

Bio sorption of hexavalent chromium using biomass of microalgae *scenedesmus* SP

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Abstract

Hexavalent chromium (Cr (VI)) is a toxic metal ion present in the water environment. The water samples collected from different points of the seepages of Sukinda Chromite mines are of Odisha, India were found to be high content of Cr (VI). Therefore, its biosorption onto the biomass of microalgae *Scenedesmus* sp. was examined in this study. The biomass of microalgae was generated using a raceway pond specially designed for their growth. Different biosorption parameters, such as initial pH, contact time, initial Cr (VI) concentration, bio-sorbent dosage, particle size distribution of the microalgae biomass and temperature, were found to affect the Cr (VI) loading onto the biomass. The maximum biosorption efficiency of Cr (VI) was found to be 93.1% at an optimum condition of contact time, 120min; Cr (VI), 10mg.L⁻¹; solid-liquid ratio, 10%(w/v); pH, 1.0; temperature, 30oC; particle size, -75+45µm; stirring, 300rpm. The presence of different functional groups, such as amides, acids, aldehydes, and halides, confirmed by the FTIR analysis technique were the reason for the high uptake of metals.

Keywords: Bio Sorption; *Scenedesmus*; Functional Group; Adsorption Parameters; Hexavalent Chromium.

1. Introduction

Hexavalent chromium or Cr (VI) is a toxic metal ion in the solution even at the level measuring in the parts per billion (ppb) [1]. Its properties favor contamination to different components in the environment [2]. Various anthropogenic activities are the major reasons for its enrichment in the water environment [3-4]. It enters into the human body due to consumption of the polluted drinking water. Since Cr(VI) is a strong oxidizing agent, its absorption in the human body causes abnormal cellular activities like generation of reactive species inside the cells, formation of Cr(III)-protein complex, and denaturation of DNA [2], [5], [6].

The Sukinda Chromites Valley, in Jajpur district, Odisha is well known for its extensive chromites ore deposits and considered as one of the richest chromites and nickel producing areas and supplies 90% of India's demand. Presently there are 14 chromite mines operating in Sukinda [7]. In this area several mines are in operation for extraction of chromites ore through open cast mining methods as shown in Figure 1. The chromites ores and waste rock materials are dumped in the open ground without considering its impact on the environment. Leaching of heavy metals is possible during the rainy season to the surface water bodies as well as to the groundwater systems. The Damsala Nala lies in the valley has been contaminated with Cr (VI). Water samples collected from various points of the Damsala Nala during pre- and post- monsoon period were found to contain high level Cr (VI). The pre-monsoonal and post-monsoonal Cr (VI) concentration were found to be maximum of 16 and 5 mg.L⁻¹, respectively. This proves that the chromium pollution is existing in the chromite valley. The government has taken the initiative as there are many perennial streams originate from Sukinda Hill range and some of them are used for beneficiation and other mining related purposes, a compilation of all the streams with their geographical location and usa-

bility can help in planning a method to safe guarding from chromium contamination. This helps to treat the stream at the point of entry before released in to Damsala nala [7].

Removal of the toxic Cr (VI) from different water systems becomes an emerging research network across the environmental research communities. Its conventional treatment options are direct chemical reduction and precipitation, composite ceramic and resin adsorption, thermal and nanomaterials catalyzed reduction, electrolysis and electro-coagulation, desalination, ion exchange, and reverse osmosis [2], [8-11]. These processes have different intensive and complex sub-processes, and they generate the toxic sludge [12]. Therefore, an alternative treatment method is very much necessary.



Fig. 1: Open Cast Mining System of Chromite Ore [7].

Multiple functional groups present in the biomass are capable of attracting both cationic and anionic species of different heavy metals from the solution in the biosorption process. This process has shown the credibility of simple way for the heavy metals removal at a low-cost operation [13-16]. In the instance of Cr(VI) removal, the biomass of bacteria, fungi, plants and their nuts, and

both micro- and macro- algae have shown capability to reduce or adsorb it from the solution [17-39]. Moreover, the advantages of biosorption are those: it uses the abundant raw biomass such as seaweed or algae, and wasted biomass generated from fermentation industries, algal wastes from agar industries, agricultural operations, food wastes, and food processing industries [40]. Furthermore, the process for the specific Cr (VI) removal can be optimized by varying simple physical, chemical and environmental parameters, such as biosorbent feed, temperature, Cr (VI) concentration, pH of the solution, contact time, agitation, redox stimulating reagents, immobilizers, and free cell reductase [26], [32], [40-43]. Simple reactor design is necessary for scaling up of the process [40].

Microalgae are photosynthetic microphytes generally found in the aquatic environments. They grow autotrophically in the photosynthesis process similar to that of the terrestrial plants. They are submerged in the water where they have an efficient access to water, CO₂ and other nutrients [44]. Therefore, they have the high growth rate compared to the terrestrial plants and can complete an entire growing cycle in every few days. Combined with their high productivity, the biomass of microalgae is possibly a rich candidate to mitigate Cr (VI) from solution. The microalgae made of different polysaccharides such as cellulose, xylan, fucoidan, mannitol, and alginic acid, which are attached to the inner fibrous skeleton as well as the outer amorphous embedding matrix within the cells [40], [45]. The polysaccharide compounds contain the large amount of deprotonated sulfate and carboxyl groups as well as the monomeric alcohol and laminaran, which are most likely responsible for the biosorption [46-48]. The biomass of both micro- and macro- algal species, such as *Chlorella vulgaris* [49-52], *Sargassum cymosum* [53], [54], *Sargassum filipendula* [46], *Peltvetia canaliculata* [42], *Halimeda gracilis* [55], *Cystoseira indica* [56], *Laminaria digitata* [13], *Oedogonium hatei* [57] and many more, have shown ability to remove Cr(VI) from the solution through the process of direct adsorption or reduction coupled with adsorption [57-58].

This research article elaborates the study of Cr (VI) biosorption from the synthetic solution using microalgae *Scenedesmus* sp. with an aim to remove Cr(VI) from the contaminated mine water sample collected from the Damsala Nala. The effects of different biosorption parameters were studied to optimize the process. Data of the biosorption process were further interpreted using different standard adsorption isotherm models.

2. Materials and methods

2.1. Collection of microalgae biomass

The microalgae biomass of the *Scenedesmus* sp. was collected from the CSIR-IMMT, Bhubaneswar, India. The *Scenedesmus* sp. (IMMTCC-13) was isolated from the brackish water of Chilika Lake of Odisha, India, and further characterized and stored in the culture collection center of the CSIR-IMMT [44]. The microalgal species were grown in a race way pond set up at the CSIR-IMMT campus. Figure 2 show the specially designed raceway pond installed at CSIR-IMMT for the large scale cultivation of *Scenedesmus* sp.



Fig. 2: Raceway Pond Installed at CSIR-IMMT [44].

2.2. Preparation of bio sorbent

The as collected biomass were washed thoroughly in the tap water. They were dried in the open air followed by drying in a hot oven at 50°C. The dried biomass was blended to powder and then sieved to different size fractions. The sieve size distributions were -45, -75+45, -100+75 and +100µm, and the respective average particle sizes were assigned as 45, 60, 87.5 and 100µm. The biomass powders were stored in a desiccator and used as biosorbent in the biosorption study.

2.3. Bio sorption experiment

The initial biosorption experiments were conducted in 200mL glass beakers containing 100mL of Cr(VI) solution. The mixing of content was maintained using a laboratory hotplate-cum-magnetic stirrer. The temperature of solution was maintained by using a thermocouple connected to the hotplate. Just prior to start the experiment, required amount of the specified biomass was added into the content. Before adding the biomass, the initial pH of the content was maintained by adding dilute H₂SO₄ (10%) solution drop wise with the help of a glass tube. Samples were collected according to the predetermined time intervals in order to analyze the Cr (VI) concentration and parallelly pH of the content was measured. Each time about 2 mL of liquid sample was drawn from the content with the help of a pipette and centrifuged at 3000 rpm for 5 min using a small Remi centrifuge. Then 1.0mL sample was taken from the supernatant with the help of a micro pipette and analyzed for the Cr (VI) concentration by the 1,5-diphenylcarbazine method [59]. The following biosorption conditions were maintained unless otherwise stated: contact time, 120 min; Cr (VI), 10mg.L⁻¹; solid-liquid ratio, 10 % (w/v); initial pH, 1.0; temperature, 30°C; particle size, -75+45µm (average 60µm).

2.4. Analysis

Since biosorption favorably a physisorption process, the functional groups present in the biomass are responsible for the biosorption kinetics. Therefore, the biomass used as biosorbent in the biosorption was analyzed using a Fourier Transmission Infrared (FTIR) spectrophotometer (JASCO-4600). Also the FTIR analysis was performed for the Cr (VI) loaded biomass obtained from the experimental runs. A bench top pH meter (PC510, EUTECH) was used to measure the pH of the solution during the experiment. Cr (VI) concentration of the samples was analyzed spectrophotometrically by the standard 1,5-diphenylcarbazine method [59]. The absorbance of pink coloured Cr (VI)-complex was taken at the wavelength 543 nm by using an UV-Visible spectrophotometer (Evolution-201, Thermo Scientific). The efficiency of biosorption (%) was calculated from the formulae in Eq.1.

$$\% = \left(\frac{C_0 - C_t}{C_0} \right) \times 100 \quad (1)$$

3. Results and discussion

3.1. FTIR analysis

In order to find out the functional groups present in the biomass of microalgae, the FTIR analysis was performed. Fig.3 shows the FTIR spectral data of the original and Cr (VI) loaded biomass. The peak at 3543.56cm⁻¹ may be related to N-H stretching of the amide [56-60]. The peak at 3400.85cm⁻¹ shows the presence of O-H stretching with hydrogen bonding in either alcohols or phenols [56-60]. The natural proteins and cellulose present in the microalgae cell wall generally contain the functional groups like N-H and O-H [40]. The peak at 2958.27cm⁻¹ may be related to the aliphatic C-H stretching which represents the aliphatic organic chains of the cellulose [56]. The peak at 2924.52cm⁻¹ may represent the O-H stretching of the carboxylic acid [40]. This defines the presence of an acidic group such as -COOH present in the cell wall of the microalgae biomass as the algae generally contains alginic acid, which is a hyper chemical compound for the biosorption of different multivalent metals [40-46]. The peak at 2852.21cm⁻¹ represents the C-H stretching in different aldehydes [61]. The peak at 1658.42cm⁻¹ may be related to the >C=O stretching in the conjugated aldehyde/amide bend proteins which are key factors for the biosorption [61]. The peak at 1536.98cm⁻¹ represents the >C=O stretching in different carboxylic acids [40]. The peaks at 1454.064 and 1402.96cm⁻¹ may be related to the >C=O stretching in the amide groups (amide I and II bands). The peak at 1148.41cm⁻¹ may represent either the characteristic absorption peak of phosphate group or the C-O stretching in the alcohols/aldehydes [40-61]. The peaks at 1117.54, 668.21 and 599.75cm⁻¹ may be related to the organic halide compounds [61]. From the above discussion it can be observed that the microalgae biomass contained different functional compounds like aldehydes, amides, acids, phosphates, and halides. They might compensate the Cr (VI) uptake onto their host biomass from the solution.

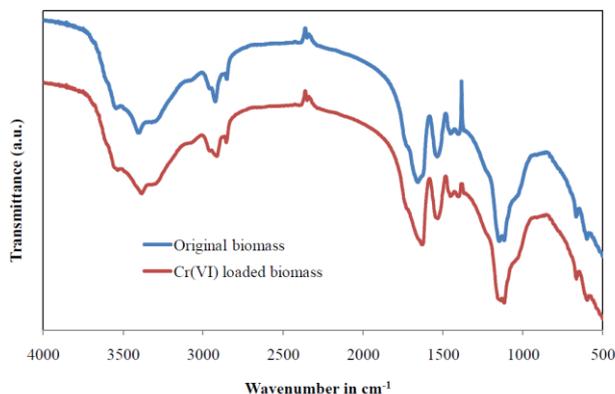


Fig. 3: FTIR Analysis of the Original and Cr (VI) Loaded Microalgae Biomass.

3.2. Effect of contact time

The biosorption of Cr (VI) using the microalgae biomass was conducted by varying different contact times, such as 30, 60, 90, 120, 150, 180, 210, 240, 270 and 300 min, while other parameters kept constant. Fig.4 shows the plot of Cr(VI) concentration and biosorption efficiency with respect to the contact time. It can be observed that the biosorption rate was initially very fast up to 90 min with the efficiency of biosorption just above 90%. Further increasing the contact time up to 300min it added only 3% more Cr (VI) biosorption. The fast rate accounted for 90.18% of the Cr (VI) biosorption within 90 min only. The biosorption rate significantly decreased after 90 min. After 150 min of the contact time it was too slow to quantify. Therefore, the biosorption time 150 min was considered as the equilibrium point of the biosorption experiment. All further biosorption experiments were conducted for 150 min.

3.3. Effect of initial pH

The initial pH of the solution is important for the biosorption of Cr (VI) as protonation of the biosorbent regulates the anionic biosorption. The effect of initial pH on the Cr (VI) biosorption was examined by varying the pH of the solution from 0.5 to 5.0, while other parameters kept constant. The biosorption efficiency during the pH variation experiment was evaluated for different initial pHs. Fig.5 shows the graph of biosorption efficiency plotted versus initial pH of the solution. With the increase of pH from 1.0 to 5.0 it decreased steadily and reached 27.5% at the pH-5.0. The maximum biosorption efficiency was 92.9% at the pH-1.0. At the lower pH the surface of biomass containing amide, carboxyl, halide and hydroxyl groups protonated and became positively charged. At the same time anionic species of Cr (VI), such as tetraoxohydrochromate (HCrO₄⁻), chromate (CrO₄²⁻) and dichromate (Cr₂O₇²⁻) ions, were exist in the acidic solution at lower pH [2]. The positively charged biomass interacted electrostatically with the anionic species of Cr (VI) resulting in a strong physiosorption of Cr (VI) onto the microalgae biomass at the lower pH range. When pH of the solution was gradually increased, surface of the biomass became negatively charged due to the decreasing in the proton concentration. The negatively charged biomass competed with the anionic chromate ions due to the electrostatic repulsion, resulting in the decrease of biosorption efficiency at the higher pH range.

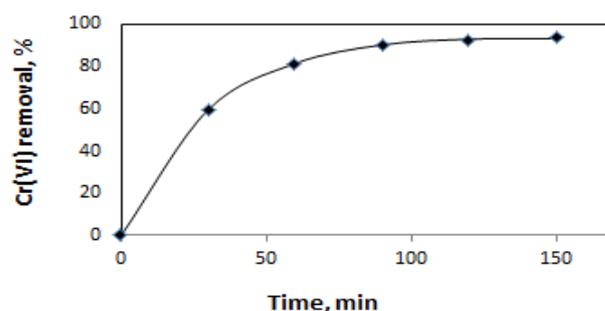


Fig. 4: Effect of Contact Time on the Cr (VI) Removal. (Conditions: Initial Cr(VI) Conc., 10 Mg/L; Solid-Liquid Ratio, 10 % (W/V); Initial Ph, 1.0; Temp., 30 Oc; Particle Size, -75+45 μ m; Stirring Speed, 200 Rpm).

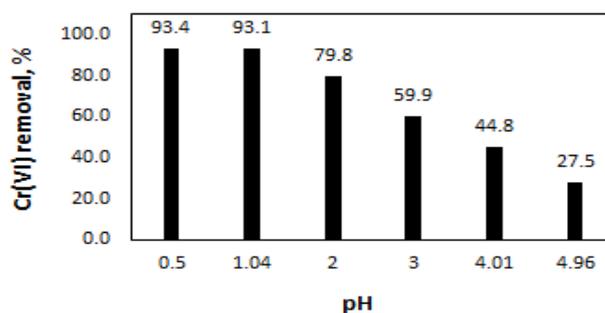


Fig. 5: Effect of Initial Ph on the Cr (VI) Removal. (Conditions: Initial Cr(VI) Conc., 10 Mg/L; Solid-Liquid Ratio, 10 % (W/V); Contact Time, 150 Min; Temp., 30 Oc; Particle Size, -75+45 μ m; Stirring Speed, 200 Rpm)

3.4. Effect of bio sorbent dosage

The biosorbent dosage in terms of solid-liquid ratio or S/L (the amount of biomass in gram added to 100mL solution, % (w/v)) was varied as 2, 5, 10, 15, 20, and 30% (w/v). The graph of biosorption efficiency plotted versus S/L is shown in Fig.6. It can be observed that the Cr (VI) removal efficiency increased rapidly with the increase of biosorbent dosage up to 10 % (w/v). This increase of the biosorption rate credited the increasing surface area while more amount of biosorbent was added. On further increasing in the biosorbent dosage there was hardly any increase in the biosorption rate achieved. Therefore, the S/L of 10 % (w/v) was chosen as an optimum biosorbent dosage for the Cr (VI) removal.

There was an obvious result of decreasing in the biosorption capacity with the increase of the biosorbent dosage (Fig.6) as it was calculated on the basis of amount of Cr (VI) adsorbed per gram of biosorbent. This may attributed to either of the overlapping, aggregation, and combination of both at the biosorbent surface resulting in the decrease of the overall biphasic interface [62-63].

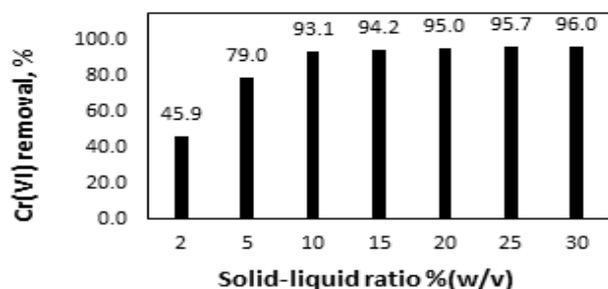


Fig. 6: Effect of Adsorbent Dose on the Cr (VI) Removal. (Conditions: Initial Cr(VI) Conc., 10 Mg/L; Initial Ph, 1.0; Contact Time, 150 Min; Temp., 30 Oc; Particle Size, -75+45 μ m; Stirring Speed, 200 Rpm).

3.5. Effect of initial Cr (VI) concentration

Since biosorption is a physical process of mass diffusion at the interface of two phases, the initial concentration of Cr (VI) as adsorbate has a major role in defining the biosorption. Fig.7 shows the graph of biosorption efficiency plotted versus initial concentration of the Cr (VI). The initial Cr (VI) concentration did not affect the biosorption efficiency, while it was increased from 5 to 10mg.L-1. When the initial Cr (VI) concentration was increased from 15 to 50mg.L-1, the biosorption efficiency decreased constantly. The biosorption capacity increased with the increase of initial Cr (VI) concentration up to 15mg.L-1, and to further increase up to 50mg.L-1 there was hardly any change. This may be due to inadequate active sites in the biosorbent for the diffusion of the increasing amount of adsorbate or mutual collision of the adsorbate hindered the diffusion at the interface of two phases or a combination of both.

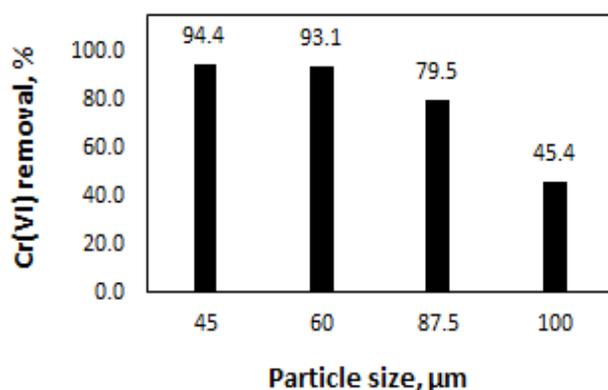


Fig. 7: Effect of Initial Cr (VI) Concentration on the Cr (VI) Removal. (Conditions: Solid-Liquid Ratio, 10 % (W/V); Initial Ph, 1.0; Contact Time, 120 Min; Temp., 30 Oc; Particle Size, -75+45 μ m; Stirring Speed, 200 Rpm).

3.6. Effect of particle size

Since biosorption is a surface phenomenon, variation of the particle size of the biosorbent is necessary for designing the bed dimension during scaling up of the process. The coarse sized biosorbent particles favour the strength of adsorption bed; however, they have less active surface area. Therefore, optimization of the particle size distribution of the biosorbent is an important parameter. Four particle size distributions, such as -45, -75+45, -100+75 and +100 μ m, respectively averaged to 45, 60, 87.5 and 100 μ m were used to evaluate the particle size effect on the biosorption process. The graph of the biosorption capacity and efficiency plotted versus the average particle size of the biosorbent is shown in Fig.8. Both the biosorption capacity as well as efficiency de-

creased with the increase of the particle size. Since the biosorption process was a mass diffusion phenomenon at the interface of two phases, the finer particle size favored the biosorption rate due to the larger exposure of potential active sites in the finer biosorbent particles.

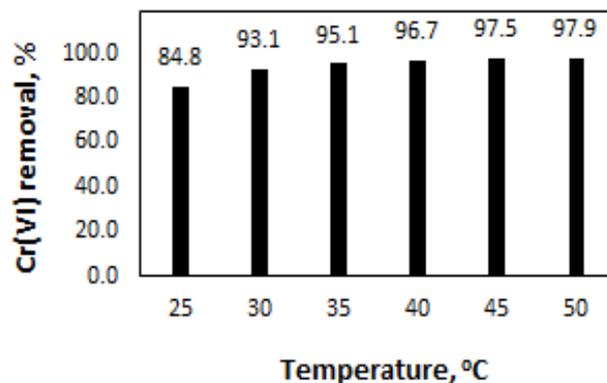


Fig. 8: Effect of Particle Size on the Cr (VI) Removal. (Conditions: Initial Cr(VI) Conc., 10 Mg/L; Initial Ph, 1.0; Contact Time, 120 Min; Temp., 30 Oc; Solid-Liquid Ratio, 10 % (W/V); Stirring Speed, 200 Rpm).

3.6. Effect of temperature

Physical adsorption is triggered thermodynamically at the interface of two phases. It depends on the randomness of adsorbate species at the surface of the biosorbents. Therefore, variation of temperature has a major role in defining the randomness at the interface of a biphasic system. The temperature was varied from 25 to 50 oC in order to evaluate its effect on the biosorption of Cr (VI) onto the microalgae biomass. Figure 9 shows the graph of biosorption capacity and efficiency plotted versus temperature. Both the biosorption capacity as well as efficiency increased with the increase of temperature. This may be due to the endothermic nature of the biosorption process.

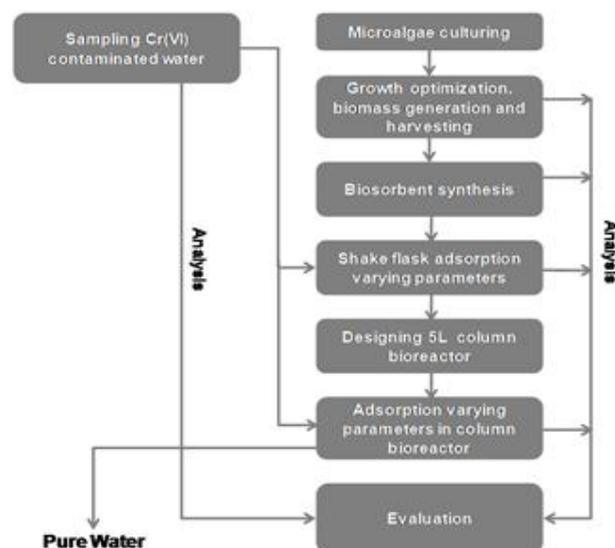


Fig. 9: Effect of Particle Size on the Cr (VI) Removal. (Conditions: Initial Cr(VI) Conc., 10 Mg/L; Initial Ph, 1.0; Contact Time, 150 Min; Particle Size, -75+45 μ m; Solid-Liquid Ratio, 10 % (W/V); Stirring Speed, 200 Rpm).

4. Conclusion

Biomass of the microalgae *Scenedesmus* sp. was used for the purpose of Cr (VI) removal from a synthetic K₂Cr₂O₇ solution. The effects of different biosorption parameters were examined for the bio-removal of Cr (VI). Presence of different functional groups in the microalgae biomass confirmed by the FTIR analysis technique compensated the Cr (VI) biosorption. The biosorption time was divided into two stages such as an initial fast rate stage followed

by a slower rate stage. The fast rate stage was accounted for more than 90% of the Cr (VI) biosorption from the solution and it lasted for 90 min. The biosorption rate decreased with the increase of three parameters such as Cr(VI) concentration, pH, and particle size; however, it increased with the increase of other two parameters such as biosorbent dosage and temperature. The biosorption propagated through the anionic biosorption mechanism. At the optimum condition (e.g. contact time, 120min; S/L ratio, 10% (w/v); Cr(VI), 10mg.L⁻¹; pH, 1.0; temperature, 30°C; particle size, 75+45µm; stirring, 300 rpm), 93.1% of Cr(VI) was removed from the solution. A tentative flowsheet for the Cr (VI) removal is shown in Fig.10.

Figure 10. Flowsheet for Cr (VI) removal from contaminated water.

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