functional groups [5]. It is usually done by using a variety of procedures that generate acidic, basic, metal or metal oxide impregnated surfaces [6]. Generally, a variety of oxidizing agents in liquid or gaseous phase like H_2SO_4, HNO_3, $HClO_4$, $(NH_4)_2S_2O_8$, H_2O_2, ClO_2, KIO_4, $KMnO_4$, ozone and ammonia have been employed which reduce hydrophobicity and enhance adsorption capacity of activated carbons [7-9].

Modified activated carbons have been successfully used in the past for the removal of toxic metals from aqueous solutions [3,8]. Nomanbhay found a maximum of 86% Cr (VI) removed by chitosan coated acid treated beads (CCAB) using its 13.5 g/L, while for chitosan coated beads (CCB) it was 64% at 18 g/L dosage and commercial activated carbon removed 52% at a

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dosage of 24 g/L [10]. Although activated carbons have been widely used as adsorbents but they have a major disadvantage of being expensive that reduces its feasibility for the management of a large quantity of industrial waste produced. Therefore, a wide range of natural carbonaceous materials and industrial wastes rich in carbon content are being used as precursors to develop a series of low-cost activated carbons with diversified properties to overcome this problem. These novel sources including wood, polymers, sawdust, lignite coal, peat, petroleum residues, waste tyres, bamboo scaffolding, coconut shell, olive and apricot pits etc. possess highly porous structures and large surface areas [11,12]. Askari *et al.* synthesized cost-effective iron-modified activated carbon derived from pistachio shells for improved dye removal from aqueous solutions [13]. Recently Chen *et al.* obtained modified activated carbon from waste wood-based panels for efficient removal of copper from aqueous solutions [14]. Similarly, activated carbon produced from coconut shell has been reported to be quite efficient for the removal of zinc, lead, cadmium, copper and nickel from wastewater [15-17]. Previous researchers have also reported cocopeat derived from coconut shells an efficient adsorbent for heavy metal removal as well as COD, BOD, ammonia and phosphate reduction [18].

During past few decades, nanostructures like metals and their oxide nanoparticles embedded in vitreous matrices, carbon-based nanomaterials like carbon nanotubes, graphene, fullerene and graphene oxide nanocomposites [19-22] have also been used for metal elimination from aqueous solutions but their synthesis involves high cost. Therefore, activated carbons obtained from cheap natural sources are preferable materials for water and wastewater treatment. Since, activated carbon is also recognized as good catalyst support so metal impregnated activated carbons derived from natural raw materials can be the best alternative.

Present study is therefore aimed at the modification of coconut shell carbon by acid activation as well as doping with manganese; the raw material for which is quite inexpensive and widely available. The products were characterized by infrared spectroscopy, scanning electron microscopy and energy dispersive X-ray (EDX) analysis. Experiments were carried out to compare the adsorption potential of acid modified coconut shell charcoal (AMCSC) and manganese doped coconut shell charcoal (MDCSC) for the removal of metals i.e. chromium (Cr) and iron (Fe) from aqueous solution. To identify the optimum conditions for the elimination of metal ions, effect of various factors i.e. biosorbent dosage, initial metal ions concentration and pH were studied. The effect of treatment on color and conductivity of the aqueous solutions was also noted.

2. Experimental

2.1. Preparation of coconut shell charcoal

Coconut shell obtained from the local market was thoroughly washed with distilled water to remove any grit and other impurities and was dried in an electric oven at 105 °C for 24 hours. The moisture free coconut shell was broken into small pieces and was burnt in a muffle furnace at 400 °C for two hours. The carbon thus obtained was ground to powder form with the help of mechanical grinder to pass through 30 and 50 mesh sieves; the fraction that passed through 30 mesh and retained on 50 mesh (-30+50) was employed for further experimental work.

2.2. Modification of coconut shell charcoal

The coconut shell charcoal (CSC) of (-30+50) mesh size was modified by the following procedure:

2.2.1. Acid modification

The coconut shell charcoal (CSC) was treated with 0.1 N hydrochloric acid for 24 hours at room temperature. The acid modified coconut shell charcoal (AMCSC) thus obtained was filtered and was extensively washed with distilled water in order to obtain a neutral product and was dried in an electric oven at 105 °C for 24 hours.

2.2.2. Manganese doping

Manganese doped coconut shell charcoal was prepared as follows: Weighed quantities of analytical reagent grade manganese chloride tetrahydrate ($MnCl_2·4H_2O$) to make 5% solution and sodium borohydride ($NaBH_4$) to make 1% solution were dissolved separately in distilled water. Manganese solution was added to AMCSC in 1:1 solid-liquid ratio while sodium borohydride solution in 5:1 solid-liquid ratio was added dropwise with continuous stirring keeping pH = 3-4 at 70 °C for 2 hours. MDCSC with 3% manganese content was thus obtained through filtration and was washed thoroughly with distilled water. The product was dried for 3-4 hours in an electric oven at 105 °C.

2.3. Characterization of charcoal

The synthesized charcoal samples *i.e.* AMCSC and MDCSC were characterized by infrared spectroscopy using Thermo Nicolet IR 200 (USA). The surface morphology studies and energy dispersive X-ray analysis were carried out using SEM S-3700N Hitachi Japan.

2.4. Adsorption studies

2.4.1. Preparation of standard solutions

A 1000 mg/L composite stock solution of chromium Cr (VI) and iron Fe (III) was prepared by dissolving appropriate quantities of potassium dichromate and ferric chloride in distilled water and working standards of desired concentrations were prepared by diluting the stock solution.

2.4.2. Adsorption experiments

Adsorption behavior of AMCSC and MDCSC was studied through optimization of parameters that influence adsorption such as adsorbent dosage, initial metal ions concentration and pH. Effect of these parameters was investigated by varying adsorbent dosage (0.1, 0.3 and 0.6 g/L), initial metal ions concentration (5, 10 and 20 mg/L) and pH (ranging from 2 to 11). The mechanism of adsorption is shown in Figure 1. In each experiment, weighed quantity of adsorbent was added to a measured volume of metal ion standard solution and after adjusting the desired pH, the mixture was agitated at invariable speed at room temperature keeping the contact time constant i.e., 8 hours. The solution thus obtained was filtered.

2.4.3. Evaluation of treated aqueous solutions

The residual metal ions concentrations of both chromium (VI) and iron (III) were analyzed in the filtrate solutions by atomic absorption spectrometer (Hitachi Z-8000) and the percentage removal of metals was calculated by the formula:

$$\mathrm{RE}(\%) = \frac{(C_i - C_f)}{C_i} \times 100 \qquad (1)$$

where, C_i and C_f are the initial and final metal ions concentrations in mg/L, respectively [23].

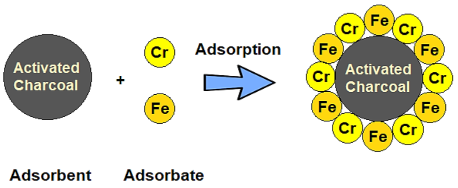

Figure 1. Adsorption mechanism of chromium and iron on activated charcoal.

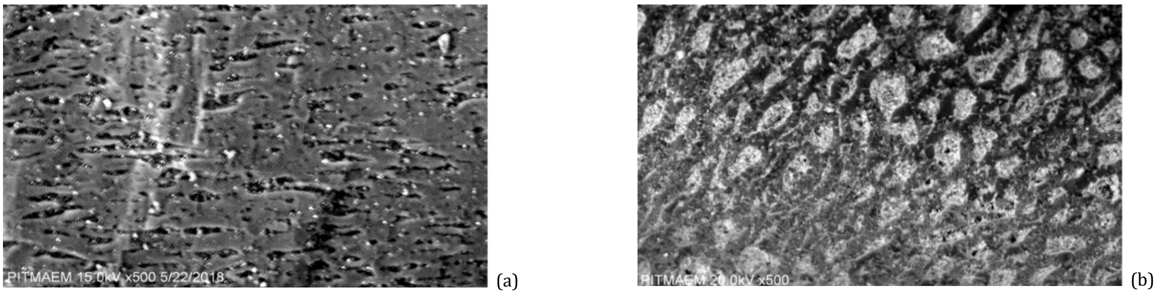

Figure 2. (a) SEM micrograph of acid modified coconut shell charcoal and (b) SEM micrograph of manganese doped coconut shell charcoal.

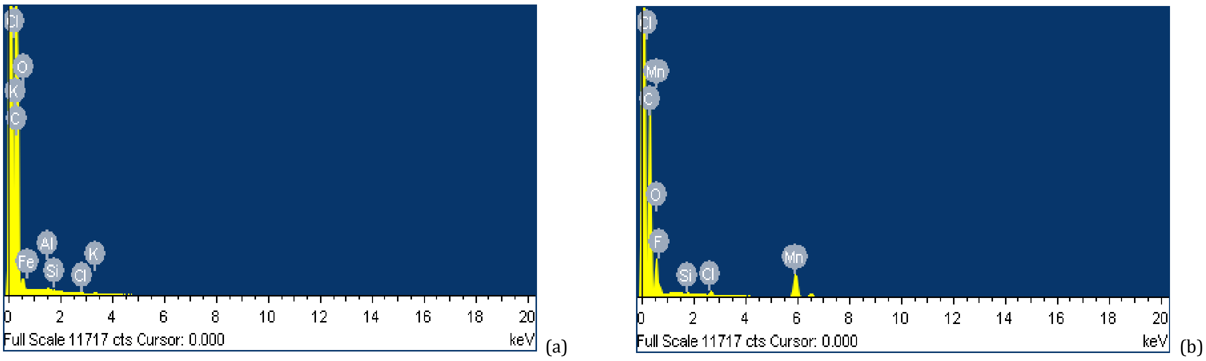

Figure 3. (a) EDX spectrum of acid modified coconut shell charcoal and (b) EDX spectrum of manganese doped coconut shell charcoal.

The effect of treatment on color and conductivity of the aqueous solutions was also studied. The change in color of each aqueous solution was noted using Tintometer Lovibond PFX895 and the conductivity was measured by Conductivity meter JENWAY 4010.

3. Results and discussion

3.1. Scanning electron microscopy

The surface morphology of the acid modified coconut shell charcoal and manganese doped coconut shell charcoal was studied using scanning electron microscopy at 500× magnification. SEM micrographs for AMCSC and MDCSC are shown in Figures 2a and 2b, respectively. The micrographs show that there are small as well as large size pores developed due to initial carbonization step which results in the release of volatile matter from the surface producing a fixed carbon mass thus enriching the carbon content and resulting in widening of pores with irregular cavities responsible for a high surface area of the activated carbon [24,25]. Figure 2b clearly depicts the porous structure of MDCSC along with manganese entrapped in the pores of coconut shell charcoal.

Sulistyani *et al.* reported that the carbon content of coconut shell activated carbon improves with the increase in activation temperature from 300 to 500 °C resulting in greater number of pores [26]. In order to develop further porosity, acid activation followed by the subsequent calcination and drying steps is performed that also increases the pore volume with the increasing temperature as well as time thus improving the surface area of carbon since, new pores are formed due to release of more volatiles [27]. Islam *et al.* observed a much lesser number of pores on the surface of carbon before carbonization as compared to those well-developed pores observed after the carbonization step probably due to the evaporation of reagent used for activation [28]. This observation is also supported by the findings of Sanni and co-workers; they observed strong influence of carbonization temperature on the morphology and pore size distribution of coconut shell activeted carbons. They also found that increasing carbonization temperature from 450 to 575 °C lead to the formation of more fine pores thus increasing the internal surface area. However, further rise in carbonization temperature up to 850 °C caused alteration of pore walls among consecutive neighboring pores thereby adversely affecting the porosity and adsorptive characteristics of the adsorbent [29].

3.2. Energy dispersive X-ray analysis

The elemental analysis was carried out using energy dispersive X-ray (EDX) analysis technique. EDX spectra (Figures 3a and 3b) illustrate the presence of carbon as the major constituent while oxygen can be seen in minor quantities in both the samples. Other elements like aluminum, silicon, chloride, potassium and iron occur in traces in AMCSC. Figure 3b shows the presence of manganese and hence, confirms its successful doping in the AMCSC matrix.

Table 1. Effect of 0.1 g/L acid modified coconut shell charcoal (AMCSC) on adsorption of Cr (VI) and Fe (III)

Synthetic solutions	pH	Conductivity		Color		Cr		Fe	
5 mg/L	**4.01**	**174 µs/cm**	**% Red**	**71 ptCo**	**% Red**	**5 mg/L**	**% Removal**	**5 mg/L**	**% Removal**
Cr+Fe	7.0	145	16.70	32	54.93	4.30	14.00	4.50	10.00
	11.0	130	25.29	29	59.15	4.10	18.00	4.30	14.00
	3.0	175	-0.57	16	77.64	3.60	28.00	3.80	24.00
	2.0	-	-	-	-	3.75	25.00	3.95	21.00
10 mg/L	**3.58**	**350 µs/cm**	**% Red**	**142 ptCo**	**% Red**	**10 mg/L**	**% Removal**	**10 mg/L**	**% Removal**
Cr+Fe	7.0	285	18.57	79	44.37	8.30	17.00	8.70	13.00
	11.0	256	26.86	67	52.82	7.90	21.00	8.30	17.00
	3.0	360	-2.86	21	85.21	6.40	36.00	6.80	32.00
	2.0	-	-	-	-	6.60	34.00	7.00	30.00
20 mg/L	**3.28**	**632 µs/cm**	**% Red**	**264 ptCo**	**% Red**	**20 mg/L**	**% Removal**	**20 mg/L**	**% Removal**
Cr+Fe	7.0	501	20.73	101	61.74	16.00	20.00	16.40	18.00
	11.0	468	25.95	87	67.04	15.10	24.50	15.60	22.00
	3.0	629	0.47	28	89.39	13.40	33.00	13.80	31.00
	2.0	-	-	-	-	14.00	30.00	14.40	28.00

* Bold values represent the initial values.

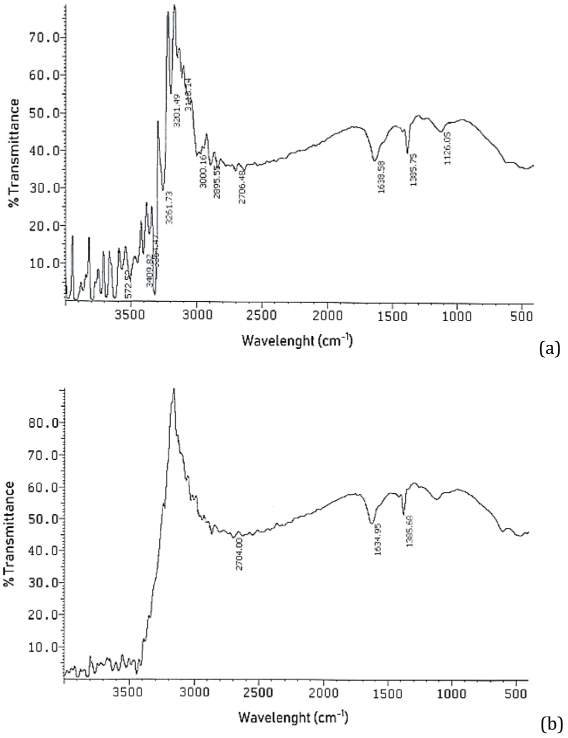

Figure 4. (a) Infrared spectrum of acid modified coconut shell charcoal and (b) Infrared spectrum of manganese doped coconut shell charcoal.

3.3. Infrared spectroscopy

IR spectra of both the acid modified coconut shell charcoal (AMCSC) and manganese doped coconut shell charcoal (MDCSC) were recorded in the range of 4000-400 cm^{-1} to identify the surface functional groups as well as the changes in the charcoal after manganese doping and are presented in Figures 4a and 4b. The spectrum for AMCSC illustrates absorption bands of various intensities combined to form a broad and strong band in the functional group region between 4000-3300 cm^{-1} and comparatively smaller bands at 3262 and 3201 cm^{-1} due to the stretching vibrations of free or bonded OH groups of alcohols and carboxylic acids. Maulidiyah *et al.* observed similar stretching vibrations for hydroxyl ions for titania doped activated coconut shell carbon in this range [30]. These bands are also associated with the presence of inter and intramolecular hydrogen bonding between hydroxyl groups along with the stretching vibrations of -NH group overlapped by the absorption bands of hydroxyl groups in this range [31,32].

Another broad band of relatively less intensity between 3000-1800 cm^{-1} can be assigned to symmetric and asymmetric stretching vibrations of hydrocarbons *i.e.* alkanes, alkenes and alkynes. The bands of medium intensity at 1639, 1484 and 1126 cm^{-1} appear due to primary amine as well as C=O stretching vibrations, O−H bending vibrations and alkyl chain stretching vibrations, respectively. The broad band below 1000 cm^{-1} is seen due to the presence of long alkyl chain [33-35]. Islam *et al.* also had the same observations for activated carbon synthesized from coconut shell [28]. It can be observed that after manganese doping, the absorption bands in the region between 4000-3300 cm^{-1} merge to form a broad band. However, the results confirm that hydroxyl, amino and carboxyl groups thought to be responsible for metal adsorption are present on the surface of both AMCSC and MDCSC [32].

3.4. Adsorption studies

A series of experiments was conducted to investigate the effect of adsorption parameters by varying adsorbent dosage, initial metal ions concentration and pH for both acid modified coconut shell charcoal and manganese doped coconut shell charcoal on the adsorption of chromium (VI) and iron (III) in the same aqueous solutions and results are illustrated in Tables 1 to 6.

Table 2. Effects of 0.1 g/L manganese doped coconut shell charcoal (MDCSC) on adsorption of Fe (III) and Cr (VI).

Synthetic solutions	**pH**	**Conductivity**		**Color**		**Cr**		**Fe**	
5 mg/L	**4.01**	**174 µs/cm**	**% Red**	**71 ptCo**	**% Red**	**5 mg/L**	**% Removal**	**5 mg/L**	**% Removal**
Cr+Fe	7.0	142	18.39	33	53.52	3.40	32.00	4.50	10.00
	11.0	126	27.59	28	60.56	3.50	30.00	3.85	23.00
	3.0	177	-1.72	16	77.46	3.00	40.00	3.35	33.00
	2.0	-	-	-	-	3.25	35.00	3.50	30.00
10 mg/L	**3.58**	**350 µs/cm**	**% Red**	**142 ptCo**	**% Red**	**10 mg/L**	**% Removal**	**10 mg/L**	**% Removal**
Cr+Fe	7.0	271	22.57	81	42.96	6.90	31.00	8.10	19.00
	11.0	237	32.28	69	51.41	6.20	38.00	7.37	26.30
	3.0	361	-3.14	23	83.80	5.90	41.00	6.25	37.50
	2.0	-	-	-	-	6.30	37.00	6.80	32.00
20 mg/L	**3.28**	**632 µs/cm**	**% Red**	**264 ptCo**	**% Red**	**20 mg/L**	**% Removal**	**20 mg/L**	**% Removal**
Cr+Fe	7.0	493	21.99	104	60.61	16.10	19.50	16.24	18.80
	11.0	431	31.80	90	65.91	13.40	33.00	14.10	29.50
	3.0	635	-0.47	29	89.01	12.00	40.00	12.70	36.50
	2.0	-	-	-	-	12.20	39.00	13.20	34.00

* Bold values represent the initial values.

Table 3. Effects of 0.3 g/L acid modified coconut shell charcoal (AMCSC) on adsorption of Fe (III) and Cr (VI).

Synthetic solutions	**pH**	**Conductivity**		**Color**		**Cr**		**Fe**	
5 mg/L	**4.01**	**174 µs/cm**	**% Red**	**71 ptCo**	**% Red**	**5 mg/L**	**% Removal**	**5 mg/L**	**% Removal**
Cr+Fe	7.0	143	17.82	29	59.15	4.10	18.00	4.30	14.00
	11.0	128	26.43	27	61.97	3.80	24.00	4.00	20.00
	3.0	175	-0.57	14	80.28	3.20	36.00	3.60	28.00
	2.0	-	-	-	-	3.15	37.00	3.30	34.00
10 mg/L	**3.58**	**350 µs/cm**	**% Red**	**142 ptCo**	**% Red**	**10 mg/L**	**% Removal**	**10 mg/L**	**% Removal**
Cr+Fe	7.0	283	19.14	77	45.77	8.20	18.00	8.50	15.00
	11.0	254	27.43	65	54.22	7.90	21.00	8.10	19.00
	3.0	360	-2.86	19	86.62	6.20	38.00	6.60	34.00
	2.0	-	-	-	-	5.97	40.30	6.03	39.70
20 mg/L	**3.28**	**632 µs/cm**	**% Red**	**264 ptCo**	**% Red**	**20 mg/L**	**% Removal**	**20 mg/L**	**% Removal**
Cr+Fe	7.0	498	21.20	99	62.50	15.90	20.50	16.20	19.00
	11.0	464	26.58	84	68.18	15.00	25.00	15.30	23.50
	3.0	629	0.47	25	90.53	13.10	34.50	13.50	32.50
	2.0	-	-	-	-	12.00	40.00	12.80	36.00

* Bold values represent the initial values.

Table 4. Effects of 0.3 g/L manganese doped coconut shell charcoal (MDCSC) on adsorption of Fe (III) and Cr (VI).

Synthetic solutions	**pH**	**Conductivity**		**Color**		**Cr**		**Fe**	
5 mg/L	**4.01**	**174 µs/cm**	**% Red**	**71 ptCo**	**% Red**	**5 mg/L**	**% Removal**	**5 mg/L**	**% Removal**
Cr+Fe	7.0	139	20.11	30	57.75	3.65	27.00	4.35	13.00
	11.0	122	29.88	25	64.79	3.40	32.00	3.75	25.00
	3.0	177	-1.72	13	81.69	3.00	40.00	3.20	36.00
	2.0	-	-	-	-	3.15	37.00	3.30	34.00
10 mg/L	**3.58**	**350 µs/cm**	**% Red**	**142 ptCo**	**% Red**	**10 mg/L**	**% Removal**	**10 mg/L**	**% Removal**
Cr+Fe	7.0	268	23.43	78	45.07	7.00	30.00	7.87	21.30
	11.0	233	33.43	66	53.52	6.00	40.00	7.18	28.20
	3.0	361	-3.14	20	85.91	5.80	42.00	5.94	40.60
	2.0	-	-	-	-	5.97	40.30	6.03	39.70
20 mg/L	**3.28**	**632 µs/cm**	**% Red**	**264 ptCo**	**% Red**	**20 mg/L**	**% Removal**	**20 mg/L**	**% Removal**
Cr+Fe	7.0	489	22.63	100	62.12	14.00	30.00	15.20	24.00
	11.0	425	32.75	87	67.04	12.20	39.00	13.80	31.00
	3.0	635	-0.47	26	90.15	11.80	41.00	12.40	38.00
	2.0	-	-	-	-	12.00	40.00	12.80	36.00

* Bold values represent the initial values.

Table 5. Effect of 0.6 g/L acid modified coconut shell charcoal (AMCSC) on adsorption of Fe (III) and Cr (VI).

Synthetic solutions	**pH**	**Conductivity**		**Color**		**Cr**		**Fe**	
5 mg/L	**4.01**	**174 µs/cm**	**% Red**	**71 ptCo**	**% Red**	**5 mg/L**	**% Removal**	**5 mg/L**	**% Removal**
Cr+Fe	7.0	140	19.54	26	63.38	4.00	20.00	4.10	18.00
	11.0	125	28.00	23	67.60	3.50	30.00	3.80	24.00
	3.0	175	-0.57	10	85.91	3.00	40.00	3.40	32.00
	2.0	-	-	-	-	3.10	38.00	3.50	30.00
10 mg/L	**3.58**	**350 µs/cm**	**% Red**	**142 ptCo**	**% Red**	**10 mg/L**	**% Removal**	**10 mg/L**	**% Removal**
Cr+Fe	7.0	280	20.00	74	47,89	8.00	20.00	8.20	18.00
	11.0	250	28.57	62	56.34	7.50	25.00	7.80	22.00
	3.0	350	0.00	16	88.73	6.30	37.00	6.60	34.00
	2.0	-	-	-	-	6.50	35.00	7.00	30.00
20 mg/L	**3.28**	**632 µs/cm**	**% Red**	**264 ptCo**	**% Red**	**20 mg/L**	**% Removal**	**20 mg/L**	**% Removal**
Cr+Fe	7.0	495	21.68	96	63.64	15.50	22.50	15.90	20.50
	11.0	460	27.21	80	69.70	14.80	26.00	15.00	25.00
	3.0	630	0.32	22	91.67	12.10	39.50	13.10	34.50
	2.0	-	-	-	-	13.00	35.00	13.60	32.00

* Bold values represent the initial values.

Table 6. Effects of 0.6 g/L manganese doped coconut shell charcoal (MDCSC) on adsorption of Fe (III) and Cr (VI).

Synthetic solutions	pH	Conductivity		Color		Cr		Fe	
5 mg/L	**4.01**	**174 µs/cm**	**% Red**	**71 ptCo**	**% Red**	**5 mg/L**	**% Removal**	**5 mg/L**	**% Removal**
Cr+Fe	7.0	140	19.54	26	63.38	4.00	20.00	4.10	18.00
	11.0	125	28.16	23	67.60	3.50	30.00	3.80	24.00
	3.0	175	-0.57	10	85.91	3.00	40.00	3.40	32.00
	2.0	-	-	-	-	3.05	39.00	3.13	37.40
10 mg/L	**3.58**	**350 µs/cm**	**% Red**	**142 ptCo**	**% Red**	**10 mg/L**	**% Removal**	**10 mg/L**	**% Removal**
Cr+Fe	7.0	280	20.00	74	47.89	8.00	20.00	8.20	18.00
	11.0	250	28.57	62	56.34	7.50	25.00	7.80	22.00
	3.0	350	0.00	16	88.73	5.12	48.80	5.02	49.80
	2.0	-	-	-	-	6.30	37.00	5.62	43.80
20 mg/L	**3.28**	**632 µs/cm**	**% Red**	**264 ptCo**	**% Red**	**20 mg/L**	**% Removal**	**20 mg/L**	**% Removal**
Cr+Fe	7.0	495	21.68	96	63.64	13.20	34.00	14.80	26.00
	11.0	460	27.21	80	69,70	11.60	42.00	13.31	33.45
	3.0	630	0.32	22	91.67	11.00	45.00	11.62	41.90
	2.0	-	-	-	-	11.40	43.00	12.04	39.80

* Bold values represent the initial values.

In past, scientists found coconut shell carbon chemically modified with nitric acid to be an efficient adsorbent for metal removal. They observed a substantial rise in metal removal efficiency with increasing the dose of nitric-treated coconut shell carbon from 1.5 to 12.0 g/L. In fact, nitric acid considerably increased the negative charge and also produced more acidic C=O groups on the adsorbent surface hence improving its hydrophilic character and making it electro-statically favourable for higher uptake of positively charged metal ions [36]. Most of the former researchers observed that the metal removal efficiency increases up to a certain limit of adsorbent dosage and further increase shows no profound effect on metal removal due to the overlapping of adsorption sites [17].

In order to study the influence of adsorbent dosage three different dosages i.e. 0.1, 0.3 and 0.6 g/L of both the adsorbents were employed keeping initial metal ions concentration 10 mg/L, pH = 3 with constant shaking speed for 8 hours at room temperature. It was found that as the dosage of AMCSC as well as MDCSC increased, the adsorption of both the metals also increased and maximum reduction occurred at 0.6 g/L. As reported in Tables 5 and 6, 0.6 g/L of AMCSC removed 48.00% Cr (VI) and 34.00% Fe (III) whereas MDCSC removed 56.10% Cr (VI) and 49.80% Fe (III). Hence, MDCSC removed both the metals more efficiently as compared to AMCSC.

Adsorption of Cr (VI) and Fe (III) on AMCSC and MDCSC was studied as a function of initial concentration of metal ions at 5, 10 and 20 mg/L while unvarying all the other process parameters. The results for both the adsorbents showed that increase in Cr (VI) ions concentration from 5 to 10 mg/L lead to an increase in reduction of metal ions followed by a slight decrease or negligible change in metal removal at 20 mg/L initial metal ions concentration. Therefore, 10 mg/L was found to be the optimum initial metal ions concentration for the adsorption of both metal ions on AMCSC as well as MDCSC. The maximum adsorption of Cr (VI) and Fe (III) on AMCSC at 10 mg/L was 48.00 and 34.00%, respectively (Table 5). Similarly, MDCSC removed 56.10 and 49.80 % of chromium (VI) and iron (III) ions respectively (Table 6). It has been observed by the previous scientists that the maximum removal of metal ions is obtained at lower concentrations while it decreases at higher concentrations due to the saturation of adsorption sites [37,38].

Influence of pH on the adsorption of Cr (VI) and Fe (III) on both the adsorbents was studied by varying the pH from 2 to 11. It can be noted from the results that both the adsorbents showed similar behavior at acidic, neutral and alkaline pH values and maximum reduction of both the metal ions was observed at pH = 3. Further reduction in pH reduced the adsorption potential of both the adsorbents. Increase in pH to neutral also had a profound decrease in the removal of metal ions again followed by a considerable increase in removal at basic pH *i.e.* 11. However, MDCSC showed better adsorption efficiency as compared to AMCSC. Table 5 shows that AMCSC removed 48.00% Cr (VI) and 34.00% Fe (III). Similarly, Table 6 reports 56.10 and 49.80% removal for Cr (VI) and Fe (III), respectively.

As reported by the previous scientists that removal of metal ions increases up to a certain pH value and after that starts decreasing due to rise in the quantity of hydroxyl ions resulting in the interference caused by diffusion of metal ions. In case of chromium ions this phenomenon can be explained by the fact that since, chromium (VI) forms different negatively charged ions depending on the pH of aqueous solution such as $Cr_2O_7^{2-}$ and $HCrO_4^-$ at acidic pH whereas at higher pH values CrO_4^{2-} are formed therefore acidic pH facilitates its adsorption [39]. Higher pH values on the other hand, cause interference due to abundance of hydroxyl ions. Moreover, at alkaline pH, both chromium and iron hydroxides start precipitating from the solution hence adsorption studies are not possible to be carried out. Bhattacharyya *et al.* established the fact that maximum adsorption of iron occurs in the pH range of 1 to 4 [40]. Babel *et al.* also confirmed pH = 4 as optimum for chromium removal using nitric acid modified coconut shell carbon as adsorbent [36]. According to some other scientist higher pH values favor adsorption of positively charged metal ions since, the surface of adsorbent is deprotonated and more negatively charged hydroxyl ions are present to attract them [10,17].

Effect of parameters variation on conductivity and color of the aqueous solutions was also studied since Fe (III) and Cr (VI) impart color to aqueous solution and color intensifies with increasing concentration from 5 to 20 mg/L that can be reduced after applying coconut shell activated carbon; same is the case with conductivity. The results show that small and in most of the cases no change in the conductivity of aqueous solutions occurred as the adsorbent dosage, initial metal ions concentration and pH were varied. However, almost similar results for change in color were observed for both the adsorbents in all the cases with a maximum of 91.67% removal.

4. Conclusion

The results revealed that acid modified charcoal and manganese doped activated charcoal prepared from coconut shell waste can be used as alternative adsorbents for the removal of metals like Cr (VI) and Fe (III) from aqueous solutions. SEM results confirmed the porous structure with high surface area due to widening of pores due to the initial carbonization step. EDX results also proved the successful doping of manganese in the activated coconut shell charcoal matrix. Infrared spectroscopy showed the presence of hydroxyl, amino and carboxyl groups on the surface of both the adsorbents, considered responsible for metal adsorption.

Preliminary adsorption studies conferred that the surface modification of acid activated coconut shell charcoal by doping with fine particles of manganese enhanced its affinity for both the metals. The results showed that MDCSC proved to be a better adsorbent as compared to AMCSC for metal removal from synthetic solutions. However, the percentage removal for chromium (VI) was found to be greater as compared to iron i.e. 56.10% at optimum conditions i.e. 0.6 g/L adsorbent dosage, 10 ppm initial metal ions concentration and pH = 3. The effect of parameters variation on color and conductivity of the aqueous solutions showed that no significant change in conductivity occurred in case of both the adsorbents however, the color was reduced with slight variation in all the aqueous solutions with a maximum of 91.67% removal. Hence, manganese doped coconut shell charcoal proved to be an efficient environment friendly adsorbent having greater adsorption potential than acid activated coconut shell charcoal. Studies can be extended further to investigate more adsorption characteristics of the synthesized adsorbents.

Disclosure statement

Conflict of interest: The authors declare that they have no conflict of interest.
Ethical approval: All ethical guidelines have been adhered.
Sample availability: Samples of the compounds are available from the author.

CRediT authorship contribution statement

Conceptualization: Zahid Mahmood; Methodology: Samreen Zahra, Farah Deeba; Investigation: Farah Deeba, Habiba Mehtab; Data Curation: Zahid Mahmood, Asma Sheikh, Hamim Bukhari; Writing - Review and Editing: Samreen Zahra; Supervision: Samreen Zahra; Project Administration: Samreen Zahra.

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