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Surfactant-assisted bioremediation of hexavalent chromium from contaminated water

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ABSTRACT

Bioremediation is an efficient and cheap process for the removal of heavy metals. Solid agricultural wastes are frequently used as biosorbent for the removal of Cr(VI). In this study, water extract of *Azadiracta indica* sawdust is used to reduce Cr(VI) to Cr(III) and thereby lowering the toxicity. Water extract of *A. indica* sawdust effectively reduces hexavalent chromium at acidic pH (pH = 2). The reaction is irreversible. Trivalent chromium produced after reduction of Cr(VI) forms soluble organo-Cr(III) complex. Coordination of Cr(III) in the water extract occurs via the chelating coordination of –OH, –NH, etc, functional groups. The presence of these functional groups were confirmed from the IR spectra of the freeze-dried water extract, and the formation of Cr(III) is proved from the UV–vis spectra of the reaction mixture after the completion of reaction. But the rate of this reduction is very slow. Addition of nonfunctional surfactants increases the rate of reduction. Anionic surfactant sodium dodecylsulphate produces maximum effect.

Keywords: Bioremediation; Hexavalent chromium; Trivalent chropmium; *Azadiracta indica* saw dust; Water extract; SDS

1. Introduction

Chromium occurs naturally in the earth crust. It is a new entry in the major toxic metal series. Chromium can exist in different oxidation states from –II to +VI. The two environmentally stable oxidation states are +III and + VI having very different toxicities and mobilities [1]. Cr(III) is an essential dietary element required in trace quantities [2]. It plays a vital role in the metabolism of glucose, lipids, and proteins. On the other hand, Cr(VI) is considered to be the toxic form of the metal [3]. It is highly soluble in water, mobile, and bioavailable and almost 500 times more toxic than the trivalent one [4]. It has now become one of the most common environmental contaminants due to its wide spread use in industry. Chromate is essential in metal plating, tanning, water cooling, wood preservation, and pigmentation industry [5,6]. In case of chromium tanning process, leather takes up only 60–80% of applied Cr, and the rest is discharged into the sewage system. Hence, Cr(VI) concentration is increasing enormously in wastewater. But the maximum level of hexavalent chromium permitted in wastewater is 0.05 mg/L [7]. Cr(VI) in high dose causes kidney, liver, and gastric damage [8]. It enters into the body in the form of chromate by sulfate uptake pathway. Reductive metabolism of Cr(VI)

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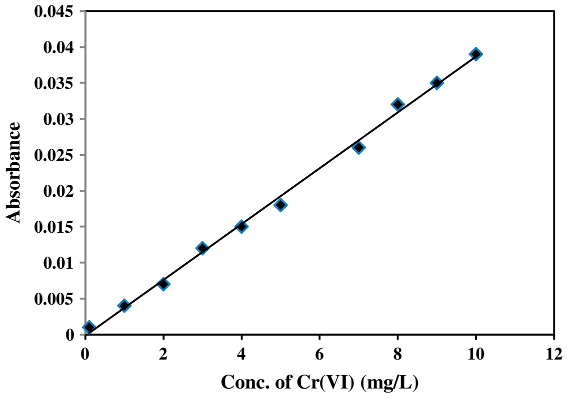


Fig. 1. Calibration curve of Cr(VI) solutions.

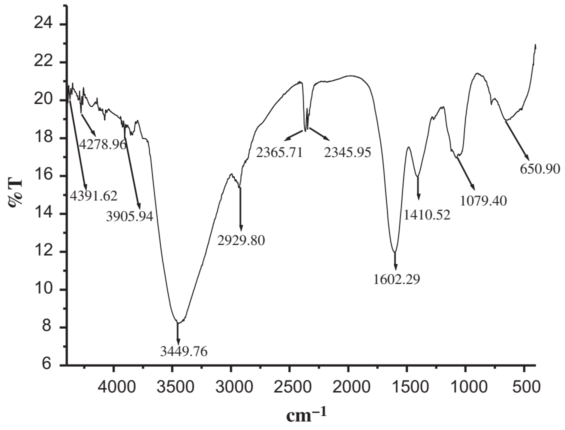


Fig. 2. IR spectra of freeze-dried water extract of neem sawdust.

inside the cell finally produces Cr(III) through the intermediates Cr(V), Cr(IV). Glutathione cysteine, ascorbate present in the cell may be primarily responsible for the reduction of hexavalent chromium. Ultimately, this Cr(III) forms adduct with DNA which induces mutation in the cell. So Cr(VI) should be removed from wastewater to protect people from its hazardous effect. The easy way of protection is to convert Cr(VI) to Cr(III). Several methods are developed to remove it from wastewater. Some of these are precipitation [9], ion exchange [10,11], ultrafiltration [12], membrane separation [13], electrocoagulation [14], solvent extraction [15], etc. However, most of these methods are often complicated, time-consuming and have high operational cost. In some cases, complete reduction of hexavalent chromium is not possible. Bioremediation is a technically feasible, economical, and environmental friendly process for Cr (VI) removal [16]. In most of the previous work, bioremediation is performed by the adsorption of Cr(VI) into the biomaterials. A number of agricultural wastes have been reported as biosorbents [17–19]. Sawdust is also used for the removal of hexavalent chromium [20–22]. Cellulose, hemicelluloses, lignin present in the biosorbents is involved in the adsorption coupled reduction. But the rate of such reaction is very slow. Not only the solid part but also the aqueous extract of biomaterials can also be used for bioremediation as it contains many reducing component which reacts with Cr(VI) and has the potential to convert it to Cr(III). The advantage of our process is that the rate of such process can be increased by using suitable catalyst. In our present work, we have used water extract of neem sawdust for bioremediation. But the rate of reduction is very slow. We have increased the rate of bioremediation with water extract of neem sawdust by the addition of surfactants as catalyst. In both the cases, Cr(III) is formed as the final product. It is confirmed by 1, 5-diphenyl carbazide method. Surfactants are widely used as catalyst in various reactions [23]. They have interesting behavior in surfaces and interfaces [24]. In our work, nonfunctional surfactant sodium

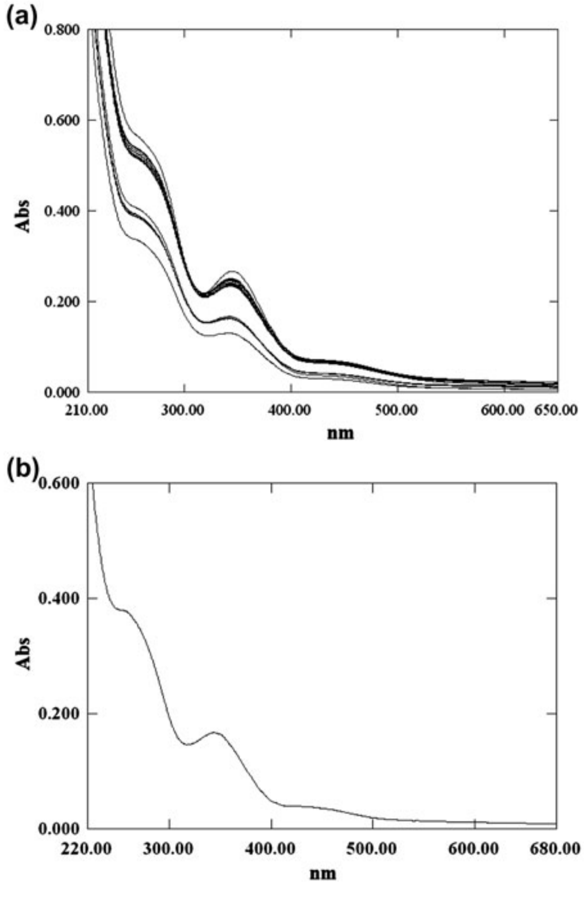


Fig. 3. (a) Scanned spectrum of surfactant-free biomaterial-added hexavalent chromium-contaminated water and (b) spectrum of surfactant-free biomaterial-added hexavalent chromium-contaminated water after 48 h.

Table 1
Cr(VI) concentration at different time intervals in absence of surfactants

Time (min)	Absorbance	Concentration (mg/L)
120	0.037	9.49
145	0.033	9.23
170	0.033	8.46
195	0.032	8.20
210	0.031	7.95
235	0.029	7.43
260	0.029	7.43
285	0.027	6.92
310	0.026	6.67
335	0.026	6.67
360	0.026	6.67
385	0.026	6.67
410	0.024	6.15
1,470	0.018	4.61
1,495	0.017	4.36
1,520	0.017	4.36
1,545	0.016	4.10
1,570	0.015	3.85
1,595	0.015	3.85
1,620	0.015	3.85
1,670	0.014	3.59
1,695	0.014	3.59
2,370	0.013	3.33
2,395	0.007	1.79
2,420	0.006	1.54
2,445	0.004	1.02
2,470	0.004	1.02
2,495	0.003	0.77

dodecylsulphate (SDS), TX-100 are used to accelerate the removal rate (reduction of hexavalent chromium to trivalent chromium), and it was found that removal rate is maximum in the presence of anionic surfactant SDS.

2. Experimental

2.1. Materials

Neem sawdust, $K_2Cr_2O_7$ (AR, BDH, India), SDS (AR, SRL, India), TX-100 (AR, SRL, India), 1, 5 diphenyl carbazide (Merck, India), and all other chemicals used were highest purity available commercially.

2.2. Methods

2.2.1. Preparation of biosorbent and water extract

Neem sawdust collected from local sawmill dried at 60˚C and then pulverized. To form the water extract, 1 gm of the sample is added to 250 ml of water mixed thoroughly with a sonicator (digital ultrasonic cleaner CD-4820). Insoluble part is filtered out.

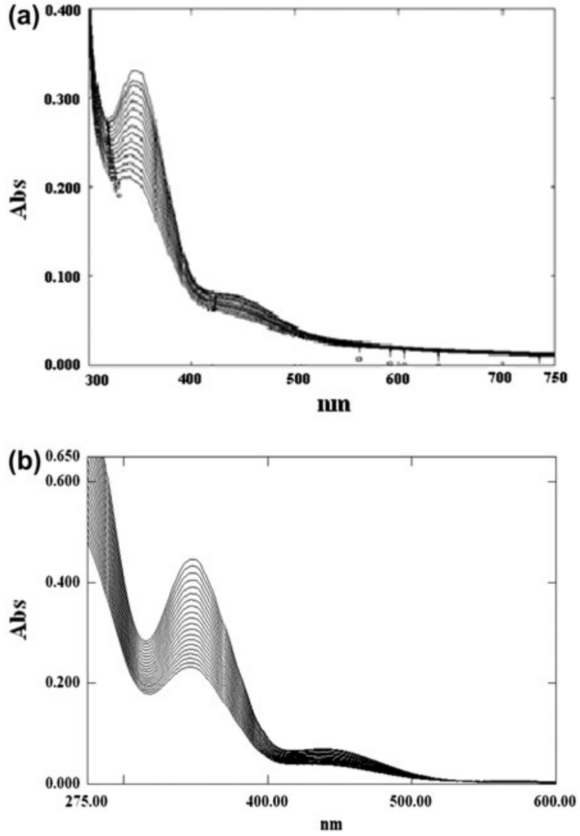


Fig. 4. (a) Scanned spectra of TX-100-catalyzed biomaterial-added hexavalent chromium-contaminated water. (b) Scanned spectra of SDS-catalyzed biomaterial-added hexavalent chromium-contaminated water.

2.2.2. Preparation of metal solution

Cr(VI) solutions were prepared using $K_2Cr_2O_7$. Stock solution (50 mg/L) was prepared by dissolving required quantity of $K_2Cr_2O_7$ in deionized water. Then, eleven set solution of concentration ranging from 0.1 to 10 mg/L were prepared from the stock.

2.2.3. Experiment

The absorbance of the Cr(VI) solution of concentration ranging from 0.1 to 10 mg/L was measured at 450 nm. A calibration curve (Fig. 1) was drawn by plotting absorbance vs. concentration.

Some amount of water extract is freeze-dried. An IR spectrum (Fig. 2) using a Perkin–Elmer FTIR model RX1 spectrometer instrument is taken.

It gives information about the functional groups present in water extract of biomaterial. Reaction is

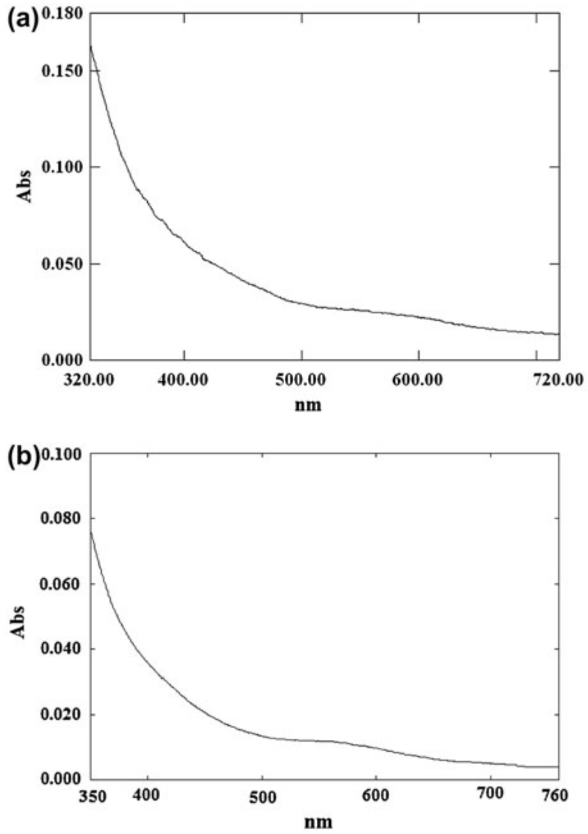


Fig. 5. (a) Overnight spectra of TX-100-catalyzed reaction mixture. (b) Overnight spectra of SDS-catalyzed reaction mixture.

started by adding the metal solution from stock to 30 ml of the aqueous extract at pH = 2. Total volume of the solution was 50 ml, and the concentration of Cr(VI) was10 mg/L. the mixture is allowed to stand for two hours. Progress of the reaction was studied by measuring the absorbance at 450 nm at regular time interval by UV–vis spectroscopy (Fig. 3(a)).

The concentration of Cr(VI) in the solution decreased with time due to reduction of hexavalent chromium by biomaterial. So absorbance value also decreased. But the rate is very slow. Even after 2 days, all the hexavalent chromium was not reduced which is evident from the spectra given in Fig. 3(b) (Table 1).

Then, the same experiment was carried out in the presence of SDS (4×10^{-2}) and TX-100 (4×10^{-2}). We get the absorbance value at different time interval from Fig. 4(a) (for TX-100) and Fig. 4(b) (for SDS).

The overnight spectra of the catalyzed biomaterial added hexavalent chromium-contaminated water (Fig. 5(a) and (b)) are similar to the spectra of aqueous solution of Cr(III).

This indicates that the reduction get completed within one day.

Table 2
Cr(VI) concentration at different time intervals in the presence of TX-100 (4×10^{-2} M)

Time (min)	Absorbance	Concentration (mg/L)
120	0.035	8.97
145	0.033	8.46
170	0.031	7.95
195	0.029	7.43
220	0.028	7.18
245	0.027	6.92
270	0.024	6.15
295	0.022	5.64
320	0.020	5.13
345	0.018	4.61
370	0.017	4.36
395	0.014	3.59
420	0.013	3.33
445	0.011	2.82
470	0.011	2.82
495	0.010	2.56
520	0.008	2.05
545	0.007	1.79
570	0.006	1.54
595	0.005	1.28
620	0.0025	0.64

Table 3
Cr(VI) concentration at different time intervals in the presence of SDS (4×10^{-2} M)

Time (min)	Absorbance	Concentration (mg/L)
120	0.034	8.72
145	0.029	7.43
170	0.024	6.15
195	0.020	5.13
220	0.017	4.36
245	0.011	2.82
270	0.008	2.05
295	0.005	1.28
320	0.004	1.02
345	0.002	0.51

Table 4
% of Cr(VI) removal in the presence and absence of surfactants

Surfactant	% Cr(VI) removal	Time (min)
Absent	92.3	2,495
TX-100	93.6	620
SDS	94.9	345

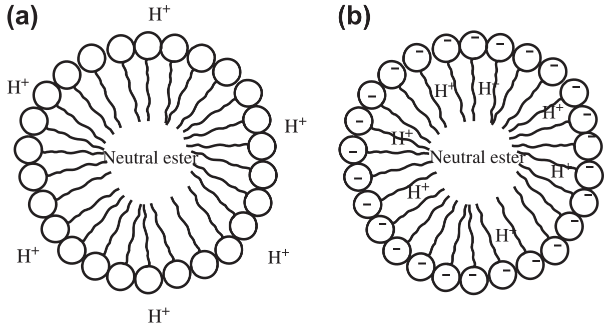
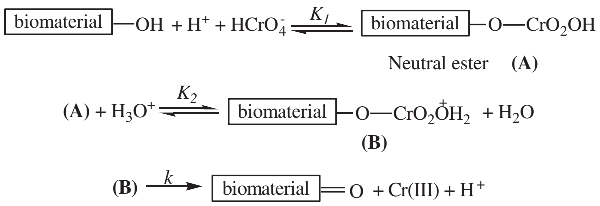


Fig. 6. Schematic representation of partitioning of neutral ester and proton in (a) SDS (b) TX-100.



Scheme 1. Reduction (24) of Cr(VI) by biomaterial.

3. Results

3.1. FTIR analysis

The spectra of the freeze-dried biomaterial shown in Fig. 3 display a good number of frequencies. The strong and broad band centered at 3,449 cm^{-1} characteristic of –OH, –NH stretches; weak band centered at 2,929 cm^{-1} assignable to the aliphatic C–H group. These groups are responsible for the reduction of hexavalent chromium to trivalent chromium.

3.2. UV–vis spectra analysis

We get the Cr(VI) concentration at different time interval by putting the absorbance values obtained from UV–vis spectra in the calibration curve. Table 1 gives the amount of Cr(VI) present in the water at different time interval in absence of surfactant.

In the presence of nonfunctional surfactants, the concentration of Cr(VI) decreases in a greater rate than in the absence of surfactant evident from Tables 2 and 3. But the decreasing rate is highest in case of SDS (Tables 3 and 4).

Nonfunctional surfactants behave here as nanoreactor (Fig. 6). Partitioning of neutral ester (Scheme 1, (A)) is possible here in both SDS and TX-100 micelles. Partitioning of proton is maximum in SDS due to electrostatic attraction. So rate is higher in SDS compared with TX-100.

4. Conclusion

Thus, the water extract of *Azadiracta indica* sawdust can effectively remove hexavalent chromium at acidic pH. Here, hexavalent chromium is reduced to trivalent chromium. Water-insoluble solid material is not required. The addition of nonfunctional surfactant greatly affects the rate of reduction. Anionic surfactant SDS accelerates the reaction most. So the reaction should be performed in the presence of SDS.

Acknowledgements

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