

Biosorption of chromium species by aquatic weeds: Kinetics and mechanism studies

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Abstract

In this paper, we have presented the results of Cr(VI) and Cr(III) removal from aqueous phase by different aquatic weeds as biosorbents. Batch kinetic and equilibrium experiments were conducted to determine the adsorption kinetic rate constants and maximum adsorption capacities of selected biosorbents. In most of the cases, adsorption followed a second-order kinetics. For Cr(III), maximum adsorption capacity was exhibited by reed mat (7.18 mg/g). In case of Cr(VI), mangrove leaves showed maximum removal/reduction capacity (8.87 mg/g) followed by water lily (8.44 mg/g). There was a significant difference in the concentrations of Cr(VI) and total chromium removed by the biosorbents. In case of Cr(VI) removal, first it was reduced to Cr(III) with the help of tannin, phenolic compounds and other functional groups on the biosorbent and subsequently adsorbed. Acid treatment significantly increased Cr(VI) removal capacity of the biosorbents whereas, alkali treatment reduced the Cr(VI) removal capacities of the biosorbents. FTIR spectrum showed the changes in functional groups during acid treatment and biosorption of Cr(VI) and Cr(III). Aquatic weeds seem to be a promising biosorbent for the removal of chromium ions from water environment.
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1. Introduction

Chromium is released into the environment through a large number of industrial operations, which include manufacturing of alloys, dyes and pigments, electroplating, metal finishing, petroleum refining, leather tanning, wood preservation, and as corrosion inhibitors in conventional and nuclear power plants [1]. Chromate is toxic, mutagenic and carcinogenic in nature. Hence, removal of Cr(VI) from industrial effluents is essential.

Conventional methods for removing dissolved heavy metal ions include chemical precipitation, chemical oxidation and reduction, ion exchange, filtration, electrochemical treatment and evaporative recovery. However, these high-end processes have significant disadvantages, including incomplete metal removal, requirement of expensive equipment and monitoring systems, high energy requirements and/or generation of toxic sludge or other waste products that require disposal [2]. This

has led to the development of alternative low-cost technologies for the removal of Cr(VI) and other heavy metals from industrial effluents.

Several recent publications reported the utilization of locally available adsorbents like fly ash, peat, microbial biomass [3–7] and agricultural byproducts [4] for heavy metal removal. The sorption capacity of different biosorbents like dried mycelium of some species of fungi, baggase, rice husk and fermented baggase were examined for cyanide and heavy metal removal from industrial effluents [8]. Adsorption of Cd(II) and Ni(II) was found to be higher than Cr(VI) and Zn(II) when phosphate treated rice husk was used as an adsorbent [9]. Adsorption of Cr(VI) with activated rice husk carbon, activated alumina [10], formaldehyde and sulphuric acid treated sawdust carbons [11] were investigated. The amount of adsorbed Cr(VI) increased with increase in dose of these adsorbents and the contact time. Many biosorbents such as fungus, seaweed, micro-algae and other plant-derived material have been studied for their metal uptake. Agarwal et al. [12] evaluated the effectiveness of low-cost agro-based materials, namely, *Tamarindus indica* seed (TS), crushed coconut shell (CS), almond shell (AS), ground nut shell

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(GS) and walnut shell (WS) for Cr(VI) removal. The state-of-the-art information regarding the remediation of Cr(III) and Cr(VI) by activated carbon and other low-cost adsorbents is available elsewhere [13].

Aquatic weeds are available in abundance and therefore attempts have been made to use them for heavy metal removal. It is reported that the roots of water hyacinth possess more metal uptake capacity compared to leaves and stem [14]. Dried Chinese Reed (*Miscanthus sinensis*) was investigated as adsorbent by Namasivayam and Holl [15] for the removal of Cr(III) from tannery wastewater. Most of the studies dealing with Cr(VI) biosorption described the process as anionic adsorption. There are a few reports on partial reduction along with anionic adsorption of hexavalent chromium by chemically modified *Saccharomyces cerevisiae* [16] and dead fungal biomass *Aspergillus niger* [2].

It is reported that in case of Cr(VI) biosorption in the pH range of 1–5, Cr(VI) was completely reduced to Cr(III), which appeared in the solution phase, or partly bound to the biomass [17]. Recently, the occurrence of the non-enzymatic reduction of Cr(VI) to Cr(III) by biomaterials or biomaterial-based activated carbons under acidic conditions were also reported [18–20]. When Cr(VI) comes in contact with organic substances or reducing agents, especially in an acidic medium, it spontaneously reduced to Cr(III), because Cr(VI) has high redox potential [17,21–24]. Therefore, it is very important to quantify the reduction of Cr(VI) by organic materials and the effects of various parameters on Cr(VI) reduction while using biosorbents for removal of Cr(VI). However, not many studies have been carried out to understand the kinetics and mechanism of Cr(VI) reduction and Cr(VI) and Cr(III) biosorption by aquatic weeds.

This study aims at comparative evaluation of various low-cost adsorbents derived from aquatic weeds for removal of Cr(VI) and Cr(III) from simulated wastewater. An attempt was also made to elucidate the mechanism of biosorption by the selected sorbents.

2. Materials and methods

2.1. Biosorbent

The biosorbents used in the present study include reed mat (*Cannomois Vvirgata*), water lettuce (*Pistia stratiotes*), arrow-leaved tear thumb (*Polygonum sagittatum*), lotus flower (*Nelumbo nucifera*), green taro (*Colocasia esculenta*), water lily flower (*Nymphaea* sp.), water hyacinth (*Eichornia crassipes*), and mangrove leaves (*Rhizophora mangle* L). All these biosorbents were collected from contaminated water bodies in and around Chennai, India.

2.2. Preparation of raw biosorbents

Collected water weeds (plants) were rinsed with distilled water and dried under sunlight for 48 h followed by oven drying at 60 °C for 48 h. The biosorbents were then cut into small pieces, ground in a blender and sieved to obtain constant size particles (between 400 and 500 μm). Adsorption experiments

were carried out using these adsorbents with a particle size of 400–500 μm .

2.3. Treatment with acid and alkali

Solutions of H_2SO_4 and NaOH at a concentration of 4N were selected for pre-treating the sorbents. Ten grams of the raw biosorbent was mixed with 100 mL of each solution and agitated (150 rpm) for 24 h. The biosorbent was washed with distilled water several times, until the pH was neutral, and then dried at 60 °C for 24 h. The raw and chemically treated biosorbent were later stored in desiccators, until further use.

2.4. Kinetic studies

The purpose of this experiment was to determine the contact time required to reach the equilibrium between dissolved and solid-bound sorbate (chromium metal ions). Experiments were carried out by agitating 100 mL of 25 mg/L Cr(III) solution with 1000 mg of adsorbent in a 250 mL conical flask. During batch experiments, solution pH was adjusted at 5 ± 0.5 using 1N NaOH and H_2SO_4 solution. The solution was kept in a mechanical shaker at 150 rpm and 30 °C. The adsorbent and adsorbate were separated by centrifugation at 8000 rpm for 5 min. Samples were collected after 15, 30, 45, 60, 120 and 180 min of contact time. The samples were analyzed for residual Cr(III) and COD concentration. Similar type of experiments were carried out for Cr(VI) adsorption also.

2.5. Sorption isotherms

Sorption isotherm studies for Cr(VI) and Cr(III) were conducted by using initial metal ion concentrations between 10 and 150 mg/L and an adsorbent concentration of 10 g/L at 30 °C for 6 h. The equilibrium data thus obtained was analyzed using Langmuir and Freundlich isotherms.

2.6. Quantification of released pigments and its hexavalent chromium reduction potential

Pigment extraction experiments were carried out by agitating 100 mL of solution with 1000 mg of sorbent in 250 mL conical flask. The adsorbent and adsorbate were separated by centrifugation at 8000 rpm for 5 min. The pigment released was measured in terms of COD. Concentrations of tannin and total phenolic compounds also were analyzed. In order to evaluate Cr(VI) reduction potential of released pigments, experiments were carried out by agitating 100 mL of 25 mg/L Cr(VI) solution along with 10 mL of pigment extract in 250 mL conical flask. The solution was kept in a mechanical shaker at 150 rpm and the temperature was maintained at 30 °C. Samples were collected after 15, 30, 45, 60, 120 and 180 min of contact time. These samples were analyzed for residual concentration of Cr(VI), total chromium, tannin and total phenolic compounds and COD. All these studies were carried out at a pH of 7.0 ± 0.1 .

2.7. Chemical oxygen demand (COD)

COD of liquid and soil samples were estimated as per standard methods [25]. Closed reflex method was followed.

2.8. Cr(VI) and total chromium analyses

Cr(VI) concentration was determined by diphenyl carbazide method [25]. Total chromium concentration was analyzed using atomic absorption spectrometer (Perkin-Elmer, USA). Cr(III) concentration was calculated by subtracting Cr(VI) concentration from total chromium concentration.

2.9. Fourier transform infrared (FTIR) analysis

Infrared spectra of the raw, treated and chromium-loaded biosorbents were obtained using a Fourier transform infrared spectrometer (Perkin-Elmer, USA). Adsorbents were dried in an oven at 60 °C for 24 h. For the FTIR study, approximately 5 mg of finely ground biomass was encapsulated in 1000 mg of KBr pellet (Sigma, USA) in order to prepare translucent sample disks.

2.10. Estimation of tannin and phenolic compounds

Dried adsorbent samples (500 mg) were successively extracted by shaking with 50 mL eluents (distilled water, methanol and phosphate buffer (100 mM)) for 3 h; allowed to settle for 5 min, thereafter filtered through Whatman (USA) No.1 filter paper. Filtrates were used to estimate tannin and phenolic compounds. Phenol contents of the extracts were determined by the modified Prussian blue assay suggested by Price and Butler [26]. Absorbance at 720 nm was determined (UV-spectrophotometer) against the reagent mixture with methanol instead of plant extract. Gallic acid was used as the standard. Tannin content was determined as described by Asquith and Butler [27]. This method is based on blue BSA method for determining protein precipitated by tannin. The absorbance was measured at 750 nm using a UV-vis spectrophotometer (Techcomp-8500, UK). Tannic acid was used as a standard for this purpose.

3. Results and discussion

3.1. Screening of biosorbents

The selected adsorbents were screened for their biosorption potential using adsorption kinetic studies. The results are summarized in Table 1. With an adsorbent dose of 10 g/L and an initial Cr(III) concentration of 25 mg/L, the removal of Cr(III) was between 78.55% (lotus) and 63.5% (green taro) for a contact time of 3 h. Under similar conditions, Cr(VI) removal varied from 99.3% (mangrove leaves) to 31.79% (water lettuce). It is clear from the results that different biosorbents have different metal uptake potential. In both the cases, residual total chromium present in the system was also analyzed. In case of Cr(VI), residual total chromium and hexavalent chromium concentrations varied significantly. Though, mangrove leaves

Table 1
Screening of various aquatic weeds for Cr(III) and Cr(VI) adsorption based on kinetic study results (3 h)

| Sorbents | Trivalent chromium | | | Hexavalent chromium | | |
|-------------------------|-------------------------|---------------------|------------------------|--------------------------|--------------------------|------------------------|
| | Initial Cr(III)=25 mg/L | COD released (mg/L) | Removal efficiency (%) | Initial Cr(VI)=25 mg/L | COD released (mg/L) | Removal efficiency (%) |
| Water lily | 7.636 | 3040 | 68.21 | 0.97 | 3320 | 58.99 |
| Lotus | 5.116 | 1680 | 78.7 | 1.31 | 1800 | 81.05 |
| Water hyacinth | 7.92 | 1400 | 67.03 | 3.74 | 1680 | 32.1 |
| Arrow-leaved tear thumb | 8.34 | 3000 | 65.28 | 16.39 | 2560 | 27.79 |
| Water lettuce | 7.18 | 1440 | 70.11 | 18.8 | 1520 | 28.42 |
| Green taro | 8.75 | 3080 | 63.57 | 3.23 | 3600 | 27.38 |
| Mangrove leaves | 7.26 | 3160 | 69.78 | 0.18 | 2840 | 67.87 |
| Reed mat | 7.04 | 1280 | 70.69 | 13 | 1200 | 25.82 |
| | | | | Total chromium (mg/L) | | |
| | | | | Residual chromium (mg/L) | Residual chromium (mg/L) | |

Initial conditions: Cr(VI) and Cr(III) = 25 mg/L, COD = 0 mg/L.

showed a high Cr(VI) removal efficiency of 99.23%, the total chromium removal was only 67.87%. This was true for other adsorbents also (Table 1). The Cr(VI) concentration in the solution decreased rapidly. However, total chromium adsorption rate was not as fast as Cr(VI) disappearance. This might be due to the reduction of Cr(VI) to Cr(III) in the system, and partial adsorption of Cr(III) on the sorbent. During the experiment, there was significant increase in solution COD in almost all cases due to the leaching of organic matter from the biosorbents. Even though, lotus, water lettuce and arrow-leaved tear thumb were showing promising results on removal of Cr(VI) and Cr(III) from aqueous phase, after the acid and alkali treatment, these sorbents became very sticky and there was considerable weight loss. Hence, these sorbents were not included in further studies.

3.2. Kinetics of metal uptake

The kinetics of Cr(III) and Cr(VI) removal by various biosorbents were also evaluated. These results are presented in Fig. 1a and b. It is evident from these results that an increase in contact time from 15 to 240 min increased the percentage removal of Cr(III) and Cr(VI). The adsorption was a very fast process for the first 30 min, and then the rate decreased and finally attained the pseudo-equilibrium within 3 h. However, the kinetics of total chromium removal, in case of experiment which started with Cr(VI), was relatively a slow process. The equilibrium was not reached even after 240 min (Fig. 1c). In case of Cr(VI), the removal might be occurring after the reduction of Cr(VI) to Cr(III) and subsequent binding of Cr(III) to the biosorbent [6,28–30]. This may be one of the reasons for the slow adsorption rate of total chromium. Moreover, the reduced Cr(III) might have formed complexes with the organic matter coming out of the biosorbent. This also might have affected the kinetics of adsorption of total chromium [29].

To describe the kinetic process, kinetic data were analyzed based on Lagergren pseudo first-order model, Ho's pseudo second-order reaction rate model. The mathematical representations of models are given in Eqs. (1) and (2).

Pseudo first-order adsorption kinetic model :

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

Pseudo second-order adsorption kinetic model :

$$\frac{t}{q_t} = \frac{1}{h} + \frac{1}{q_e} t \quad (2)$$

where $h = k_2 q_e^2$.

The adsorption rate constant (k_1) for Cr(VI) and Cr(III) sorption were calculated from the slope of the linear plot of $\ln(q_e - q_t)$ versus time. In the latter case, kinetic data were plotted between t/q_t against t . The kinetic rate constants obtained from first- and second-order pseudo kinetic model are given in Table 2. The high correlation coefficient value of 0.97–1.0 for all the biosorbents indicate that Cr(III) and Cr(VI) sorption on to the biosorbents followed a pseudo second-order kinetic expression. For Cr(VI) and total chromium removal, mangrove

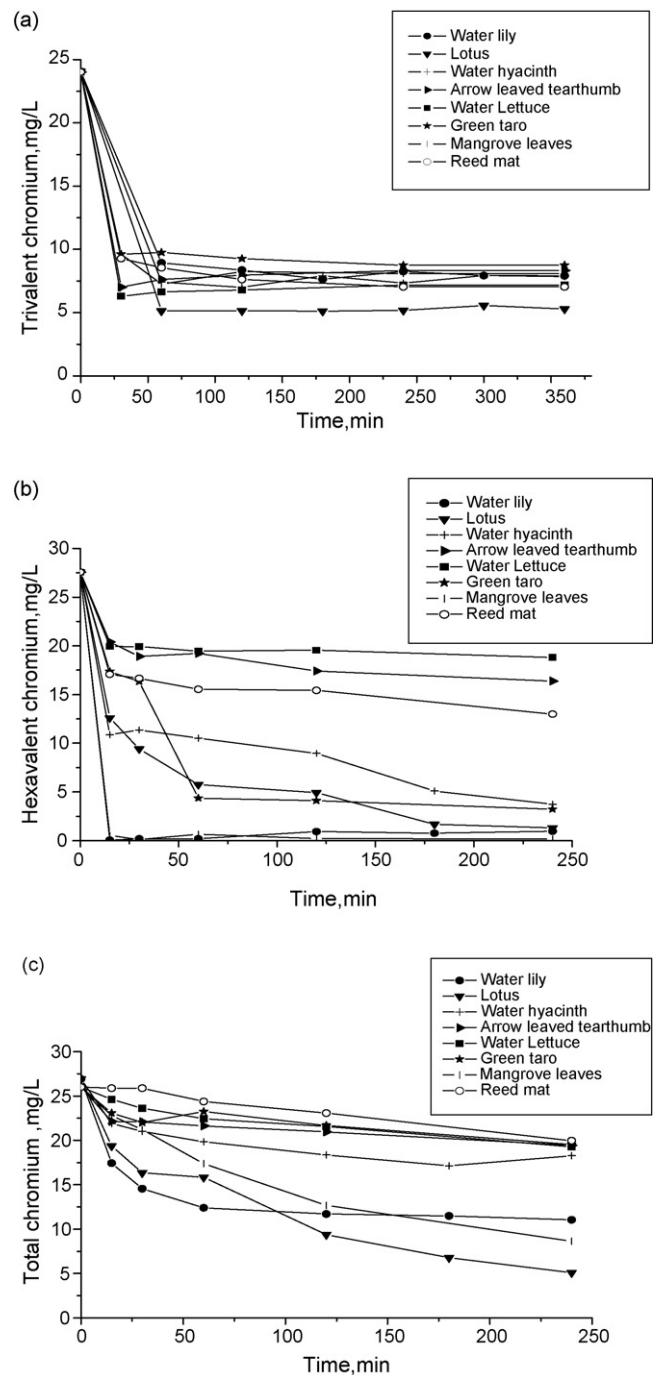


Fig. 1. Kinetic of Cr(III), Cr(VI) and total chromium removal by different aquatic weeds. (a) Trivalent chromium; (b) hexavalent chromium; (c) total chromium.

leaves showed a higher value followed by water lily, indicating that Cr(VI) sorption/reduction on these biosorbents is much faster than the Cr(VI) removal by water hyacinth and reed mat. The quick removal of Cr(VI) by water lily and mangrove leaves may be due to the availability of large quantity of organic material/groups capable of reducing Cr(VI) to Cr(III) and then adsorbing it to the surface. Similar observations are reported by many researchers. Lytle et al. [31] reported that Cr(VI) taken from the fine lateral roots of wetland plants was rapidly reduced

Table 2
Adsorption rates constants obtained from Lagergren pseudo first-order model and pseudo second-order model for selected biosorbents

| Metals | Adsorbent | Lagergren pseudo first-order model | | | Pseudo second-order model | | | | |
|-------------------------|--------------------|---|------------------------------|--------|--|------------------------------|--|--------|--------|
| | | Reaction rate k_1 (h^{-1}) | q_e (mg/g^{-1}) | r^2 | Reaction rate k_2 ($\text{g mg}^{-1} \text{h}^{-1}$) | q_e (mg/g^{-1}) | h ($\text{mg g}^{-1} \text{h}^{-1}$) | r^2 | |
| Trivalent chromium | Water lily | 7.021 | 1.114 | 0.9595 | 16.298 | 1.286 | 26.954 | 0.9989 | |
| | Water hyacinth | 4.205 | 1.093 | 0.9517 | 19.843 | 1.440 | 41.152 | 0.9999 | |
| | Green taro | 11.840 | 1.416 | 0.9984 | 11.793 | 1.205 | 17.123 | 0.9988 | |
| | Mangrove leaves | 5.746 | 1.056 | 0.9916 | 18.953 | 1.149 | 25.000 | 0.9996 | |
| | Reed mat | 1.450 | 1.347 | 0.8428 | 7.246 | 1.566 | 17.762 | 0.9990 | |
| Hexavalent chromium | Water lily | 2.182 | 1.876 | 0.9588 | 1.691 | 2.432 | 10.000 | 1.0000 | |
| | Water hyacinth | 0.191 | 1.267 | 0.8732 | 0.467 | 1.907 | 1.697 | 0.9550 | |
| | Green taro | 0.210 | 1.427 | 0.9364 | 0.452 | 2.224 | 2.238 | 0.9835 | |
| | Mangrove leaves | 0.470 | 1.177 | 0.9008 | 2.076 | 2.496 | 12.937 | 0.9998 | |
| | Reed mat | 0.210 | 1.534 | 0.9951 | 0.135 | 1.998 | 0.538 | 0.9517 | |
| Total chromium | Water lily | 1.715 | 0.776 | 0.9549 | 6.337 | 1.179 | 8.811 | 0.9998 | |
| | Water hyacinth | 0.211 | 1.078 | 0.9608 | 0.183 | 1.358 | 0.337 | 0.9447 | |
| | Green taro | 0.294 | 1.229 | 0.9801 | 0.231 | 1.512 | 0.528 | 0.9709 | |
| | Mangrove leaves | 0.449 | 1.952 | 0.9959 | 0.209 | 2.291 | 1.096 | 0.9968 | |
| Acid treated adsorbents | Reed mat | 0.218 | 1.336 | 0.9715 | 0.081 | 1.920 | 0.298 | 0.9032 | |
| | Trivalent chromium | Water lily | 0.939 | 0.288 | 0.977 | 6.997 | 0.280 | 0.548 | 0.9716 |
| | | Water hyacinth | 0.437 | 0.128 | 0.9885 | 26.253 | 1.313 | 45.249 | 0.9962 |
| | | Green taro | 0.722 | 0.104 | 1.000 | 31.664 | 0.825 | 21.552 | 0.9996 |
| | | Mangrove leaves | 0.769 | 0.597 | 0.996 | 0.855 | 0.903 | 0.697 | 0.9674 |
| Reed mat | | 0.636 | 0.167 | 0.8186 | 36.270 | 0.752 | 20.492 | 0.9963 | |
| Hexavalent chromium | Water lily | 1.975 | 1.503 | 0.977 | 1.2300 | 2.4540 | 7.4074 | 0.9999 | |
| | Water hyacinth | 0.958 | 1.659 | 0.985 | 0.387 | 2.630 | 2.675 | 1.000 | |
| | Green taro | 1.128 | 1.619 | 0.975 | 1.002 | 3.089 | 2.978 | 0.998 | |
| | Mangrove leaves | 4.364 | 3.809 | 0.996 | 1.004 | 2.681 | 15.060 | 0.996 | |
| | Reed mat | 0.933 | 1.915 | 0.998 | 0.261 | 2.827 | 2.086 | 0.998 | |
| Total chromium | Water lily | 1.366 | 1.109 | 0.996 | 0.625 | 1.493 | 1.393 | 0.965 | |
| | Water hyacinth | 0.741 | 1.596 | 0.997 | 0.287 | 2.285 | 1.501 | 0.998 | |
| | Green taro | 0.901 | 1.739 | 0.993 | 1.001 | 2.848 | 1.162 | 0.999 | |
| | Mangrove leaves | 2.007 | 2.818 | 0.999 | 1.001 | 2.562 | 7.924 | 0.999 | |
| | Reed mat | 0.900 | 1.781 | 1.000 | 0.204 | 2.753 | 1.547 | 0.998 | |

to Cr(III). Gardea-Torresdey et al. [29] reported that Cr(VI) bound to an oat byproduct was easily reduced to Cr(III) by positively charged functional groups, and subsequently adsorbed by available carboxyl groups. During Cr(VI) reduction, some of the organic carbon of the biosorbents were completely oxidized into inorganic carbon (HCO_3^- and CO_2). The reduction rate of Cr(VI) increased with decreasing solution pH as the protons were consumed during Cr(VI) reduction. It is also reported that Cr(VI) was completely reduced to Cr(III) by contact with the brown seaweed *Ecklonia* biomass below pH 5 [17]. The converted Cr(III) appeared in the solution and was partly bound to the biomass [32]. Similar results were reported in case of fungal biomasses, such as *A. niger*, *Rhizopus oryzae*, *Saccharomyces cerevisiae* and *Phenicillium chrysogenum* [6,33].

3.3. Kinetics of Cr(VI) and Cr(III) adsorption by acid and alkali treated biosorbents

It is reported that untreated adsorbents have less adsorption capacity for chromium ion than chemically treated adsorbents because they lack appropriate chemical functional groups on

their surfaces [25]. To enhance the removal efficiency of metal ions by the biosorbent, various pre-treatments can be used. Pre-treatment may be in terms of hardening the cell wall structure through a cross-linking reaction using epichlorohydrin [34], or increasing the negative charge on the cell surface by NaOH treatment [35], or increasing the positive charge on the cell surface and opening of the available sites for the adsorption by acid treatment [17,36]. Therefore, biosorbents were subjected to alkali and acid treatments prior to biosorption studies.

It was observed that, after the alkali and acid treatments, weight of biosorbents reduced considerably (Fig. 2). This might be due to the removal of lignin and other compounds from adsorbent materials. The kinetics of biosorption of Cr(III) and Cr(VI) by the acid washed mangrove leaves are presented in Fig. 3.

The pre-treatment of biosorbents with 4N H_2SO_4 enhanced the Cr(VI) sorption whereas, there was a decrease in Cr(III) adsorption. This could be attributed to the fact that acid hydrolysis yields relatively pure amino sugar, D-glucosamine [37], which is more easily protonated at adsorption pH. Thus, extraction of finely powdered biosorbents in acids could expose more binding sites. Enhanced biosorption of metal ions by acid

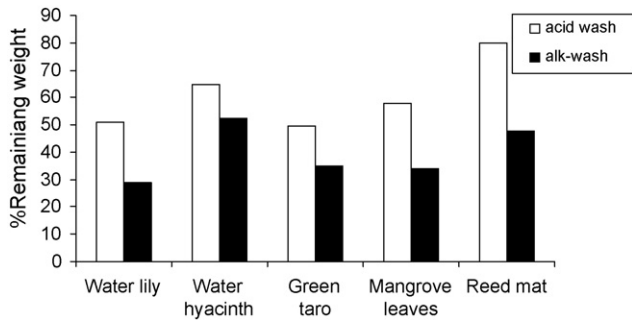


Fig. 2. Weight loss of biosorbents during acid and alkali wash.

treated biosorbents have been reported while employing pine bark as adsorbent material [38,39]. For the pH range used in the present experiments (5 ± 0.5), Cr(VI) behaves as an oxoanion as $\text{Cr}_2\text{O}_7^{2-}$, HCrO_4^- , CrO_4^{2-} in aqueous solution with an overall negative charge [40]. Acid treatment might have increased the overall positive charge of the adsorbents [17,36]. As a result, the sorbent was able to attract more negatively charged metal ions. On the other hand, Cr(III) behaves as a cation

$\text{Cr}(\text{OH})^{2+}$, $\text{Cr}(\text{OH})^+$, $\text{Cr}_3(\text{OH})^{5+}$ with an overall positive charge [41,42]. The accessibility of cations might have decreased due to the increase in sorbent surface positive charge.

It may also be noted that, after the acid wash, the organic matter content in the sorbent as well as in the reaction mixture was reduced (data not shown). This reduction resulted in a slower rate of Cr(VI) conversion to Cr(III). Hence, after the acid wash, a part of the Cr(VI) removal might be due to the adsorption of Cr(VI) directly to the biosorbent. After the adsorption, Cr(VI) and Cr(III) were selectively eluted from the adsorbents and were analyzed. It was observed that in raw adsorbents, only 2–4% of total chromium adsorbed was in Cr(VI) form whereas in acid treated adsorbents it was 11–12%.

Treatment of the biosorbents with 4N NaOH significantly reduced the removal rate of Cr(VI). The decrease in Cr(VI) removal may be due to the net increase in the surface negative charge of the adsorbents or masking of surface groups by corresponding sodium salts [35,43]. This treatment also affected the physical characteristics of the adsorbent, thereby hindered the operational stability. There was drastic swelling of biomass, which may be due to the polymer chain breakage.

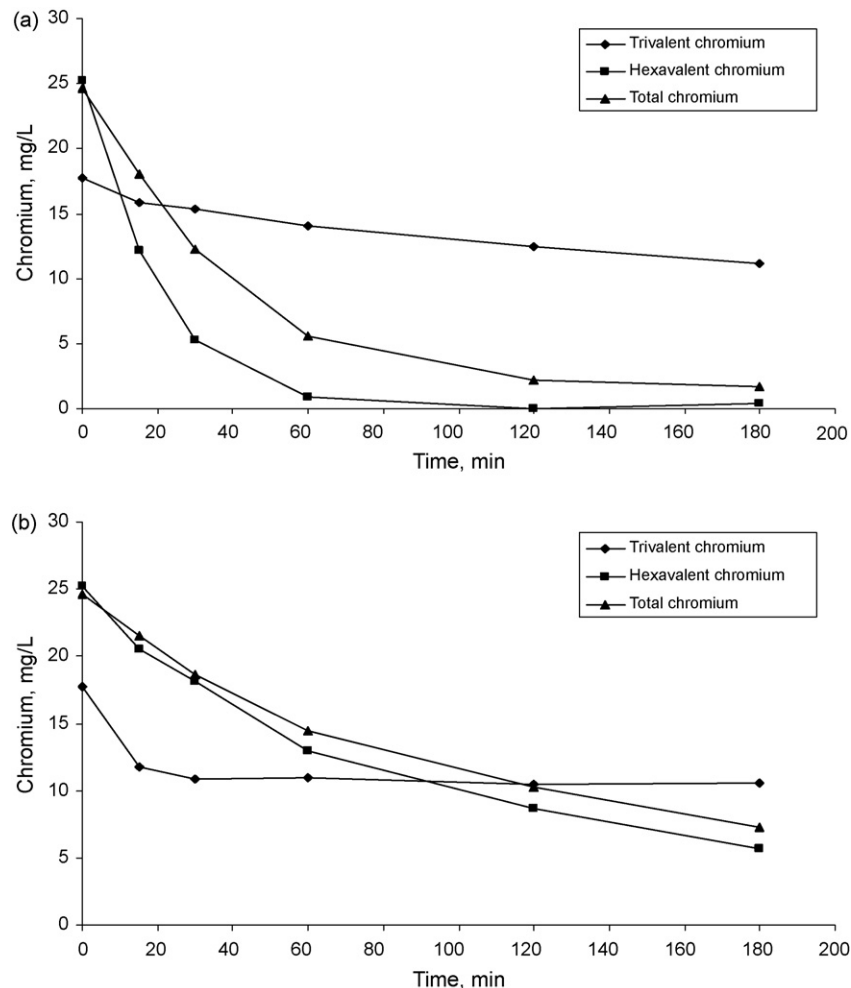


Fig. 3. (a) Kinetics of Cr(III), Cr(VI) and total chromium removal by acid washed mangrove leaves. (b) Kinetics of Cr(III), Cr(VI) and total chromium removal by acid washed reed mat.

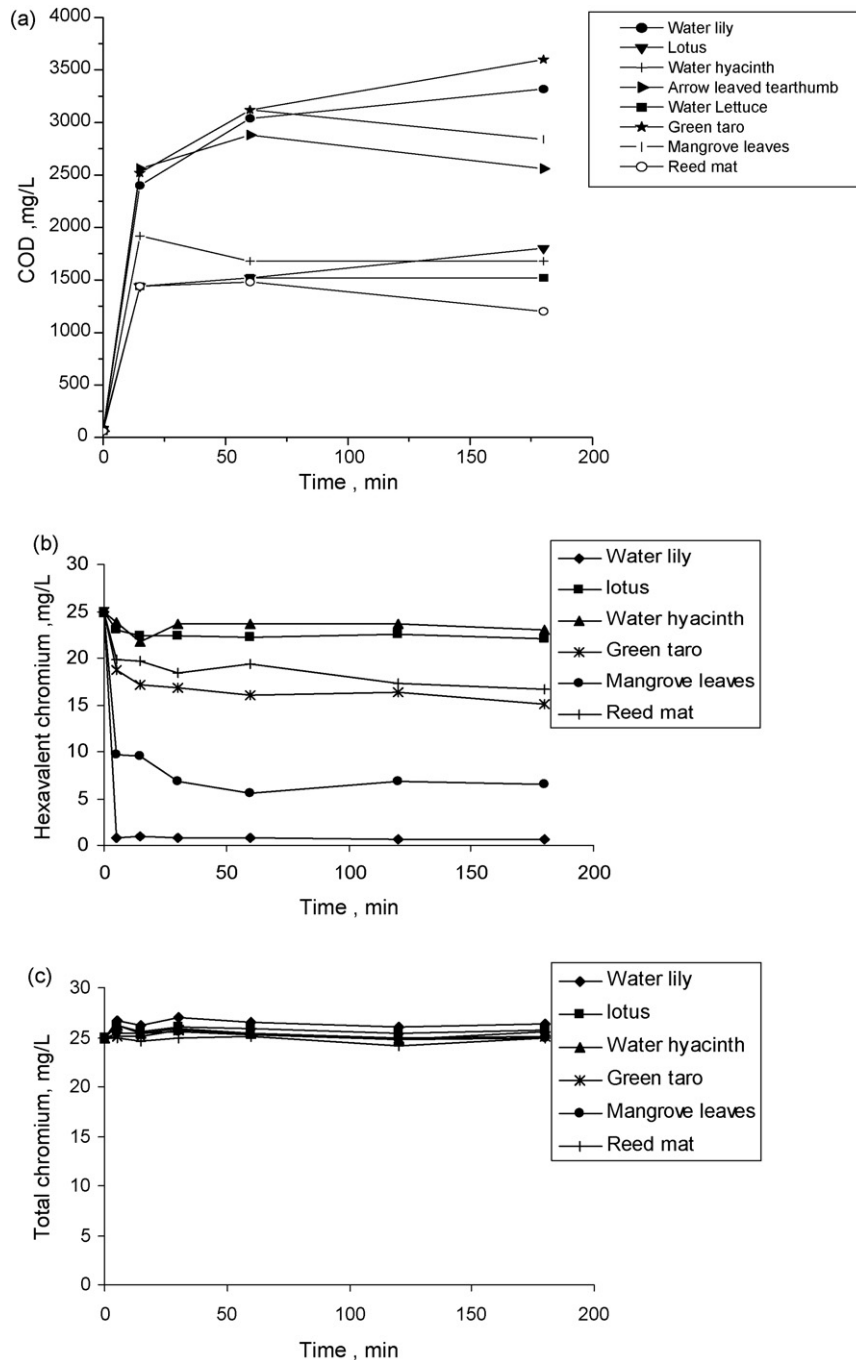


Fig. 4. (a) Kinetics of organic substance leaching out from various raw biosorbents. (b) Kinetics of Cr(VI) reduction by the released organic matter. (c) Total chromium concentration with respect to time during Cr(VI) reduction by released organic matter.

3.4. Role of released organic material on Cr(VI) reduction

From the kinetics studies, it was clear that Cr(VI) removal from the system was due to the reduction of Cr(VI) to Cr(III) and adsorption. It was also noticed that during the course of experiment, significant amount of dissolved organic matter was released into the system (Fig. 4a). From these results, it is clear that there is a correlation between the amount of organic matter released and the percentage of Cr(VI) reduced. In order to find the role of organic matter released on Cr(VI)

removal, kinetic experiments for Cr(VI) removal were carried out using the released organic matter. These results are presented in Fig. 4b. The rate of Cr(VI) reduction was very fast and the system reached the equilibrium within 15 min. In most of the cases, the Cr(VI) reduction efficiency was directly proportional to the initial COD of the system. The organic material released from mangrove leaves and water lily showed significantly high Cr(VI) reduction (81–99%), whereas Cr(VI) reduction by organic material released from water hyacinth and reed mat were insignificant. Total chromium concentrations in

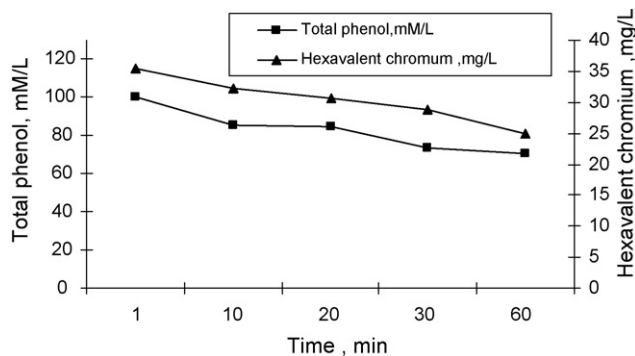


Fig. 5. Kinetics of Cr(VI) reduction and corresponding decrease in the concentration of phenolic compounds.

all the systems were analyzed with respect to time and it was found that the concentration of total chromium remained the same all throughout the study (Fig. 4c). From this study, it is clear that the organic material released from mangrove leaves and water lily had certain components which have high reduction potential. However, there was no significant Cr(VI) reduction in presence of high concentrations of glucose or molasses under similar conditions [44].

3.5. Characterization of released organic material

The characterization of organic material released from various biosorbents using different eluents was carried out and the results are presented in Table 3. The amount of total phenol and tannin was maximum in water lily followed by mangrove leaves. The minimum amount of total phenol and tannin was found in water hyacinth. From the earlier kinetic studies, it was found that maximum Cr(VI) reduction occurred in presence of water lily and mangrove leaves. From these observations, it is evident that total phenol and tannin present in the system has a significant role in Cr(VI) reduction. Analysis of total phenol was carried out for water lily as well as mangrove leaves after Cr(VI) removal/reduction. It was observed that corresponding to Cr(VI) removal, there was a reduction in total phenol also (Fig. 5). It is reported that poly phenolic compounds can chelate metal ions *in vitro* [45]. While discussing the adsorption mechanism of hexavalent chromium by condensed tannin gel, Nakano et al. [46] described the esterifica-

tion of chromate with tannin molecules, reduction of Cr(VI) to Cr(III), formation of carboxylic group by tannin molecules and ion exchange of Cr(III) by carboxyl/hydroxyl groups [17,32]. Similar reactions might have taken place in the present system also.

3.6. Equilibrium studies

Adsorption equilibrium studies were carried out with the raw and acid treated biosorbents. All the adsorption studies were conducted at a pH of 4.5–5.5. The adsorption equilibrium data were analyzed using the well-known Langmuir and Freundlich isotherm models. The results are presented in Tables 4a–4d. From the results, it is clear that the adsorption data is fitting well with both Langmuir and Freundlich models, though Langmuir fit was giving a better correlation coefficient. In case of Cr(III), the maximum specific adsorption capacity varied from 7.184 mg/g (reed mat) to 6.07 mg/g (green taro).

For Cr(VI), maximum removal/reduction capacity was exhibited by mangrove leaves (8.87 mg/g) followed by water lily (8.43 mg/g). For the same experiment, the total chromium adsorption was also evaluated. As shown in Table 4b, adsorption of total chromium was significantly lower than Cr(VI) reduction/removal. This clearly shows that Cr(VI) was getting reduced to Cr(III) and was partially adsorbed by the sorbents. Among all the adsorbents, mangrove leaves showed maximum total chromium removal capacity (5.72 mg/g).

Adsorption equilibrium studies were also conducted with acid treated biosorbents. These results are presented in Tables 4c and 4d. As expected, the adsorption capacity of acid wash adsorbents for Cr(III) was less compared to the raw adsorbents. However, there was a significant increase in adsorption capacity in case of Cr(VI) and total chromium. The Q_{\max} value for acid washed mangrove leaves increased to 11.38 mg/g for total chromium. Generally, acid treatment is being used for cleaning the cell wall and replacing the natural mix of ionic species bound on the cell wall with protons and sulphates [47–49]. As discussed earlier, in the given experimental condition (pH 4.5–5.5), Cr(VI) exists in anionic form whereas Cr(III) preferably exists in cationic form. This must be the reason for higher removal of Cr(VI) and lower adsorption of Cr(III) by the acid treated adsorbents.

Table 3
Estimation of tannins and total phenolic compounds leached out from various biosorbents

| Sorbents | Tannin concentration | | | Total phenolic compounds | |
|-------------------------|------------------------|---------------|-----------------|--------------------------|-----------------|
| | Distilled water (mg/g) | Buffer (mg/g) | Methanol (mg/g) | Distilled water (mM/g) | Methanol (mM/g) |
| Water lily | 43.87 | 45.05 | 43.43 | 224.16 | 282.78 |
| Lotus | 8.98 | 12.62 | 6.34 | 15.20 | 9.43 |
| Water hyacinth | 9.24 | 11.68 | 2.42 | 9.63 | 5.57 |
| Arrow-leaved tear thumb | 21.39 | 25.08 | 12.51 | 29.59 | 31.04 |
| Green taro | 20.58 | 22.83 | 6.60 | 30.52 | 17.71 |
| Mangrove leaves | 26.74 | 31.71 | 12.08 | 51.75 | 46.45 |
| Reed mat | 11.20 | 14.40 | 2.24 | 22.39 | 33.64 |

Table 4a
Langmuir and Freundlich isotherm constants for Cr(III) adsorption by selected raw biosorbents

| Adsorbents | Raw adsorbents | | | | | |
|-----------------|-------------------|-------|-------|---------------------|-------|-------|
| | Langmuir isotherm | | | Freundlich isotherm | | |
| | Q_{\max} (mg/g) | b | r^2 | K | $1/n$ | r^2 |
| Water lily | 6.112 | 0.031 | 0.979 | 0.332 | 0.748 | 0.972 |
| Water hyacinth | 6.614 | 0.050 | 0.957 | 1.439 | 0.420 | 0.918 |
| Green taro | 6.072 | 0.034 | 0.991 | 0.206 | 0.874 | 0.994 |
| Mangrove leaves | 6.544 | 0.032 | 0.926 | 0.524 | 0.609 | 0.990 |
| Reed mat | 7.184 | 0.042 | 0.989 | 1.850 | 0.247 | 0.990 |

Table 4b
Langmuir and Freundlich isotherm constants for total chromium adsorption (Cr(VI) was used as the sorbate) by selected raw biosorbents

| Adsorbents | Total chromium | | | | | |
|-----------------|-------------------|-------|-------|---------------------|-------|-------|
| | Langmuir isotherm | | | Freundlich isotherm | | |
| | Q_{\max} (mg/g) | b | r^2 | K | $1/n$ | r^2 |
| Water lily | 5.110 | 0.027 | 0.984 | 0.248 | 0.645 | 0.999 |
| Water hyacinth | 0.342 | 0.917 | 0.995 | 0.151 | 0.161 | 0.995 |
| Green taro | 1.418 | 0.042 | 1.000 | 0.120 | 0.501 | 0.999 |
| Mangrove leaves | 5.724 | 0.044 | 0.997 | 0.191 | 0.797 | 0.992 |
| Reed mat | 1.662 | 0.039 | 0.999 | 0.126 | 0.515 | 1.000 |

Table 4c
Langmuir and Freundlich isotherm constants for Cr(III) adsorption by selected acid washed biosorbents

| Adsorbents | Langmuir isotherm | | | | | |
|-----------------|-------------------|-------|-------|---------------------|-------|-------|
| | Langmuir isotherm | | | Freundlich isotherm | | |
| | Q_{\max} (mg/g) | b | r^2 | K | $1/n$ | r^2 |
| Water lily | 2.112 | 0.051 | 0.933 | 0.180 | 0.414 | 0.752 |
| Water hyacinth | 6.227 | 0.086 | 0.969 | 1.277 | 0.360 | 0.988 |
| Green taro | 3.580 | 0.096 | 0.987 | 0.959 | 0.291 | 0.997 |
| Mangrove leaves | 2.633 | 0.049 | 0.927 | 1.356 | 0.076 | 0.983 |
| Reed mat | 3.200 | 0.129 | 0.999 | 0.601 | 0.395 | 0.982 |

3.7. Fourier transform infrared (FTIR) analysis of adsorbents

The FTIR spectrum of raw, acid and alkali treated adsorbents before and after sorption of both hexavalent and trivalent chromium were used to determine the vibration frequency changes in the functional groups, in the adsorbents. The spectra of adsorbents were measured within the range of 400–4000 cm^{-1} wave number. As shown in Table 5 and Fig. 6a and b, the FTIR spectrum of mangrove leaves displays a number

of absorption peaks, indicating the complex nature of the biosorbent. The broad absorption peak around 3389 cm^{-1} is indicative of the existence of –OH and –NH stretching, thus showing the presence of hydroxyl and amine groups on the adsorbent. The band at 2929 cm^{-1} can be assigned to the –CH stretch. The absorption bands at 1622 cm^{-1} (mainly C=O stretch) and 1500 cm^{-1} (mainly –NH stretch) can be attributed to the amide I and II bands of amide bond due to the protein peptide bond. It was clear that the carboxylate ions gave rise to two bands: C=O stretch at 1493 and 1375 cm^{-1} . A band at about 1250 cm^{-1} ,

Table 4d
Langmuir and Freundlich isotherm constants for total chromium adsorption (Cr(VI) was used as the sorbate) by selected acid washed biosorbents

| Adsorbents | Total chromium | | | | | |
|-----------------|-------------------|-------|-------|---------------------|-------|-------|
| | Langmuir isotherm | | | Freundlich isotherm | | |
| | Q_{\max} (mg/g) | b | r^2 | K | $1/n$ | r^2 |
| Water lily | 7.559 | 0.009 | 0.890 | 2.344 | 0.410 | 0.992 |
| Water hyacinth | 6.378 | 0.063 | 0.996 | 1.153 | 0.361 | 0.907 |
| Green taro | 5.747 | 0.549 | 0.998 | 0.762 | 0.494 | 0.965 |
| Mangrove leaves | 11.377 | 0.555 | 0.963 | 5.011 | 0.224 | 0.962 |
| Reed mat | 3.393 | 0.202 | 0.999 | 1.407 | 0.206 | 0.992 |

Table 5
FTIR wave number and corresponding functional groups in various raw biosorbents

| Range | Group | Assignment and remarks | Water lily | Water hyacinth | Green taro | Mangrove leaves | Reed mat | Acid treated adsorbents (mangrove leaves) | |
|----------------|--|---|------------|----------------|------------|-----------------|----------|---|---|
| | | | | | | | | Observation | Remarks |
| 3520–3320(m-s) | NH ₂ in aromatic amines | NH stretch | 3432 | 3403 | – | – | 3442 | – | – |
| 3420–3250(s) | OH in alcohols and phenols | OH stretch | 3785 | 3738 | 3763 | 3389 | – | – | – |
| 2990–2850(m-s) | CH ₃ and –CH ₂ in aliphatic compound | CH antisym and asym stretch | 2924 | 2997 | 3000 | 2929 | 2988 | % Transmission decreasing | Treatment of acid hydrolysis |
| 2700–2250(br) | Amine salts | NH ₂ stretch | 2309 | 2310 | 2325 | 2308 | 2369 | – | – |
| 2140–2100(m) | –C=C– in alkyline | C=C stretch | 2107 | 2122 | – | 2114 | 2120 | – | – |
| 2000–1650(br) | Substituted benzene ring | Several bands from overtone and combination | 1907 | 1911 | 1920 | 1907 | 1898 | – | – |
| 1710–1690(s) | C=O in carboxylic acids | C=O stretch | 1704 | 1705 | 1707 | 1706 | 1678 | % Transmission increasing | It is may be ester hydrolysis to a carboxylic acid. Under acidic conditions |
| 1680–1620(s) | C=O and NH ₂ in primary amides | C=O stretch | 1636 | 1622 | 1624 | 1622 | 1624 | % Transmission decreasing | Hydrolysis under acidic conditions |
| 1515–1485(m) | Benzene ring in aromatic compounds | Ring stretch | 1489 | 1496 | 1487 | 1493 | 1510 | – | – |
| 1400–1310(s) | COO– group in carboxylic acid | Antisym stretch | 1353 | 1397 | 1404 | 1375 | 1350 | % Transmission increasing | Hydrolysis of carboxylic acid esters |
| 1360–1320(vs) | NO ₂ in aromatic nitro compounds | NO ₂ antisym stretch | 1334 | 1343 | – | 1342 | – | – | – |
| 1285–1240(vs) | AR–O in alkyl ethers | C–O stretch | 1235 | 1282 | 1281 | 1250 | 1298 | – | – |
| 1260–1150(s) | Hydrated sulphonic acid | SO ₃ stretch | 1180 | 1188 | 1184 | 1192 | 1146 | – | – |
| 1250–1200(s) | C–O–C in vinyl ethers | C–O–C stretch | 1230 | – | 4 | – | 1219 | – | – |
| 1060–1025(vs) | CH ₂ –OH in primery alcohols | C–O stretch | 1046 | 1043 | 1019 | – | 1050 | – | – |
| 950–900(vs) | CH–CH ₂ in vinyl compounds | CH ₂ | 909 | 903 | 903 | 909 | 911 | % Transmission decreasing | Acid hydrolysis |
| 900–865(vs) | CH–CH ₂ in vinyl compounds | CH ₂ | 859 | 849 | 898 | – | 879 | – | – |
| 630–535(s) | C–CO–C– in ketones | C–CO–C bend | 549 | 628 | 655 | – | – | – | – |

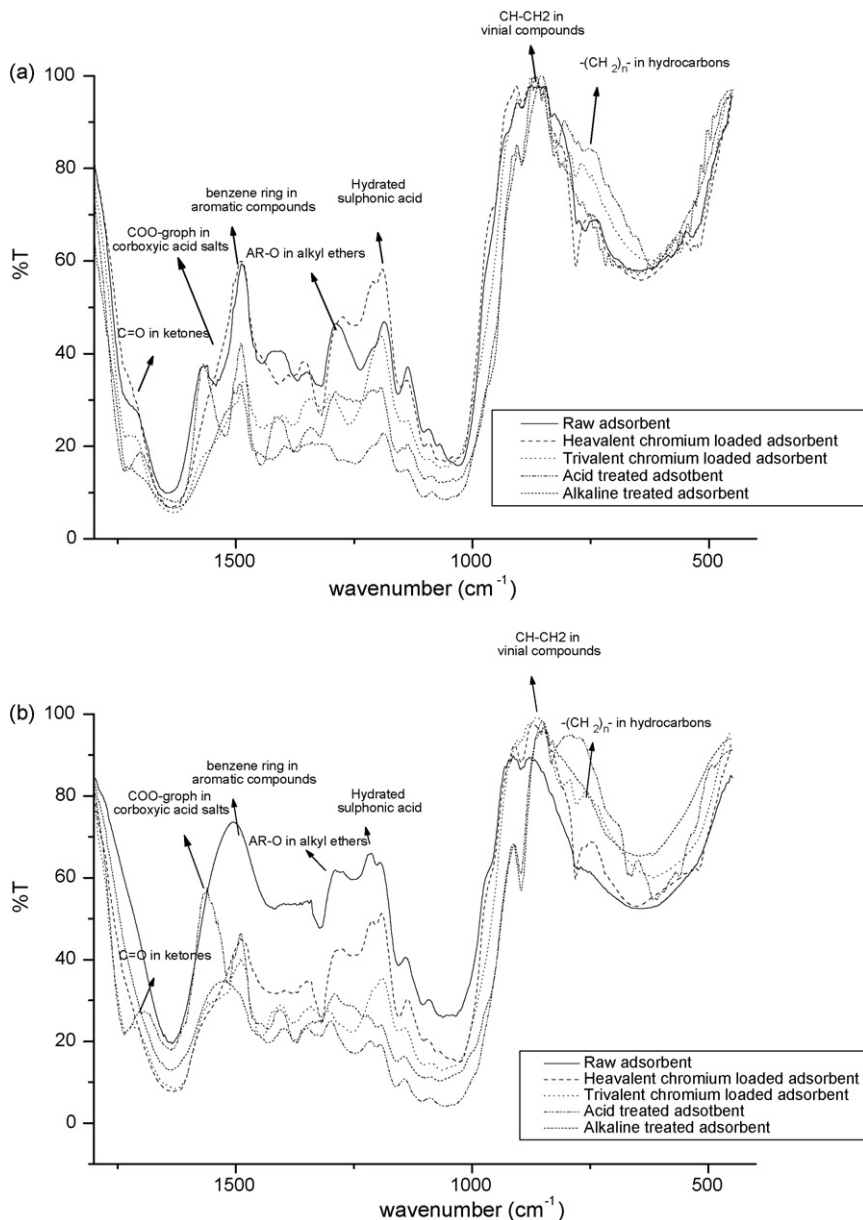


Fig. 6. (a) FTIR spectrum for mangrove leaves. (b) FTIR spectrum for reed mat.

representing $-\text{SO}_3$ stretching, was also observed in the FTIR spectrum of mangrove leaves.

Significant changes of the functional group were visible after acid treatment. Acid treatment was used for cleaning the cell wall and replacing the natural mix of ionic species bound on the cell wall with protons and sulphates [47–49]. The acid hydrolysis converts amide and ester groups to corresponding carboxylic acids [50]. The results (Fig. 6) show the changes in functional group, i.e. carboxylic acids at 1706 cm^{-1} , esters at 1250 cm^{-1} , amides at 1627 cm^{-1} and amines at 2309 cm^{-1} in the acid washed adsorbent compared to the raw one.

Treatment of the biosorbents with 4N NaOH significantly reduced the adsorption capacity, as discussed earlier. FTIR spectrum of alkali treated mangrove leaves is given in Fig. 6a. There were significant functional group changes after the alkali wash. Alkali treatment might have formed corresponding metal salts

with functional groups on the adsorbent. The changes are visible for carboxylic acids in 1701 cm^{-1} , esters in 1250 cm^{-1} , amides in 1625 cm^{-1} and amines in 2309 cm^{-1} .

The change of the functional group are visible in Cr(VI) loaded adsorbents also (Fig. 6a and b). Cr(VI) is a powerful oxidizing agent, which might have oxidized primary and secondary alcohols to corresponding ketones, carboxylic acids and other compounds having “benzyl” hydrogen to benzoic acids, and Cr(VI) got reduced to Cr(III).

To confirm the difference in functional groups after the biosorption of Cr(III) and Cr(VI), FTIR study was carried out using Cr(VI) and Cr(III) loaded mangrove leaves. The absorption spectrum of chromium-loaded adsorbent (at pH 4.5) was compared with that of raw mangrove leaves. A change of absorption bands can be seen when comparing the FTIR spectra of pristine and chromium-loaded biomass (Fig. 6a). This figure

also shows the changes in the spectrum of the biosorbent after sorption of Cr(III). An interesting phenomenon was the sharp decrease in the band intensity at 1406 cm^{-1} corresponding to C=O stretching after metal binding. Although, slight changes in other absorption frequencies were observed, it was difficult to interpret how these absorption peaks were related with Cr(III) biosorption.

4. Conclusions

In the present study, various aquatic weeds were screened for Cr(VI) and Cr(III) biosorption potential. Batch kinetic and equilibrium experiments were conducted to determine the adsorption rate and adsorption capacities of various biosorbents. Among the biosorbents screened, reed mat has shown maximum Cr(III) adsorption capacity whereas, mangrove leaves performed better in case of Cr(VI) removal. In most of the cases, adsorption followed second-order kinetics. In case of Cr(VI), first it was reduced to Cr(III) with the help of tannin, phenolic compounds and other functional groups on the sorbent surfaces and subsequently got adsorbed. Acid treatment significantly increased the Cr(VI) removal capacity of almost all the biosorbents. However, there was a reduction in Cr(III) adsorption capacity by the acid washed adsorbents. FTIR spectrum showed the functional group changes during adsorption of different chromium species. In summary, aquatic weeds seemed to be a promising biosorbent for both Cr(VI) and Cr(III).

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