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Surfactant-assisted enhancement of bioremediation rate for hexavalent chromium by water extract of Sajina (*Moringa oleifera*) flower

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ABSTRACT

The presence of hexavalent chromium in waste water is a serious environmental problem due to its toxicity and carcinogenicity. Bioremediation is an efficient alternative to the conventional chemical methods of treatment. Bioremediation of toxic hexavalent chromium is done by the reduction of hexavalent chromium to relatively less toxic trivalent chromium. In this study, water extract of Sajina flower, which contains different types of reducing components such as sugar, amino acid, is used as reductant and the rate of bioremediation is increased by treatment with anionic and neutral surfactants. Here surfactants are used as catalyst in the bioremediation process. Sodiumdodecyl sulfate (SDS) is found to be the best catalyst. In the absence of surfactants, 60.37% of the total chromium(VI) is reduced within 285 h, whereas the removal percentage increases up to 96.25 and 99.37% in the presence of TX-100 and SDS, respectively, in minimum time.

Keywords: Hexavalent chromium; Nontoxic; Water extract; Sajina flower; Surfactant

1. Introduction

Large amount of organic and inorganic pollutants are discharged into the environment due to the progress in civilization and growth in industrial activities. Metals are not like the organic pollutants because they are not biodegradable and can accumulate in living tissues. Some metals are essential micronutrients for both plants and animals in low doses. But higher doses dramatically affect the health of most living organism [1–3]. Chromium is such a type of metal. Chromium occurs naturally in water from alluvial aquifers in the western part of the Mojave Desert [4]. It can exist in several oxidation states ranging from +2 to +6. However, the major forms are +6 and +3. Cr(III) is essential for humans in low levels because it is involved in the metabolism of glucose, lipid, and protein [5]. But the hexavalent form is a strong oxidizing agent and a potential carcinogen [6]. It causes liver damage, pulmonary congestion, and skin irritation resulting in ulcer formation [7]. Hexavalent chromium is a water-soluble species and can move freely in the subsurface and can readily enter the cell through sulfate uptake pathway. Chromium is used in many industrial activities such as metal plating, mining activities, smelting, battery manufacture, tanneries, petroleum refining, paint manufacture, pesticides, pigment manufacture, printing, and photographic industries [8]. The unused chromium is then discharged into water both in Cr(III) and Cr(VI) forms.

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Cr(III) is oxidized in different ways and converted into Cr(VI). Thus the level of Cr(VI) in water is going on increasing. The permissible limit of Cr(VI) in surface water by the US EPA is below 0.05 mg/L [9]. As Cr(VI) is highly toxic it must be removed from water to protect the living organisms in aquatic systems. The conventional method is to reduce Cr(VI) to 300-times less-toxic Cr(III) [10,11] and thereby lowering the concentration of Cr(VI). Many chemical processes such as ion exchange, liquid–liquid extraction, and electrocoagulation etc. have been proposed for this purpose [12–14]. But the methods are very expensive. This problem leads to the use of waste materials to reduce Cr(VI)–Cr(III) and thereby reducing the toxicity. Bioremediation is an effective and economical method for removing various toxic heavy metals. Different kinds of biosorbents, such as fungi [15–17], yeast [18], bacteria [19], algae [20], and lignocellulosic materials [21–28], are used for chromium and other toxic metal removal. In these cases, powdered biomaterials are used and it has been reported that Cr(VI) is completely reduced to Cr(III) by these solid biomaterials at low pH. Reaction proceeds through adsorption-coupled reduction mechanism. But the reaction is very slow. Method for increasing the rate of such process is not available in previous literatures. Again the water extract of such type of biomaterials can also reduce Cr(VI) as they contain several compounds that have the potential to reduce Cr(VI). But the mechanism is still unknown. In the present work, the water extract of dried and powdered Sajina flower is used for the bioremediation of hexavalent chromium. Sajina flower (*Moringa oleifera*) is rich in sugars and proteins. The aqueous extract of the mature flowers contains free natural sugars, D-mannose and D-glucose in the ratio of 1:5 [29]. It also contains polysaccharide which on hydrolysis gives D-glucose, G-galactose, and D-glucuronic acids in a molar ratio of 1:1.9:0.9 [29]. Again the presence of amino acids such as glutamic acid, arginine, proline, tyrosine, isoleucine, leucine, phenylalanine, and aspartic acid has also been reported [30]. So it is rich in hydroxyl and phenolic groups. These groups serve as the electron donor group in the water extract of biomaterials [31–34]. Among the sugars present in the cell wall of biomaterials, glucose has the highest electron-donating efficiency [35]. Presence of reducing sugar in the water extract of Sajina flower is confirmed by the positive response in the Molish test. In the monomeric form of cellulose, active hydroxyl groups are present. So Carboxylic acid, hydroxyl etc. groups play a major role in the binding of metal ions from solution. But the rate of reduction is very slow. In our previous work, we have used surfactants to increase the rate of oxidation of organic compound such as 2-propanol, L-sorbose, etc. by Cr(VI) [36–38]. So the surfactants can be used here to speed up the bioremediation procedure. Here cationic surfactant, anionic surfactant Sodiumdodecyl sulfate (SDS) and neutral surfactant Triton-X-100 are used to increase the rate of bioremediation. SDS is found to be the best catalyst for this process. Water-soluble organo-Cr(III) complex is formed. It is characterized by UV–vis spectroscopy.

2. Experimental

2.1. Materials

Dried and powdered Sajina flower, $K_2Cr_2O_7$ (AR, BDH, India), SDS (AR, SRL, India), TX-100 (AR, SRL, India), H_2SO_4 (QUALIGENS, India), α-naphthol (AR, SRL, India), methanol (AR, SRL, India) and all other chemicals used were of highest purity available commercially.

2.2. Methods

2.2.1. Preparation of water extract

Sajina flower was collected from a field of Bankura, WB, India. It was dried and powdered with a mixer grinder. One gram of this was added to 250 mL of water mixed thoroughly with a sonicator (Digital ultrasonic cleaner CD-4820). It was kept for one night. Then the insoluble part was filtered out to get the water extract of Sajina flower which was used in the whole experiment to reduce toxic Cr(VI).

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

Absorbances of the prepared solutions were recorded with a UV–vis spectrophotometer [UV-1601 (Shimadzu)] at 450 nm. By plotting the absorbance value against concentration, a calibration curve (Fig. 1) is drawn.

Ten millilitre of water extract of Sajina flower was mixed with 10 mL of 100 mg/L Cr(VI). At this pH, no reaction occurred. At low pH, the dominant form of Cr(VI) is $HCrO_4^-$ where the water extract of Sajina flower was positively charged. Hence the low pH value of 2.0 led to a higher percentage removal of Cr(VI). So concentrated sulfuric acid was added to maintain pH 2. The final volume of the solution was 25 mL. The mixture was centrifuged by Centrifuge-Z206A (Hermle Labortechnik GmbH) for 10 min at

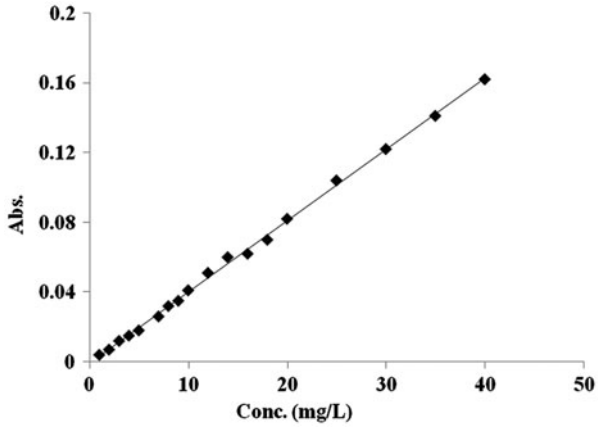

Fig. 1. Calibration curve of hexavalent chromium concentration ranging from 40 to 1 mg/L.

3000 rpm. After 1 h of mixing, absorbance of Cr(VI) was measured at 450 nm at regular time intervals (30 min) on the first day. On the second day, absorbance of Cr(VI) was again measured (at 450 nm) at regular time intervals (30 min). The rate of reduction decreased with increasing time. So the next measurements were made after a 24-h interval. Same procedure was followed in the presence of the surfactants.

From this scanned spectra, we got the absorbance value of Cr(VI) at different times at 450 nm. Concentrations of Cr(VI) in the solution at different time intervals can be calculated from the absorbance values with the help of the calibration curve (Fig. 1). Figs. 2 and 3 also show the decreasing absorbance value of Cr(VI) by the water extract of Sajina flower in the presence of surfactant TX-100 and SDS.

To prove that the hexavalent chromium was finally reduced to trivalent chromium by the water extract of Sajina flower, a spectrum (Fig. 4) of the reaction mixture (SDS catalyzed) is taken and it was seen that the spectrum was identical with the Cr(III) spectrum in aqueous solution.

Some amount of water extract of Sajina flower (with and without Cr(VI)) is freeze-dried. An IR spectrum (Fig. 5) using a Perkin-Elmer FTIR model RX1 spectrometer instrument detects the functional group involved in bioremediation.

3. Results

3.1. UV analysis

It was found that the absorbance of Cr(VI) at 450 nm decreased with time as the Cr(VI) was reduced to Cr(III) when it came in contact with the biomaterial. Fig. 6 shows that the absorbance of Cr(VI) at 450 nm continuously decreases with time in a slow rate due to the reduction of hexavalent chromium to trivalent chromium by the reducing component present in the water extract of Sajina flower. From Figs. 2 and 3 it is clear that the absorbance of Cr(VI) at 450 nm decreases

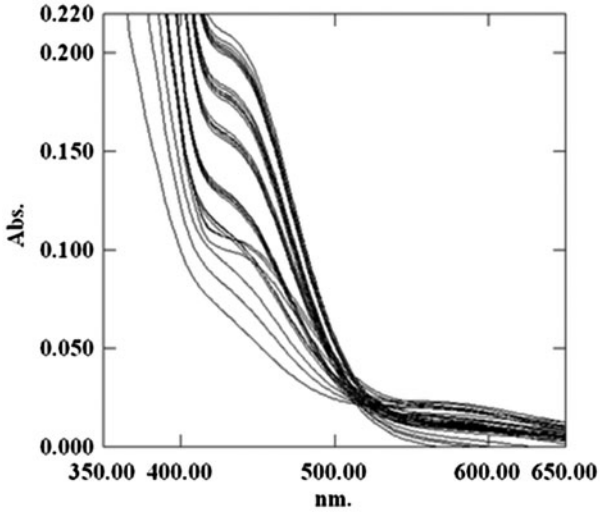

Fig. 2. Scanned spectra of surfactant-free biomaterial-added hexavalent chromium-contaminated water showing the decrease in the absorbance of Cr(VI) at definite time intervals. Cr(VI) = 40 mg/L, water extract of biomaterial = 10 mL, pH 2, temp. = 30 °C.

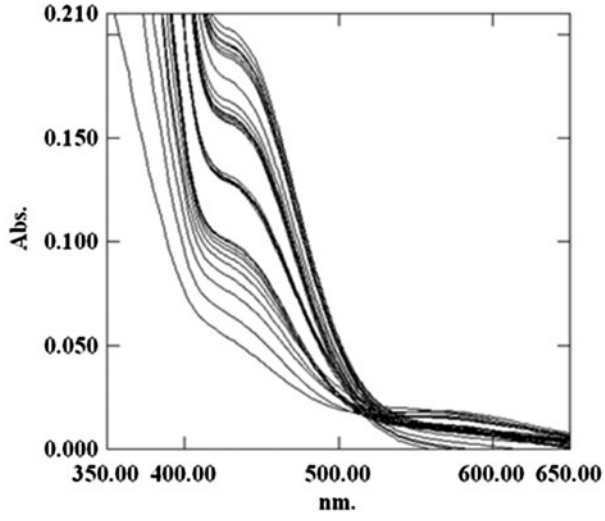

Fig. 3. Scanned spectra of TX-100-catalyzed biomaterial-added hexavalent chromium-contaminated water showing the decrease in the absorbance of Cr(VI) at definite time intervals. Cr(VI) = 40 mg/L, water extract of biomaterial = 10 mL, pH 2, TX-100 = 3×10^{-2} M, temp. = 30 °C.

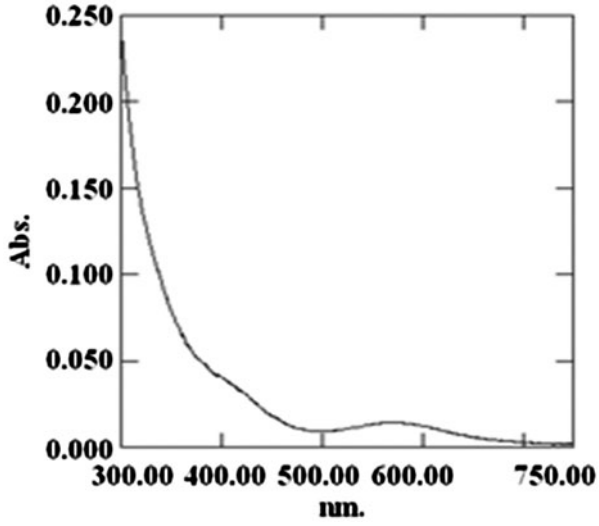

Fig. 4. Scanned spectra of SDS-catalyzed biomaterial-added hexavalent chromium-contaminated water showing the decrease in the absorbance of Cr(VI) at definite time intervals. Cr(VI) = 40 mg/L, water extract of biomaterial = 10 mL, pH 2, SDS = 3×10^{-2} M, temp. = 30 ℃.

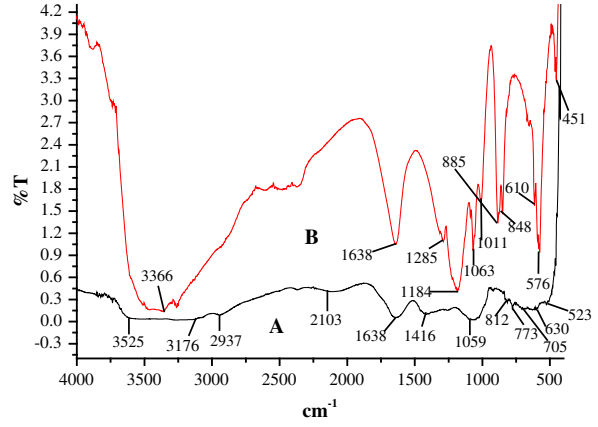

Fig. 5. Spectrum of SDS-catalyzed biomaterial-added hexavalent chromium-contaminated water after completion of the reaction. Initially [Cr(VI)] = 40 mg/L, water extract of biomaterial = 10 mL, pH 2, SDS = 3×10^{-2} M, temp. = 30 ℃.

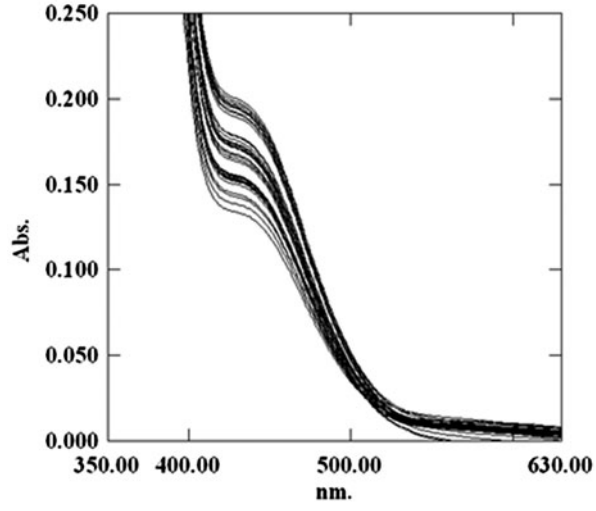

Fig. 6. Spectrum of biomaterial-added hexavalent chromium-contaminated water after 285 h (a) in the absence of surfactants (b) in the presence of TX-100 and (c) in the presence of SDS.

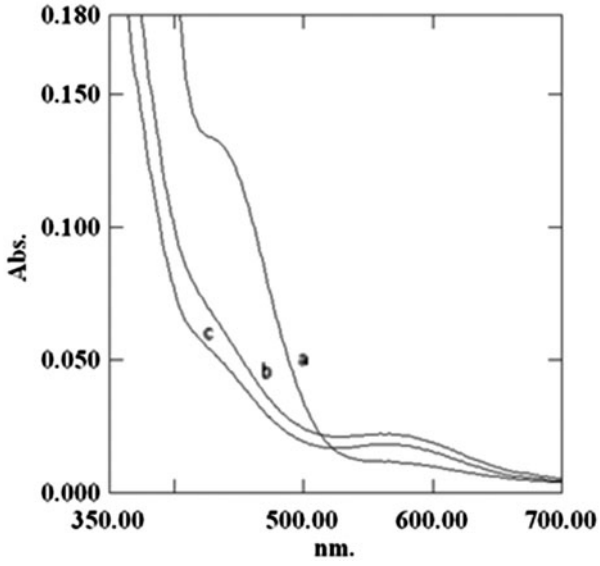

Fig. 7. (A) IR spectra of freeze-dried water extract of Sajina flower in the absence of hexavalent chromium in the solution. (B) IR spectra of freeze-dried water extract of Sajina flower in the presence of hexavalent chromium in the solution.

rapidly in the presence of surfactants compared to surfactant-free water extract of Sajina flower. The highest efficiency of SDS as catalyst is also evident from the spectra given in Fig. 7.

It shows that the absorbance of Cr(VI) at 450 nm is lowest in the case of SDS-catalyzed reaction mixture, i.e. the reduction of Cr(VI) is most effective in the presence of SDS.

3.2. IR analysis

The mechanism of Cr(VI) removal by the water extract of Sajina flower was elucidated on the basis of the FTIR analyses. CH_2 stretching frequency in this case appears at 2,937 cm^{-1}. In the range 1,400–1,450 cm^{-1} some weak bands are present, corresponding to the bending vibration of CH_2 and CH groups [39]. In case

of untreated Sajina flower, the peak due to –OH group appears at 3,176 cm^{-1}. Whereas in case of Cr-laden material this peak appears at 3,366 cm^{-1} indicating the decrease in hydrogen bonding. We also observed the emergence of a strong broad peak at 1,638 cm^{-1} which has been assigned to the C=O group of amide [40]. Again the $\%T$ value at 1,638 cm^{-1} increases in the case of Cr(VI)-laden water extract. Band at 1,063 cm^{-1} is assigned to the C–O stretching mode of vibration [41] which is shifted to a larger value (1,063 cm^{-1}) in the case of Cr-laden water extract. Peaks located near 1,100–1,000 cm^{-1} are related to the C–O bond, which is characteristic for polysaccharides, it also relates to –CN stretching [42]. Peak at 800–850 cm^{-1} suggests the presence of sulfonate group on the cell surface [43]. Changes were observed in the region of 1,655–750 and 3,450–2,800 cm^{-1}. These changes indicate that Cr(VI) was complexed by carboxyl, amide, polysaccharides, and sulfonate functional groups present in the water extract of Sajina flower.

4. Discussion

Cr(VI) may exist in the aqueous phase in different anionic forms such as chromate (CrO_4^{2-}), dichromate ($Cr_2O_7^{2-}$), or hydrogen chromate. The following equilibria may be written for the Cr(VI) anions present in aqueous solution [44].

$$H_2CrO_4 \leftrightarrow HCrO_4^- + H^+ \; K_1 = 1.21 \quad (1)$$

$$Cr_2O_7^{2-} + H_2O \leftrightarrow 2\,HCrO_4^- \; K_2 = 35.5 \quad (2)$$

$$HCrO_4^- \leftrightarrow CrO_4^{2-} + H^+ \; K_3 = 3 \times 10^{-7} \quad (3)$$

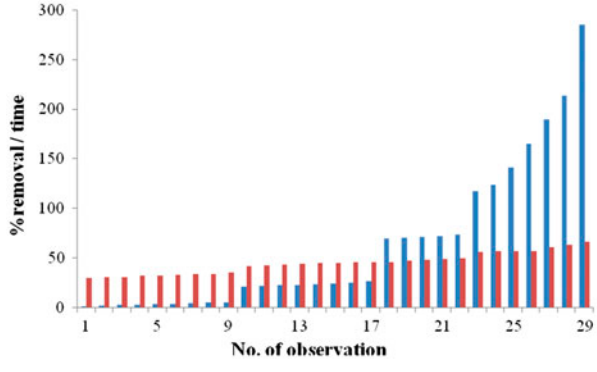

Fig. 8. Removal percentage of Cr(VI) at different time (min) intervals in the absence of surfactants. Red (shorter) bar represents the percentage of removal and blue (long) bar represents the time.

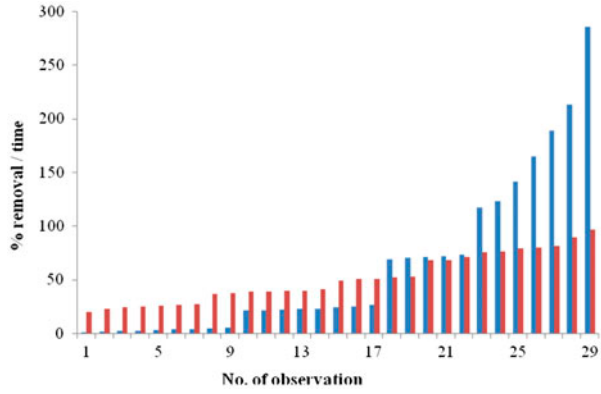

Fig. 9. Removal percentage of Cr(VI) at different time (min) intervals in the presence of surfactant TX-100. Red (shorter) bar represents the percentage of removal and black (long) bar represents the time.

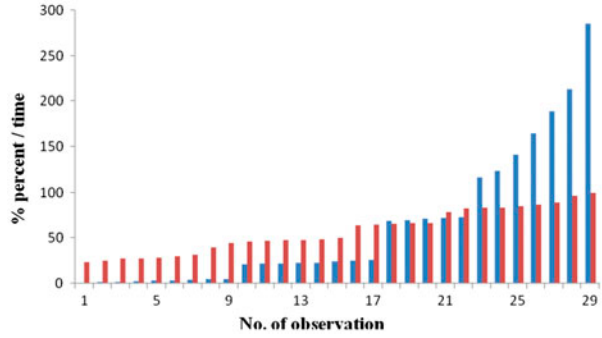

Fig. 10. Removal percentage of Cr(VI) at different time (min) intervals in the presence of surfactant SDS. Red (shorter) bar represents the percentage of removal and black (long) bar represents the time.

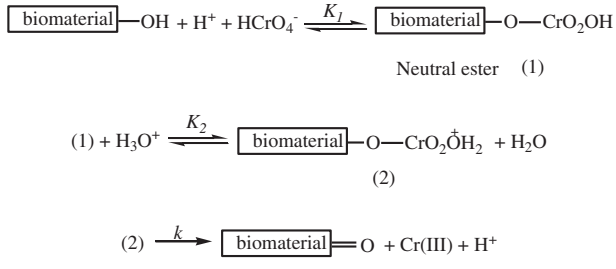

Fig. 11. Reduction of Cr(VI) by biomaterial.

Inside the solution, the hexavalent chromium is reduced to Cr(III) and the reaction can be written as:

$$HCrO_4^- + 7H^+ + 3e \rightarrow Cr^{3+} + 4H_2O \quad (4)$$

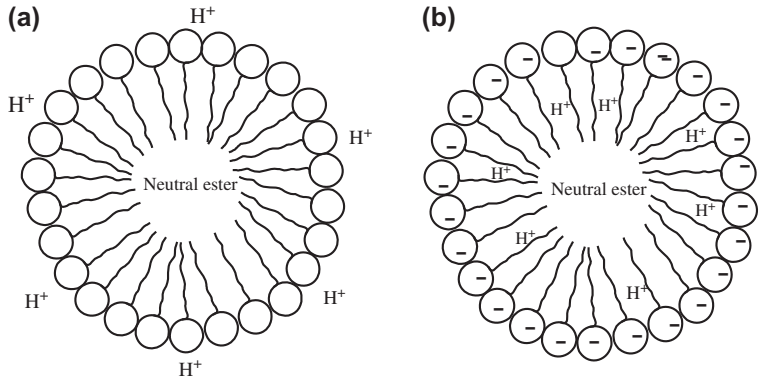

Fig. 12. Schematic representation of partitioning of neutral ester and proton in (a) TX-100 and (b) SDS.

Other forms of hexavalent are also reduced by the same way. The water-soluble organic compound supplies the electron required for the above reduction and they become oxidized. The following reactions can be written for the oxidation of the biomass [45].

$$C(org) \rightarrow CO_2 \text{ and/or}$$

$$C(org) \rightarrow C \text{ (org oxidized)}$$

Initially pH of all the reaction mixtures increases slowly from pH 2. It occurs as H^+ ion is consumed during the reduction of Cr(VI) following reaction (4). But near the end of the reaction, pH of the solutions decrease to a lower value (1.85 for uncatalyzed reaction mixture, 1.81 for TX-100-catalyzed reaction mixture and 1.80 for SDS-catalyzed reaction mixture). So it can be said that after the formation of Cr(III) it undergoes cation exchange with the protonated biomaterial [47]. But the pH lowers to a small extent because at this low pH protons have a high ability to compete with Cr(III) [46]. When surfactants are present in the reaction mixture, the rate of Cr(VI) reduction is much higher and almost goes to completion in the presence of SDS within 285 h, whichis evident from Figs. 8–10. In previous literature, catalysis of bioremediation process is not mentioned.

In all the cases, concentrations of surfactants are above their critical micellar concentration (CMC). CMC is the concentration above which the surfactants begin to form globular aggregate called micelle. So they form micelle in the solution. The hydrophobic tails group together to create a non-polar interior with the head groups located at the surface of the glob in contact with the aqueous solution. Reactive species present in the solution will distribute itself between the aqueous phase and the micellar phase. As the concentration of the reactive species is higher in the micellar phase, the rate of Cr(VI) reduction by the water extract of Sajina flower increases in the presence of surfactant. The mechanism of the reaction occurring inside the micelle can be written as shown in Fig. 11.

Biomaterial first reacts with Cr(VI) and forms a neutral ester (1) [47]. Non-functional surfactants act as nanoreactors. Partitioning of neutral ester (Figs. 11 and 12) is possible here in TX-100 and SDS micelles. But the partitioning of proton is maximum in anionic surfactant SDS due to electrostatic attraction, and intermediate in neutral surfactant TX-100. So the rate is highest in the presence of SDS.

5. Conclusion

The present work demonstrates that the water extract of Sajina flower is able to efficiently reduce Cr(VI). Bonded carboxyl group, amide, polysaccharide, and sulfonate were the functional groups responsible for binding of Cr(VI) to the water extract of this biomaterial. Anionic surfactant SDS greatly increases the bioremediation rate. Cr(VI) of concentration 40 mg/L is totally reduced to Cr(III) within 285 h in the presence of SDS. But in the absence of surfactant it takes about 570 h to complete the reduction.

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