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Decontamination of Cr(VI) and Mn(II) from aqueous media by untreated and chemically treated banana peel: a comparative study

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ABSTRACT

Untreated banana peels (UTBPs), alkali-hydrolyzed banana peels (AlBPs), acid-hydrolyzed banana peels (AcBPs), and bleached banana peels (BBPs) were used as adsorbents separately for the removal of Cr(VI) and Mn(II) from aqueous solution during batch experiments. Different parameters like pH, temperature, contact time, adsorbent dose, and initial concentration were studied. The maximum removal capacities for Cr(VI) were UTBP (45%), AlBP (87%), AcBP, (67%) and BBP (40%). While for Mn(II), the maximum removal capacities of theses adsorbents were UTBP (51%), AlBP (90%), AcBP (74%) and BBP (67%) at optimum conditions. The maximum removal of Cr(VI) and Mn(II) was obtained at initial concentration 3 mg/L, adsorbent dose of 4 g/L, pH 6, and contact time 60 min. It was noted that the metal ions removal capacity of these adsorbents was AlBP > AcBP > UTBP > BBP, which indicated that chemical treatment of banana peels enhances the biosorption of metal ions. This study showed that chemically treated banana peel can be used as suitable and cost-effective adsorbent for the removal of Cr(VI) and Mn(II) ions from aqueous solutions.

Keywords: Biosorption; Decontamination; Alkali-hydrolyzed; Acid-hydrolyzed; Bleached; Cost-effective

1. Introduction

The presence of heavy metals in the environment is of major concern because of their toxicity, bioaccumulation, and threat to human life and the environment. Large numbers of industries release excessive amount of heavy metals to the environment, which is a great problem all over the world. Heavy metals are non-biodegradable and persist in the environment for a long time making a potential threat to human and other living organisms. Various industries like metal plating, mining operations, tanneries, smelting, alloying industries, and storage batteries industries release large amount of heavy metals to aquatic system [1] Cr exists in aqueous medium in two forms, trivalent and hexavalent. These two forms have different biological activities [2]. Cr(VI) is more toxic than Cr(III) and is a primary contaminant and is carcinogenic [3]. Various industries use Cr for various industrial applications and discharge large quantity into the environment. Cr enters into the body through breathing, eating, drinking, or skin contact of chromium and its compounds. Cr(III) is present in vegetables, yeast, and fruits. Cr enters into food which is stored in steel containers. Cr(VI) is

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more dangerous to human health and can cause various allergies like skin rash [4].

Cr(VI) can cause other serious health problems like respiratory infections, weakness in immune system, liver and skin problems, lung cancer, and death. Metallic Cr is not so much toxic as hexavalent chromium. Inhalation of hexavalent chromium can affect badly the larynx, pharynx, and lungs. Cr (III) and Cr(VI) are present in the wastewater discharge from textile, tannery, metallurgical industries, and paints and pigments industries [5].

Mn and its compounds are widely used in the manufacture of products, ranging from disinfectants and health foods to plant fertilizers and batteries. While manganese oxides and carbonates are used in textile printing, glass and ceramics coloring, potassium permanganate is used as a discoloring agent [6].

There are a number of techniques used for removal of heavy metals such as electrolysis, chemical precipitation, oxidation reduction, solvent extraction, ion exchange, and adsorption [7–12]. Adsorption paid great attention because of low-cost materials as adsorbent for the removal of heavy metals and organic pollutants from industrial wastewater. Agricultural wastes are now becoming viable alternative since they are abundantly available, much cheaper, and have various functional groups such as carboxylic acid, esters, carboxylate, esters, hydroxyl, phenolic, and amino, that can act as adsorption sites for heavy metals ions and organic pollutants [13–16].

In the present work, various adsorbents like alkali-hydrolyzed banana peel (AlBP), acid-hydrolyzed banana peel (AcBP), untreated banana peel (UTBP), and bleached banana peel (BBP) were used as low-cost adsorbent for the removal of Cr(VI) and Mn(II) from aqueous medium. The effect of various parameters such as contact time, adsorbent dose, initial metal ions concentration, and pH was also studied.

2. Materials and methods

2.1. Preparation of adsorbents

Banana peels were obtained from local fruit fields in northern part of Pakistan. The banana peels were dried, alkali-hydrolyzed in round-bottom flask under reflux for three h. The pulp was washed thoroughly with distilled water to remove lignin and peptic materials and was dried in oven at 105˚C for 24 h.

2.2. Acid hydrolysis with 10% HCl

Hundred grams dried raw banana peels were taken in round flaks, 35 mL of 10% HCl (liquor ratio 1:15) and 1,500 mL water were added into it and then reflux for three h. After three h, the AcBP was cooled, filtered through bukner's funnel and then washed with distilled water till neutrality. The neutrality of the sample was checked by treating filtrate with methyl orange. In acid hydrolysis the glycosidic linkage in hemicelluloses and lignin depolymerises through α and β aryl ether cleavage to give soluble products.

2.3. Alkaline hydrolysis

Hundred grams dried raw banana peels were taken in round flaks, 20 mL of 10% NaOH (liquor ratio 1:15) and 1,500 mL water were added into it and then reflux for 3 h. After 3 h, the AlBP were cooled, filtered through bukner's funnel, and then washed with distilled water till neutrality. The neutrality of the sample was checked by treating filtrate with phenolphthalein. In alkaline hydrolysis, NaOH reacts with any free –COOH or acidic –OH that is present in the pre-hydrolyzed banana peel.

2.4. Bleaching of the pulp

Hundred grams of dry sample obtained from alkaline hydrolysis was taken in bottles, 1.5 g sodium chlorate and 0.5 mL glacial acetic acid were added to it and heated at 60˚C for three h in steam bath. The contents were filtered using bukner's funnel and then washed with distilled water till it become neutral. During bleaching, all peptic compounds and lignin were removed and completely white pulp was obtained.

2.5. Batch sorption experiments

The rate of various parameters on the adsorption process was studied by varying initial metal ions concentration (3, 6, 9, 12, and 15 mg/L), adsorbent dose (1, 2, 3, 4, 5, and 6 g/L), contact time (10, 30, 45, 60, 90, and 120 min) and solution pH (2, 4, 6, 8, 10, and 12) to obtain the equilibrium. The change in metal ions concentration in the aqueous solutions before and after equilibrium sorption was determined using the following equation.

$$q_e = \frac{V(C_0 - C_e)}{W} \tag{1}$$

where q_e is the adsorbed metal ions (mg/g adsorbent) on untreated and chemically treated banana peel, V is the solution volume (L), W is the sorbent amount (g), and C_0 and C_e are the initial and equilibrium metal ions concentration, respectively. The percentage metal ions removal was calculated using the following equation.

$$R\ (\%) = \frac{C_0 - C_e}{C_0} \times 100 \tag{2}$$

3. Results and discussion

3.1. Effect of initial concentration on Cr(VI) and Mn(II) removal

Effect of Cr and Mn concentration on the removal of Cr(VI) and Mn(II) was studied by changing the initial concentration and the results are summarized in Table 1. Cr and Mn solutions of different concentration (4, 6, 8, 10, and 12 mg/L) were taken at pH 4, 25℃, contact time 60 min, agitation speed 300 rpm and the adsorbent dose 5 g/L which result in the removal of Cr(VI) with change in concentration. Table 1 shows that increasing the initial metal ion concentration, decreases the Cr(VI) and Mn(II) removal. At lower concentration, the ratio of number of moles of metal ions to the surface area of adsorbent is large and adsorption takes place without any interuption. As the concentration increases, the surface area of the adsorbent becomes saturated and the removal of metal ions decreases [17].

Table 1
Effect of initial concentration on Cr(VI) and Mn(II) removal by (UTBP), (AcBP), (BBP) and (AlBP)

Initial concentration (mg/L)	Metal ions removal by UTBP (%)		Metal ions removal by AcBP (%)		Metal ions removal by BBP (%)		Metal ions removal by AlBP (%)	
	Cr (VI)	Mn (II)	Cr (VI)	Mn (II)	Cr (VI)	Mn (II)	Cr (VI)	Mn (II)
4.0	45	53	67	74	40	67	87	90
6.0	42	64	61	63	34	54	75	77
8.0	38	72	50	56	29	43	60	66
10.0	30	80	46	47	16	36	41	49
12.0	21	78	39	36	11	25	33	30

3.2. Effect of adsorbent dose on Cr(VI) and Mn(II) removal

The effect of sorbent dose on Cr(VI) and Mn(II) removal is shown in the Table 2. Different amount of adsorbents (1, 2, 3, 4, 5, and 6 g/L) was taken at constant pH 4, and equilibrated for 40 min at initial metals ion concentration of 3 mg/L. The effect of adsorbent dose on Cr(VI) and Mn(II) removal by UTBP, AcBP, BBP, and AlBP is shown in Table 2. The percentage adsorption increases from 50% at lower adsorbent dose (1 g/L) to 95% at higher adsorbent dose (4 g/L). The Cr(VI) ions removal capacity of adsorbents decreases at higher adsorbent dose above 4 g/L. Other investigations have shown similar results for Cr(VI) sorption. The competition of Cr(VI) ions for the available sites increases at higher adsorbent dose which decreases its removal [18].

3.3. Effect of contact time on Cr(VI) and Mn(II) removal

The effect of contact time on Cr(VI) and Mn(II) removal by UTBP, AcBP, BBP, and AlBP is shown in Table 3. Other parameters such as temperature 25℃, pH 4, agitation speed 300 rpm, initial metal ions concentration 10 mg/L, and the adsorbent dose 4 g/L were kept constant. Table 3 shows that the metal ions removal initially increases with increase in time up to 60 min and removal percentage reached to maximum. Further increase in time from 60 to 120 min brings no significant change in the equilibrium concentration. The increase in metal ions removal with increase in time is due to the higher interaction between the sorbent surface and metal ions. No increase in metal ions removal occurred after the 60 min as equilibrium has established.

Table 2
Effect of adsorbent dose on Cr(VI) and Mn(II) removal by (UTBP), (AcBP), (BBP) and (AlBP)

Adsorbent dose g/L	Metal ions removal by UTBP (%)		Metal ions removal by AcBP (%)		Metal ions removal by BBP (%)		Metal ions removal by AlBP (%)	
	Cr (VI)	Mn (II)	Cr (VI)	Mn (II)	Cr (VI)	Mn (II)	Cr (VI)	Mn (II)
1.0	53	37	65	48	41	47	47	47
2.0	64	54	78	63	57	58	63	60
3.0	72	60	84	79	62	68	74	78
4.0	80	93	92	94	70	85	82	90
5.0	78	87	87	83	68	76	74	81
6.0	70	75	82	80	65	63	71	75

Table 3
Effect of contact time on Cr(VI) and Mn(II) removal by (UTBP), (AcBP), (BBP) and (AlBP)

	Metal ions removal by UTBP (%)		Metal ions removal by AcBP (%)		Metal ions removal by BBP (%)		Metal ions removal by AlBP (%)	
Contact time (min)	Cr (VI)	Mn (II)	Cr (VI)	Mn (II)	Cr (VI)	Mn (II)	Cr (VI)	Mn (II)
10	18	27	21	26	15	25	24	30
30	27	36	34	42	24	38	31	43
45	43	53	47	67	41	61	49	65
60	75	80	78	83	65	75	86	84
90	75	78	78	76	65	70	86	80
120	75	74	78	72	65	67	86	77

3.4. Effect of pH on Cr(VI) and Mn(II) removal

The effect of pH on Cr(VI) and Mn(II) removal by UTBP, AcBP, BBP, and AlBP was investigated during batch experiments. Table 4 shows that pH of solution influences the biosorption of metal ions. Other parameters were kept constant such as temperature 25°C, contact time 60 min, agitation speed 300 rpm, initial metal ions concentration 3 mg/L, and the adsorbent dose 4 g/L. Table 4 shows that the metal ions removal is higher at lower pH, reaching to maximum at pH 4–6.0. As the pH of solution was increased, the percentage removal increased and reached to maximum value at pH 6. The decrease in removal of metal ions is due to the lowering of attraction between the positively charged metal ions and the negatively charged adsorbent. When pH increases beyond 6.0, removal of metal ions decreases due to the competition of metal hydrates and OH^- ions where the latter is more prominent species. At higher pH, the metal ions removal decreases due to the formation of soluble hydroxyl complexes [19]. Decreasing pH below 4 also decreases the removal of metal ions because at lower pH, higher concentration of H^+ ions is present in the reaction mixture.

Table 4
Effect of pH on Cr(VI) and Mn(II) removal by (UTBP), (AcBP), (BBP) and (AlBP)

	Metal ions removal by UTBP (%)		Metal ions removal by AcBP (%)		Metal ions removal by BBP (%)		Metal ions removal by AlBP (%)	
pH	Cr (VI)	Mn (II)	Cr (VI)	Mn (II)	Cr (VI)	Mn (II)	Cr (VI)	Mn (II)
2.0	15	45	23	40	20	37	24	40
4.0	22	62	31	66	28	60	33	61
6.0	73	86	85	78	79	74	80	85
8.0	62	70	72	68	63	61	76	72
10.0	50	57	59	53	44	46	51	53
12.0	19	30	20	25	13	20	15	30

3.5. Adsorption isotherm study

In the present study, Freundlich and Langmuir adsorption isotherms were used to describe the relationship between the adsorbed amount of metal ions and its equilibrium concentration in solution. The metal ions uptake capacity of BBP is lower than all others and that of AlBP is highest.

3.5.1. Freundlich adsorption isotherm

The linear form of Freundlich adsorption isotherm is given as [20],

$$\ln q = \ln K + \frac{1}{n}\ln C_e \tag{3}$$

where n and K are Freundlich adsorption isotherm constants, which are indicative for the intensity and capacity of adsorption, respectively. The values of K and n can be obtained by plotting log q_e vs. log C_e (Figs. 1 and 2). Linear plots were obtained from ln$q$ vs. ln C_e with slope $1/n$ and can be seen from Figs. 1 and 2. The values of n are larger which show that the adsorbent is effective. The greater $1/n$ values indicate that the metal ions concentration in solution is less than the adsorbed amount (Fig. 3).

The Cr(VI) and Mn(II) adsorption capacities of various adsorbents are shown in Tables 5 and 6. It

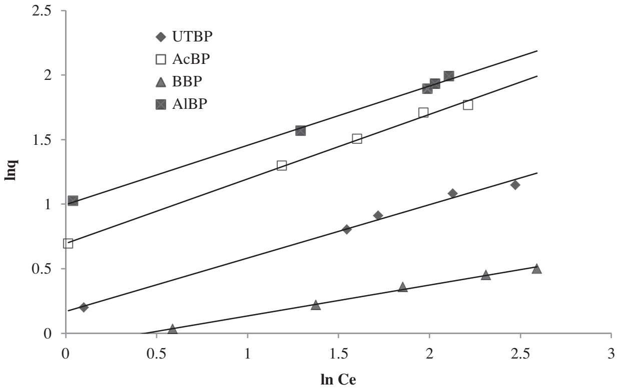

Fig. 1. Freundlich adsorption isotherm of Cr(VI) on UTBP, AcBP, BBP and AlBP.

Table 5
Comparison of adsorption isotherms constants of Cr(VI) on various adsorbents

Isotherm	Parameters	Adsorbents			
		UTBP	AcBP	BBP	AlBP
Freundlich	$1/n$	0.3994	0.4880	0.2337	0.4672
	K_F (mg/g)	1.4631	1.4983	1.3597	1.4014
	R^2	0.993	0.997	0.995	0.980
Langmuir	q_{max} (mg/g)	3.3557	4.4889	2.4644	5.1098
	K (L/mg)	0.8533	0.9429	0.7505	0.9466
	R^2	0.9987	0.9847	0.9876	0.9945

Table 6
Comparison of adsorption isotherms constants of Mn(II) on various adsorbents

Isotherm	Parameters	Adsorbents			
		UTBP	AcBP	BBP	AlBP
Freundlich	$1/n$	0.3844	0.7461	0.5328	0.8431
	K_F (mg/g)	1.574	2.8800	2.3115	2.7245
	R^2	0.997	0.995	0.989	0.995
Langmuir	q_{max} (mg/g)	2.8636	4.1516	2.7359	3.6010
	K (L/mg)	0.9397	0.9940	0.9359	0.9573
	R^2	0.998	0.995	0.999	0.995

can be seen from the table that the adsorption capacity of UTBP is much lower and chemical modification of adsorbent increases the adsorption capacity of adsorbent.

3.5.2. Langmuir adsorption isotherm

Langmuir adsorption isotherm is represented by the following equation:

$$\frac{C_e}{q} = \frac{1}{q_{max}K} + \frac{C_e}{q_{max}} \tag{4}$$

The equilibrium data for the adsorption of Cr(VI) and Mn(II) using various adsorbents fit into Langmuir adsorption isotherm model (Fig. 4). The applicability of Langmuir adsorption isotherm shows that the adsorption of Cr(VI) and Mn(II) on untreated and modified banana peel is monolayer. It also suggests, that there is no interaction between adsorbed species and the adsorption sites are equivalent. The values of K and q_{max} show that AlBP is an affective adsorbent for the removal of Cr(VI) and Mn(II) from aqueous media (Tables 5 and 6).

By plotting C_e/q against $C_{e,}$ straight lines were obtained with intercept $1/q_{max}K$ and slope $1/q_{max}$ where q_{max} is the amount of adsorption (mg/g) corresponding to a complete monolayer coverage and K (L/g) is the binding energy constant. Tables 5 and 6 show the results obtained for Cr(VI) and Mn(II) from Langmuir plot (Table 7 and Fig. 5).

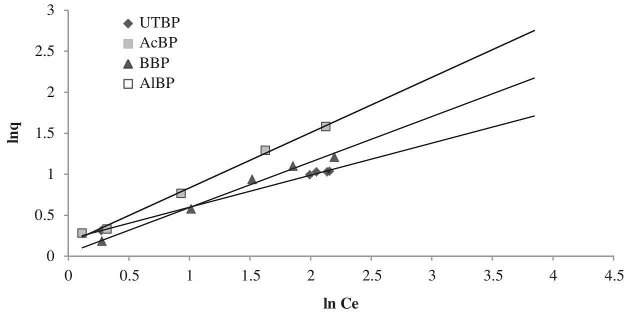

Fig. 2. Freundlich adsorption isotherm of Mn(II) on UTBP, AcBP, BBP and AlBP.

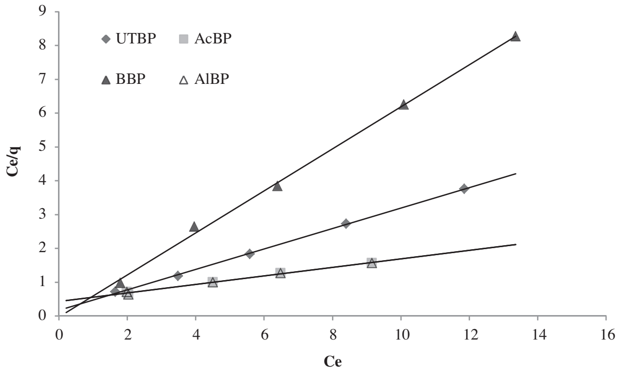

Fig. 3. Langmuir adsorption isotherm of Cr(VI) on UTBP, AcBP, BBP and AlBP.

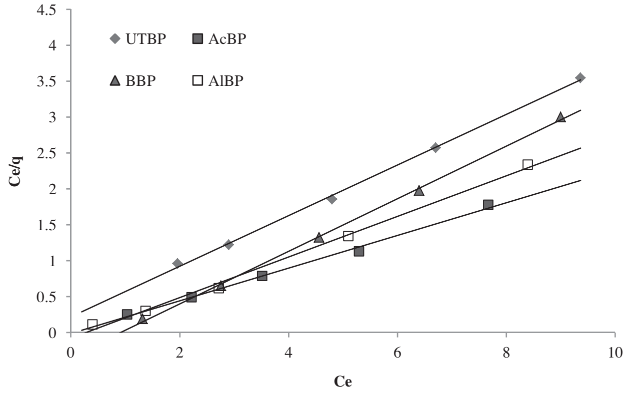

Fig. 4. Langmuir adsorption isotherm of Mn(II) on UTBP, AcBP, BBP and AlBP.

Table 7
Comparison of Cr(VI) and Mn(II) removal by UTBP, AcBP, BBP and AlBP

Adsorbents	Cr(VI) removal (%)	Mn(II) removal (%)
UTBP	45	51
AcBP	67	74
BBP	40	67
AlBP	87	90

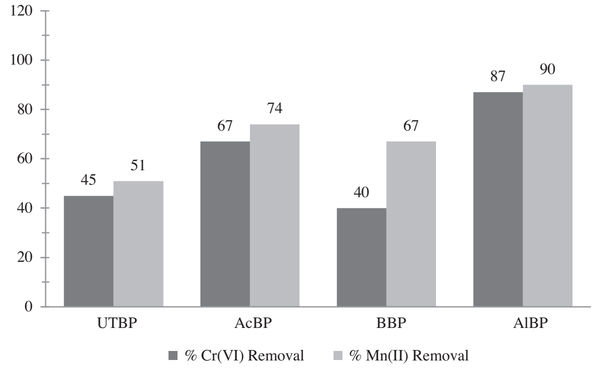

Fig. 5. Comparison of Cr(VI) and Mn(II) removal by UTBP, AcBP, BBP and AlBP.

4. Conclusion

Banana peel can be used as a low-cost and efficient adsorbent for the removal of heavy metals from waste water. In this present study, various low-cost adsorbents such as UTBP, AcBP, AlBP, and BBP are used for the removal of Cr(VI) and Mn(II) from aqueous solutions. It is clear from the results that the metal ions removal capacity of AlBP is much higher than AcBP, BBP, and UTBP. Furthermore, it is also clear from the results that metal ions removal capacity of chemically treated banana peel is much higher than untreated sample which show that modification with various chemicals increase the removal efficiency of banana peel. It was also found that AcBP removes Mn(II) (90%) than Cr(VI) (87%) at optimized conditions from aqueous solution. The metal ions removal efficiency of various adsorbent used in this work in higher for Mn(II) than Cr(VI). The series of metal ions removal by these adsorbent is AlBP > AcBP > BBP > UTBP.

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