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Reliable bioremediation of hexavalent chromium from wastewater using mango leaves as reductant in association with the neutral and anionic micellar aggregation as redox accelarators

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ABSTRACT

Chromate, the invisible danger of environment is found to be degrading both animal and plant kingdom with its carcinogenic oxidizing ability by contaminating ground water. To prevent uncontrolled Cr(VI) contamination, various chemical methods for reduction of hazardous Cr(VI) to less toxic Cr(III) have been established of which aqueous reduction, ion exchange, liquid–liquid extraction, and electrocoagulation are found to be effective. Bioremediation, a greener approach is always of greater interest. The aim of the present study is to utilize mango leaves for the reduction of hexavalent chromium and to accelerate the reduction process by the use of surfactants. A 168 h study reveals that in absence of surfactants 58% of the total chromium(VI) is reduced, whereas removal percentage increases upto 75% in the presence of neutral surfactant TX-100 and upto 79% in the presence of anionic surfactant SDS.

Keywords: Hexavalent chromium; Nontoxic; Water extract; Mango leaves; Surfactant

1. Introduction

Heavy metal pollution has become one of the most serious environmental problem.They are not biodegradable and accumulate in the living tissues. Chromium is a toxic heavy metal of this type. It can exist in different oxidation state. Hexavalent and trivalent species are the most stable under environmental and physiological conditions [1–4]. Chromate is a known carcinogen and suspected mutagen and teratogen [5]. As soluble Cr(VI) can readily cross cell membranes [6] and can be taken up by both prokaryotic and eukaryotic cells [7]. Exposure to Cr(VI) by inhalation, touch, and ingestion can induce headaches, coughing, impaired breathing, ulcerated skin, corneal damage, nausea, vomiting, gastrointestinal convulsions, etc. So the level of chromium should be controlled in wastewater, natural water, and drinking water. Removal of hexavalent chromium contaminant from polluted industrial aqueous effluents is an important step in pollution control of surface water and ground water. Hexavalent chromium is used in several industries such as metal finishing, petroleum refining, iron and steel industries, leather tanning,

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inorganic chemicals production, textile manufacturing and pulp producing, electroplating etc. [8]. Effluents from tannery factories have been reported to contain 1,300–2,500 mg L^{-1} of Cr(VI) [9], whereas the permissible limit of Cr(VI) in surface water by the US EPA is below 0.05 mg/L [10]. On the other hand the inorganic trivalent chromium salts are typically insoluble [11], nontoxic and it is considered essential in mammals for the maintenance of glucose, lipid, and protein metabolism for many living organisms [12]. Conventional technologies such as ion exchange, liquid–liquid extraction and electrocoagulation, etc. have been employed to clean up hexavalent chromium ions from contaminated waters, but these technologies are not cost-effective. It is well known that cellulosic waste materials can be employed as cheap adsorbents to remove heavy metal ions. It utilizes the properties of certain kinds of inactive or dead biomass to bind and accumulate these pollutants by different mechanisms, such as adsorption, chemisorption, complexation, ion exchange, etc. [13]. However, it has been proved that Cr(VI) is easily reduced to Cr(III) by contact with organic materials under acidic conditions because of its high redox potential value [14]. Gardea-Torresdey et al. reported that Cr(VI) could be bound to an oat byproduct, but easily reduced to Cr(III) by positively charged functional groups, and subsequently adsorbed by available carboxyl groups [15]. Different types of biomaterials such as algae [16], fungi [17], and sawdust [18–23] are used for chromium removal. However, Cr(VI) reduction was found to be also pH dependent. The ability of mango leaves sawdust was studied for the ability to bind Cr(VI) under acidic condition. Mangifera indica (mango) leaves are an important source of phytochemicals which are mainly phenolic compounds mangiferin, quercetin. Mango contains various classes of polyphenols, carotenoids, and ascorbic acid [24]. These compounds reduces hexavalent chromium to trivalent chromium. Change in functional groups of the sawdust after reduction of hexavalent chromium is seen by IR spectroscopy. The soluble Cr(III) is complexed with organic ligands in the presence of cellular organic compounds to form stable and soluble organo Cr(III) complex [25]. Formation of Cr (III) species is characterized by UV spectroscopy. Rate of chromic acid oxidation of organic substrate such as tartaric acid, sorbitol, etc. can be increased by the use of surfactants [26–28]. So here the surfactants are used to speed up the bioremediation procedure. Surfactants dissolve completely in water at very low concentrations, but above a certain level, the critical micelle concentration, the molecules form globular aggregates, called micelles. Reactant species localizes in the relatively small volume of the micelles compared to the bulk solution. This leads to increase in rate of reaction. Formation of micelle is seen from optical images of the reaction mixture and the incorporation of reactant molecules inside the micelle has been confirmed by dynamic light scattering method.

2. Experimental

2.1. Materials

Mango leaves, $K_2Cr_2O_7$ (AR, BDH, India), SDS (AR, SRL, India), TX-100 (AR, SRL, India), H_2SO_4 (Merck, India), and all other chemicals used were of highest purity available commercially.

2.2. Methods

2.2.1. Preparation of water extract and metal solution

Mango leaves were collected from a village of Bankura, WB, India. It was dried and powdered with mixer grinder. Then it was washed with deionized distilled water several times then dried in an oven at 60˚C for 24 h. About 0.5 g of the mango leaves sawdust was added to 250 ml of water mixed thoroughly with a sonicator (Digital ultrasonic cleaner CD-4820). It was kept for one night for leaching of soluble organic matter from lignocellulosic materials. Then the water insoluble part was filtered out to obtain a clear solution and to understand the role of only the water soluble part of the mango leaves sawdust and then volume is made up to 250 ml.

Stock solution (100 mg/L) of hexavalent chromium was prepared by dissolving required quantity of $K_2Cr_2O_7$ in deionised water. Then a number of solutions of concentration ranging from 40 to 1 mg/L were prepared from the stock.

Absorbances of the prepared Cr(VI) solutions were taken at 450 nm. By plotting the absorbance value against concentration a calibration curve (Fig. 1) is drawn.

2.2.2. Experiment

Water extract of mango leaves was mixed with Cr(VI) solution. The pH of this mixture was near 5 at that time, i.e. in the acidic range. The initial pH of the solution was made 2 with 0.01 M HCl/0.01 M NaOH using a pH meter. At lower pH 2, the dominant form of Cr(VI) is $HCrO_4^-$ and hence the low pH value of 2.0 results in a higher percentage removal of Cr(VI). The mixture was centrifuged for 10 minutes at 3,000 rpm. The mixture was kept in an oven at 30˚C for about 2 d. On the second day, the absorbance of Cr(VI) in

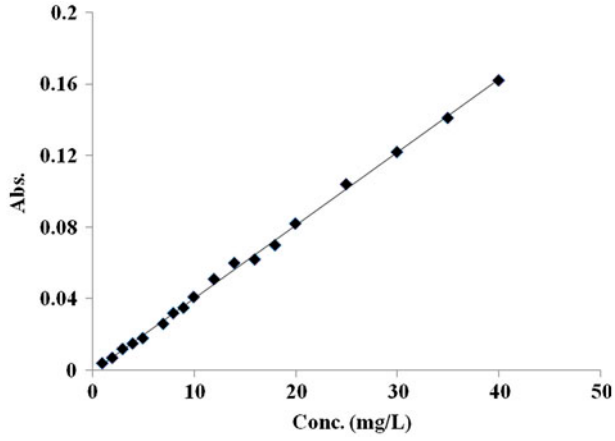

Fig. 1. Calibration curve of hexavalent chromium of concentration ranging from 40 to 1 mg/L.

the mixture is measured at 450 nm at regular time interval (1 h). But the reduction rate of Cr(VI) decreases with time. So the next measurement of absorbance was taken at long time interval. Same procedure was followed in presence of surfactants. Figs. 2–4 shows the decrease in absorbance of Cr(VI) at 450 nm by the water extract of biomaterial in absence and presence of surfactants.

Water extract of mango leaves finally reduce the hexavalent chromium into nontoxic trivalent chromium

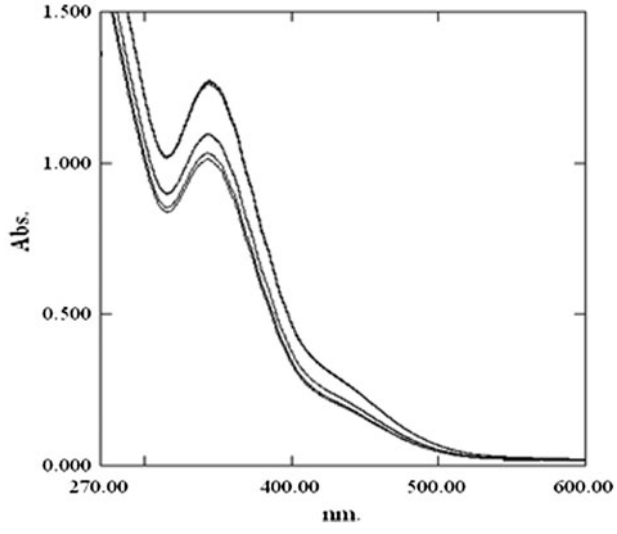

Fig. 2. Scanned spectra of surfactant free biomaterial added hexavalent chromium contaminated water showing the decrease in absorbance of Cr(VI) at definite time interval. [Cr(VI)] = 40 mg/L, water extract of biomaterial = 10 ml, pH 2, Temp. = 30 °C.

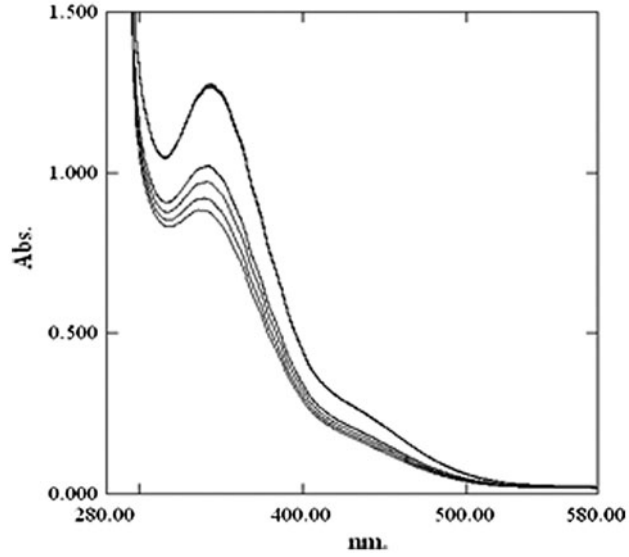

Fig. 3. Scanned spectra of TX-100 catalyzed biomaterial added hexavalent chromium contaminated water showing the decrease in absorbance of Cr(VI) at definite time interval. [Cr(VI)] = 40 mg/L, water extract of biomaterial = 10 ml, pH 2, TX-100 = 3×10^{-2} M, Temp. = 30 °C.

in presence and absence of surfactants and it is shown by spectrum of surfactant free reaction mixture and TX-100, SDS catalyzed reaction mixture (Fig. 5).

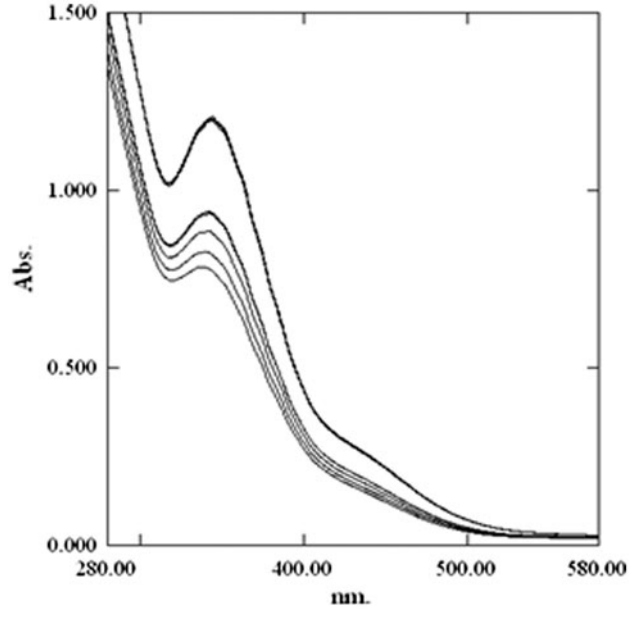

Fig. 4. Scanned spectra of SDS catalyzed biomaterial added hexavalent chromium contaminated water showing the decrease in absorbance of Cr(VI) at definite time interval. [Cr(VI)] = 40 mg/L, water extract of biomaterial = 10 ml, pH 2, [SDS] = 3×10^{-2} M, Temp. = 30 °C.

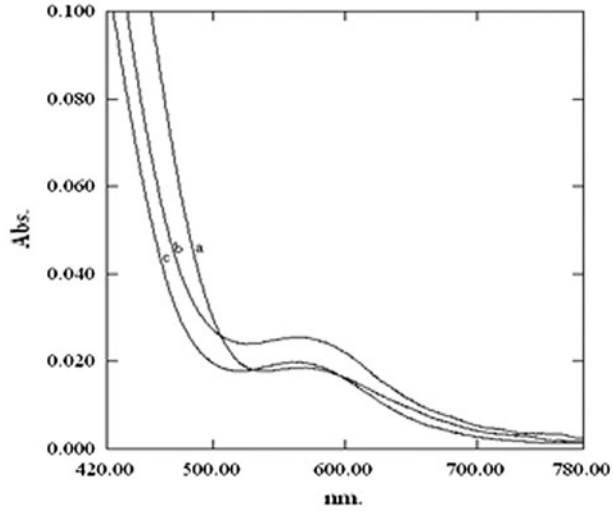

Fig. 5. (a) Spectrum of surfactant free biomaterial added hexavalent chromium contaminated water after completion of reaction, (b) TX-100 catalyzed biomaterial added hexavalent chromium contaminated water after completion of reaction, and (c) SDS catalyzed biomaterial added hexavalent chromium contaminated water after completion of reaction. Initially [Cr(VI)] = 40 mg/L, water extract of biomaterial = 10 ml, pH 2, [TX-100] = 3×10^{-2} M, [SDS] = 3×10^{-2} M, Temp. = 30°C.

3. Results

3.1. UV analysis

Percentage removal of Cr(VI) with time is plotted (Figs. 6–8) to see the catalytic action of SDS and TX-100. It is found that the absorbance of Cr(VI) at 450 nm decreases with time as the Cr(VI) is reduced to Cr(III) when came in contact with the biomaterial. The reducing component present in the water extract of mango leaves reduces hexavalent chromium to trivalent chromium in a slow rate as is shown in Fig. 2. From Figs. 3 and 4 it is clear that the absorbance of Cr(VI) at 450 nm decreases rapidly in the presence of surfactants compared to surfactant free water extract of mango leaves. Concentration of Cr(VI) remained in the solution is determined from the above UV spectra by comparing with the calibration curve (Fig. 1). Hence, the amount of Cr(VI) removed is also determined. Now the percentage removal at different time interval is plotted against the number of observation both in absence (Fig. 6) and in presence of surfactants (Figs. 7 and 8). The plots show that percentage of Cr(VI) removal is greater in the presence of surfactants. The highest efficiency of SDS as catalyst is also clear from the plot given in Fig. 8.

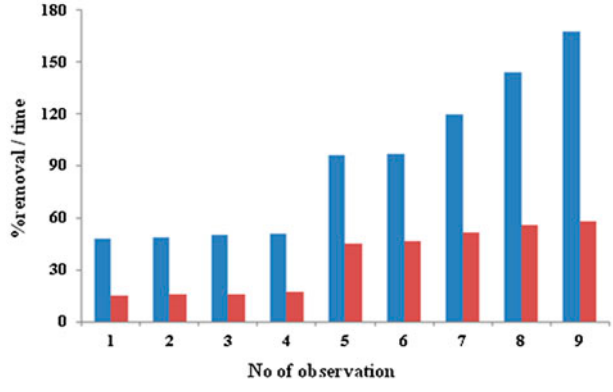

Fig. 6. Cr(VI) concentration (mg/L) at different time (hour) intervals in absence of surfactants. Red (shorter) bar represents the percentage of removal and black (long) bar represents the time.

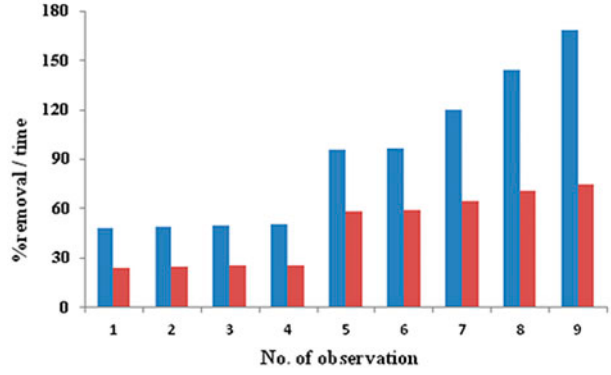

Fig. 7. Cr(VI) concentration (mg/L) at different time (hour) intervals in presence of surfactant TX-100. Red (shorter) bar represents the percentage of removal and black (long) bar represents the time.

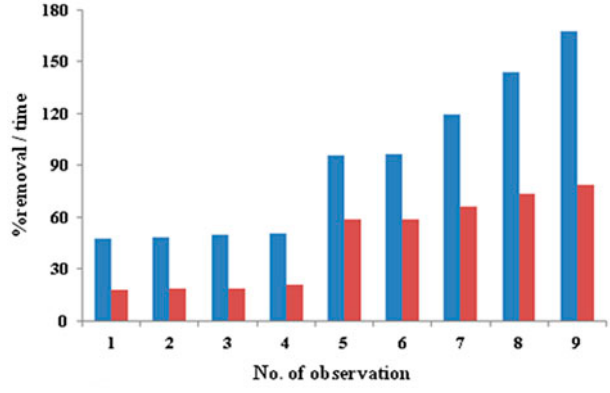

Fig. 8. Cr(VI) concentration (mg/L) at different time (h) intervals in presence of surfactant SDS. Red (shorter) bar represents the percentage of removal and black (long) bar represents the time.

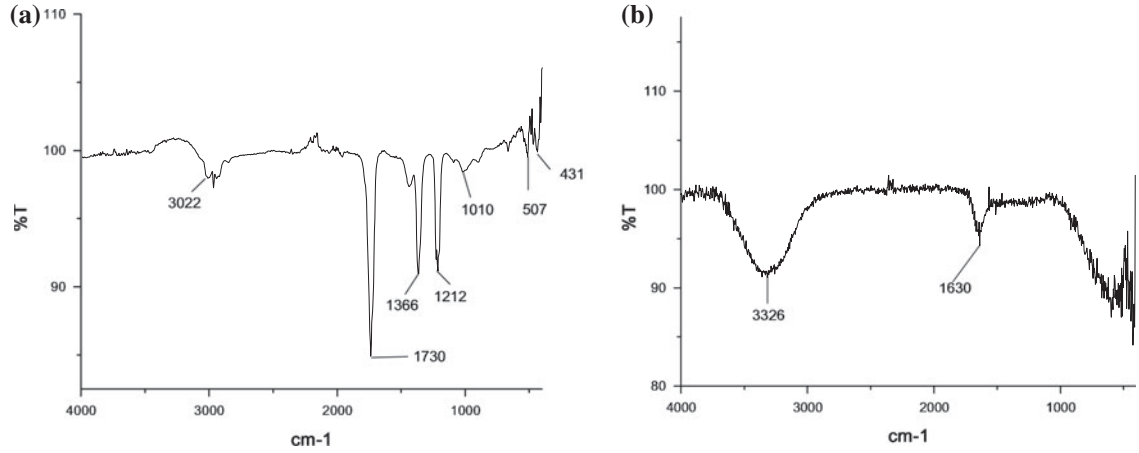

Fig. 9. (a) IR spectra of water extract of mango leaves in absence of hexavalent chromium in the solution and (b) IR spectra of water extract of mango leaves in presence of hexavalent chromium in the solution.

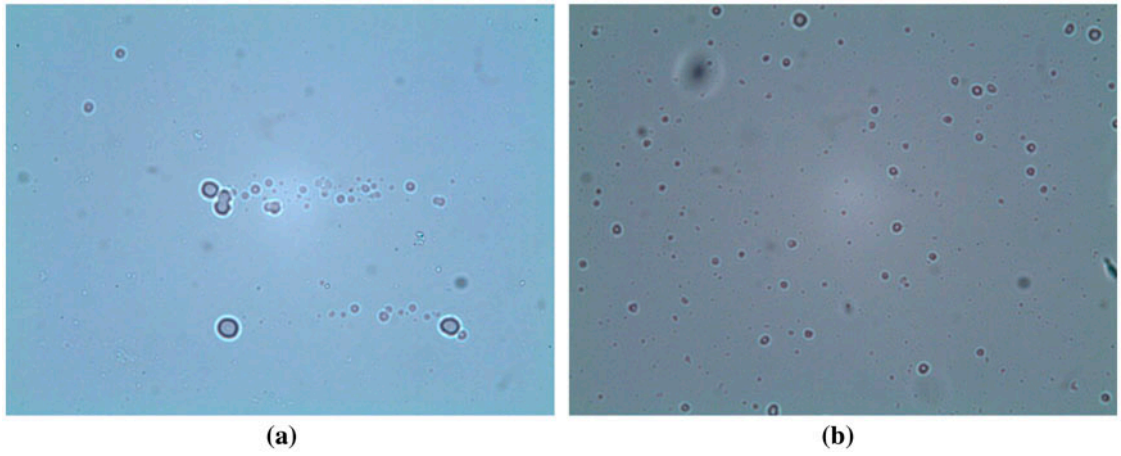

Fig. 10. Optical micrograph images of mixtures of water extract of mango leaves and surfactants in water: (a) water extract of mango leaves: TX-100 = 10:1 and (b) water extract of mango leaves: SDS = 10:1. Formation of TX-100 (Fig. 11(a)) and SDS micelle (Fig. 11(b)) is also confirmed from the TEM images of the water extract of mango leaves in presence of the above surfactants. These micelles are responsible for the catalyzation of the bioremediation process.

3.2. Preparation of sample for FTIR

Acclimatize The FTIR spectra of the water extract, before and after Cr(VI) uptakes, are obtained to characterize the surface structure and functional groups associated with Cr(VI) biosorption. Infrared spectra (Fig. 9(a)) of the water extract of mango leaves prepared earlier at pH 2 is taken using a Fourier transform infrared spectrometer (SHIMADZU PRESTIGE). Then 10-ml potassium dichromate solution of concentration 100 mg/L was mixed with 10-ml water extract of mango leaves sawdust at low pH. Total volume of the solution was 25 ml. A FTIR spectrum (Fig. 9(b)) of this solution was taken with SHIMADZU PRESTIGE. By comparing these two spectra the groups involved in complexation with Cr(VI) can be determined.

3.3. FTIR Analysis

The band at 3,022 cm^{-1} indicates the presence of –OH group. Peak at 1,730 cm^{-1} is the characteristic band for carbonyl stretching associated with the carbonyl groups present in lignin [29]. The peak at 1,366 cm^{-1} appears due to in plane O–H. The intense peak at 1,212 cm^{-1} is C–O stretching vibrations of ethers and alcohols. In case of untreated mango leaves

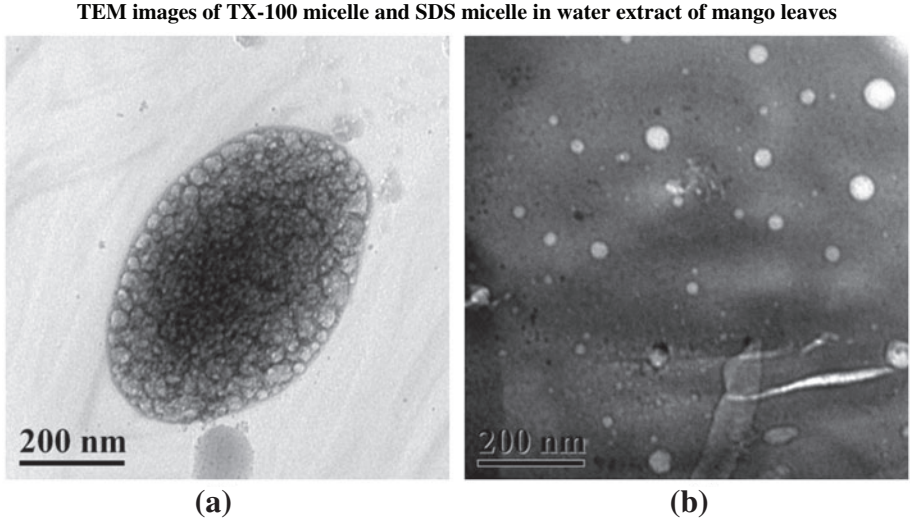

Fig. 11. TEM image of (a) blank TX-100 micelle in presence of acid and (b) SDS micelle in presence acid.

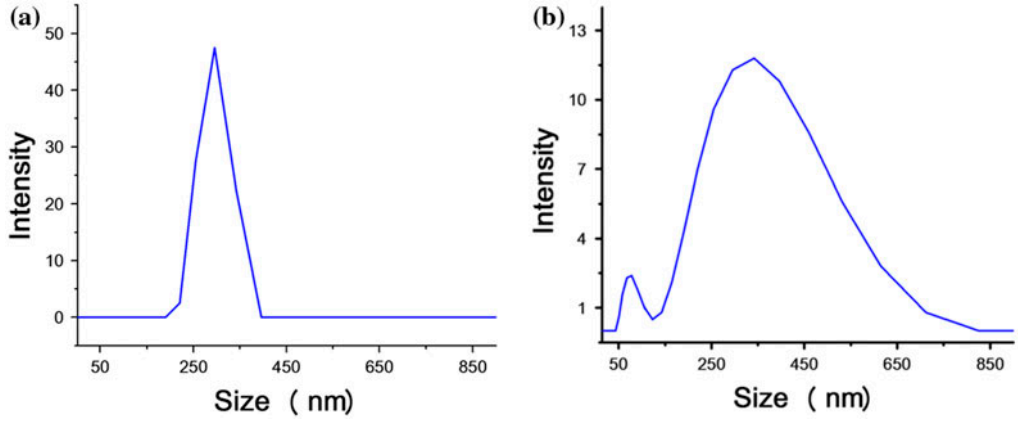

Fig. 12. DLS data showing increase in size of aggregates formed by SDS: (a) only SDS (3×10^{-2} mol dm^{-3}) and (b) SDS (3×10^{-2} mol dm^{-3}) in presence of Cr(VI) and biomaterial.

the peak due to –OH group appears at 3,022 cm^{-1}. Whereas in case of Cr laden material this peak appears at 3,326 cm^{-1} indicating the decrease in hydrogen bonding. The intensity of the peaks were either minimized or shifted slightly in case of treated and adsorbed sawdust, respectively. These results are similar to the ones reported earlier.

3.4. Optical micrographs for micelle

The optical micrographs are taken for mixtures of 10:1 concentration ratio of substrate (water extract) and surfactant in 100× magnification in an optical microscope. The images (Fig. 10) show that micelles are formed in presence of both TX-100 and SDS.

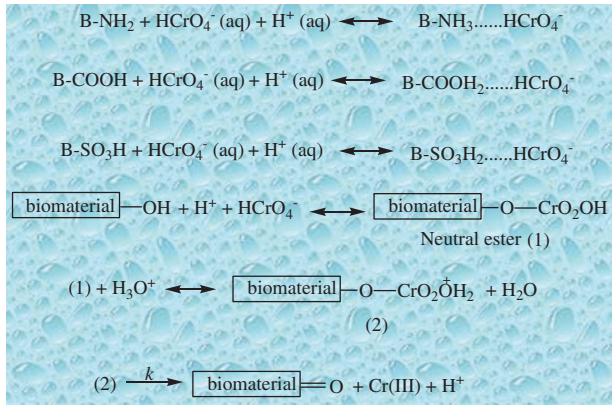

Fig. 13. Reduction of Cr(VI) by biomaterial in aqueous medium.

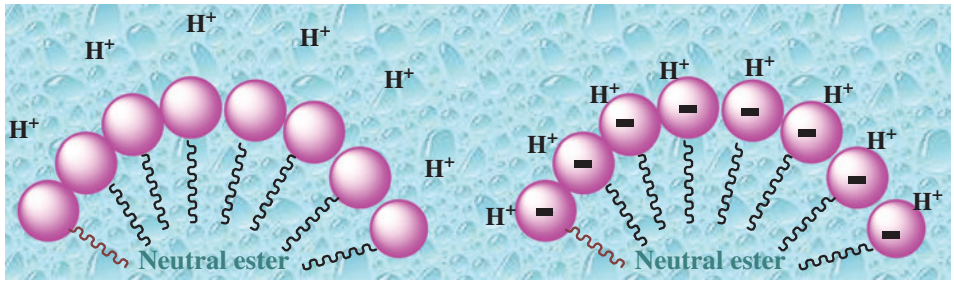

Fig. 14. Schematic representation of portioning of neutral ester and proton in (a) TX-100 and (b) SDS.

3.5. Dynamic light scattering

The size of the aggregated surfactant was determined by dynamic light scattering method using a Zetasizers Nano- ZS apparatus from Malvern Instruments Ltd. The beam of a 4 mW He–Ne laser (operating at a wavelength of 633 nm) was focused into the cuvette containing the surfactant solution. The intensity of scattered light was recorded in backscattering geometry at an angle of 90°. All measurements were achieved in triplicate. Plot of intensity vs. size of micelle (Fig. 11) showed that size of SDS micelle increases in presence of biomaterial and Cr(VI). So it can be said that rate of reduction increases in presence of micelle due to the incorporation of reaction mixture into the micellar core.

4. Discussion

In the pH range of 1.0–6.0 chromium ions coexist in different forms, such as $Cr_2O_7^-$, $HCrO_4^-$, $Cr_3O_{10}^{2-}$, and $Cr_4O_{13}^{2-}$, of which $HCrO_4^-$ predominates. At pH values greater than 6 lesser adsorption of Cr(VI) occurs may be due to the dual competition of both the anions $Cr_2O_4^{2-}$ and OH^- [30]. Protons and electrons are consumed during the reduction of Cr(VI) species as follows

$$Cr_2O_7^{2-} + 14\,H^+ + 6e \leftrightarrow 2Cr^{3+} + 7H_2O \quad E^0 = 1.33V \quad (1)$$

$$CrO_4^{2-} + 8\,H^+ + 3e \leftrightarrow 2Cr^{3+} + 4H_2O \quad E^0 = 1.48V \quad (2)$$

$$HCrO_4^- + 7\,H^+ + 3e \leftrightarrow Cr^{3+} + 4H_2O \quad E^0 = 1.35V \quad (3)$$

$$H_2CrO_4 + 6\,H^+ + 3e \leftrightarrow Cr^{3+} + 4H_2O \quad E^0 = 1.33V \quad (4)$$

Polyphenols, polysaccharides, low molecular weight carbohydrates and proteins, present in water extract of mango leaves whose redox potential are lower than that of chromate species under acidic condition provide the electrons for the above reactions. Biomaterial first reacts with $HCrO_4^-$ to form a neutral aster (Fig. 12). The neutral ester is protonated in acidic pH. The protonated neutral ester then dissociates to give Cr(III).

Initially, the pH of the solution was two but near the end of the reaction pH of all the uncatalyzed and catalyzed reaction mixture decrease slightly from the initial value. So it can be said that after formation of Cr(III) it undergoes cation exchange with the protonated biomaterial [31]. To interpret the observation in presence of micellar catalyst the applicability of the pseudo-phase kinetic model proposed by Menger and Portnoy [32] must be taken into consideration. According to this model the portioning of the reactant occurs between micellar phase and aqueous phase. Neutral ester is equally portioned in both the TX-100 and SDS micelle (Fig. 13). But the portioning of proton occurs maximum in SDS micelle due to the electrostatic attraction between the negative head group of SDS and proton (Fig. 14).

5. Conclusion

The results of the current investigation clearly demonstrated that water extract of mango leaves has strong potentials to reduce toxic and soluble Cr(VI) to the less toxic and less soluble Cr(III) and hence can be employed as a bio-agent for Cr(VI) detoxification from the contaminated effluents. In this study, a significant rate acceleration of Cr(VI) reduction in presence of surfactants was observed.

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