Evaluation of the effectiveness of dolochar as an adsorbent for chromium (VI) removal from synthetic samples

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Abstract - The present study was conducted to investigate the effectiveness of dolochar as an adsorbent, for chromium (VI) removal from synthetic water samples. Adsorption studies were conducted in the range of 10-50 mg/l initial chromium (VI) concentration and at temperature in the range of 20-40ºC. The experimental data were analyzed by the Freundlich isotherm and the Langmuir isotherm. The rate of adsorption as shown in figure was found better fit to pseudo-second-order kinetics with good correlation.In this paper an attempt has been made to investigate the sieve size analysis so as to reutilize it as a good absorbent to absorb the pollutants present in water. The adsorption behavior of dolochar using batch process has been studied to remove hexavalent chromium from mine drainage. Batch study have been conducted by varying adsorbent dose, adsorbate concentration, pH, particle size, time, temperature on removal of chromium (VI) of these metal ions. The adsorption of Chromium (VI) is found to be better in acidic pH in comparison to alkaline media. It was found that more than 100% of the removal was achieved under optimal condition. The experimental results obtained at various concentration at 30ºC showed that the adsorption pattern of the dolochar.

Keywords: Adsorption; Dolochar; chromium (VI) removal; Kinetics; Isotherms

I. INTRODUCTION

The sponge iron manufacturing industries in India use iron ore, coal and dolomite to produce sponge iron which results in generation of huge quantity of waste due to the use of inferior quality of coal. For the production of 100 tonnes of sponge iron, the amount of iron ore and coal requirement is 154 and 120 tonnes respectively in which case the solid waste generate is around 45 tonnes and out of which 25 tonnes are char and widely known as dolochar [1-2]. From 1980 onwards, the production of sponge iron in India has been exponentially increased, so also dolochar. Now-a-days it is a major challenge to utilize such waste generated by sponge iron industries. Therefore, efforts are to be made for controlling pollution arising out of the disposal of wastes by conversion of these unusable wastes into utilizable raw materials for various beneficial uses. If these materials can be suitably utilized, the pollution and disposal problems may be partly reduced [3].

These materials may possess environmental pollution in the nearby locality, so its commercial recovery by any suitable process will give added advantage to the economy and efficient utilization of resources as well as environmental pollution control [4]. So here we used dolochar as an adsorbent for removing hexavalent chromium from mine drainage.

Odisha accounts for about 98% of the total proved chromite (chromium ore) reserves of the country, of which about 97% occur in the Sukinda Valley, over an area covering approximately 200 sq. km., in the Jajpur district [5]. Sukinda valley in Odisha has made it to the top ten of the world's 30 most polluted places. Seventy years of intensive open-cast chromite mining have resulted in a scarred landscape, toxic water and soil, ruined agricultural fields, degraded forestland, and populations that are being slowly poisoned. Over 30 million tonnes of hexavalent chromium bearing overburden, generated by 13 chromite mines, have completely altered the landscape of the

region. Many of the mines there do not have an environmental management plan, untreated or partially treated waste water from the mines, generated while washing the ore and excess water from the mine pits is let out into the open fields of the surrounding villages [6]. It eventually drains into the Damasala nala, a tributary of the Brahmani that empties out into the Bay of Bengal. So the presence of heavy metals Cr (VI) in high concentration in ground water can cause an adverse effect on human health and making that water not potable. For reducing hexavalent chromium from mine discharge water, adsorption method is mostly used. It is a cost effective method.

In this case an attempt has been made to remove hexavalent chromium from mine drainage by using dolochar. Chromium is toxic metal found in different industrial discharges and effluents [7]. Presence of heavy metals in human environment is of a major concern due to their tendency to accumulate in living organisms, and by that find their way into the human body causing various diseases and disorders. The major ill effects caused by Cr (VI) ions in human body are liver and kidney damage and cause internal hemorrhages, respiratory irritation, skin ulcer etc. Chromium may affect the eyes. Low chromium levels may cause high cholesterol [8, 9]. Chromium salts (chromates) are also the cause of allergic reactions in some people.

Adsorption is a versatile treatment technique practiced widely in fine chemical and process industries for waste water [10], However in order to find some utility of dolochar as an adsorbent and taking into account its carbon content and inherent porosity, adsorption studies with regard to some heavy metal ions like Cr(VI) were attempted. The influence of several operating parameters for adsorption of chromium(VI), such as contact time, initial concentration, pH, particle size and adsorbent dose, temperature etc. were investigated in batch shaking process.

II. MATERIALS AND METHODS

A. .Mechanism of chromium removal

Removal of chromium has been investigated by using phytoextraction, reverse osmosis, adsorption, precipitation, ion-exchange, membrane and biological processes [11–15]. The traditional techniques are based on chemical precipitation coupled to pre- or post-oxidation/reduction followed by filtration in order to concentrate the species of interest. The main disadvantage of these techniques is the production of sludges containing toxic compounds of which the final disposal is often the general landfill [16]. Therefore, the use of other alternative techniques (such as adsorption, ion exchange, membrane and biological processes) based on physical, chemical and biological mechanisms are advisable in order to protect the environment and at the same time recover valuable metal. Nevertheless, many of these approaches are marginally cost-effective or difficult to implement in developing countries. The main advantages of ion exchange are the recovery of metal value, the selectivity, the less sludge volume produced and the meeting of strict discharge specifications [17]. Gode and Pehlivan [18] have proved that ion-exchange resins can be used for the efficient removal of chromium from water and wastewater. Rengaraj et al. [19] have studied the removal of chromium from water and electronic process wastewater by ion-exchange resins. Sule and Ingle [20] have studied the adsorption of Cr^{3+} species by Chelex-100 chelating resin and Cr^{6+} by the anion-exchange resin. In another report by Zhao et al. [21], they have analyzed the removal of hexavalent chromium from wastewater, by using an ion-exchange bed with the strongly basic ion-exchange resin and found that all of expanded beds provided better adsorption than the fixed-bed. The parameters that influence adsorption, initial Cr^{6+} concentration, agitation time, pH, resin amount, temperatures, isotherm and kinetic, were investigated at 30ºC (room temperature). In addition, the equilibrium and kinetic parameters of Cr^{6+} at pH 2 were analyzed at 20, 30, and 40ºC respectively. Of all the various water treatment techniques, adsorption is generally preferred for the removal of heavy metal ions due to its high efficiency, easy handling, availability of different adsorbents and cost effectiveness [22–26].

B. Experimental technique

Adsorbate

The synthetic chromite solution was used for optimizing different adsorption parameters for batch study, and the optimized methods were applied to remove chromium (VI) from synthetic samples to evaluate the results.

A stock solution of chromium (VI) was prepared (1000 mg/l) by dissolving required amount of, potassium dichromate ($K_2Cr_2O_7$) in distilled water. Potassium dichromate ($K_2Cr_2O_7$) was used without any purification. Different concentration of this solution was prepared varies from 20 to 60 mg/l. The pH of the solution was adjusted to the required value by adding either dilute H_2SO_4 or NaOH solutions.

Adsorbent: Dolochar

Dolochar sample was collected from one of the sponge iron plants of Odisha, India and washed with distilled water for several times to remove dirt and dust particles and dried at 105ºC for few hours. The material was then

subjected to fine grinding using laboratory ball mill. Therefore, dolochar was crushed in a small ball mill with 50 numbers of small balls for 1 hour. The fine dolochar from ball mill was collected and dried to remove the moisture. Then this fine dolochar was kept in airtight packet for the experimental use.

Adsorption method

Batch adsorption experiments were performed by contacting 2g of the selected activated samples with 100ml of the aqueous solution of different initial concentration (10, 20, 30, 50 mg/l) at low pH (2). The experiments were performed in a thermal shaker at controlled temperature (30±1ºC) for a period of 1 h at 150rpm using 250 ml Erlenmeyer flasks containing 100ml of different chromium (VI) concentrations at room temperature. Continuous mixing was provided during the experimental period with a constant agitation speed of 150rpm for better mass transfer with high interfacial area of contact. The remaining concentration of chromium in each sample after adsorption was determined by atomic-absorption spectrophotometer after filtering the adsorbent with Whatmen filter paper to make it carbon free. The pH of the final solution was measured at the end of the experiment. The pH of the solution was adjusted to the required value by adding either dilute H_2SO_4 or NaOH solutions. The batch process was used so that there is no need for volume correction. The chromium (VI) concentration retained in the adsorbent phase was calculated according to

$$q_e = \frac{(C_i - C_e)V}{W} \quad \text{.....(1)}$$

where Ci and Ce are the initial and equilibrium concentrations (mg/L) of chromium (VI) solution, respectively; V is the volume (L); and W is the weight (g) of the adsorbent.

The effect of adsorbent dosages (5–30 g/l) on the equilibrium adsorption of chromium (VI) on the selected carbon was investigated by employing different initial concentrations (10, 20, 30 and 50 mg/l) at different temperature (10–50ºC). For these experiments, the flasks were shaken, keeping the pH at low (2) and agitation speed (150 rpm) for the minimum contact time required (1 hour) to attain equilibrium, as determined from the kinetic measurements detailed above.

Analytical method

Atomic-absorption spectrophotometry utilizes the phenomenon that atoms absorb radiation of particular wavelength. By atomic-absorption spectrophotometer, the metals in water sample can be analyzed [28, 29]. It detects concentration of Cr (VI) in ppm level in the solution and volume of sample required is only 1 ml for one analysis. A UV-Visible spectrophotometer was used for the estimation of hexavalent chromium by complexing with 1,5-diphenyl carbazide in acid solution. The purple-violet colour developed due to complexion with hexavalent chromium at low pH was measured at 540nm [30].

III. RESULT AND DISCUSSION

A. Sieve size analysis

This is known as particle size analysis or mechanical analysis. It is a method of separation of soils into different fraction based on particle size (dolochar is analyze instead of soil). It expresses quantitatively the proportions, by mass, of various sizes of particles present in the dolochar sample. 300 gm of dolochar sample was taken and sieved through a nest of sieves which is consists of 4.75mm, 2mm, 1mm, 600µ, 425µ, 300µ, 150µ, 75µ and pan. The total arrangement was placed in a mechanical sieve shaker and was shake it for 10 minutes. The Table.1 and Fig.1.shows the particle size/ sieve size analysis and particle size distribution curve of dolochar respectively.

B. Chromium adsorption

B.1 Adsorbent dose study

The effect of adsorbent dosage on the percentage removal chromium (VI) has been shown in Fig. 2. It can be seen from the figure that initially the percentage removal increases very sharply with the increase in adsorbent dosage. The adsorption capacities for chromium (VI) increased from 62 to 100, 60 to 90, 57 to 88 and 53 to 81% at 10, 20, 30, 50mg/l initial feed concentration respectively with the increase in the adsorbent dosages varies from (5 to 30g/l) at constant temperature (30ºC) and pH (2). A maximum removal of 100% was observed at adsorbent dosage of 25g/l at pH 2 for initial chromium (VI) concentration of 10mg/L. Therefore, the use of 20g/l adsorbent dose is justified for economical purposes.

B.2 Contact time study

The relationship between contact time and chromium adsorption on dolochar at different initial chromium concentrations is shown in Fig.3. The adsorption capacities increased from 58 to 92, 42 to 70, 30 to 62 and 23 to 48% with the chromium concentration of 10, 20, 30, 50mg/l at a constant speed 150rpm. The time dependent behavior of hexavalent chromium adsorption was measured by varying the contact time in the range of 5 to 80 minute to determine the metal ion adsorption capacity of the dolochar. Therefore the use of time is decided 60 min for all experiments.

B3 Adsorbate study

The effect of chromium concentration in the solution on the adsorption has been shown in Fig.4. It can be seen from the figure that with increased initial feed concentration of chromium (VI), there was decrease in percentage of adsorption of chromium. The adsorption capacities for chromium (VI) decreased from 90 to 61, 97 to 65, 99 to 70% at adsorbent doses 10, 20, 30 g/l with the increase in the initial feed concentration from 2 to 15 mg/l at constant temperature 30 ºC and pH 2. Therefore the use of adsorbate dose 20mg/L is justified for economical purposes.

B.4 Effect of particle size

The influence of particle size was studied for different initial feed concentration of Cr (VI) at constant temperature 30ºC and pH 2. Fig.5 shows the experimental results obtained from a series of experiments performed using different particle sizes of dolochar. The adsorption capacities for chromium (VI) decreased from 96 to 61, 92 to 60 and 88 to 57 and 85 to 53% at 10, 20, 30, 50mg/l initial feed concentration respectively with the increase in the particle size from 45 to 600micron because the higher adsorption with smaller adsorbent particle may be attributed to the fact that smaller particles give large surface areas. The result showed that there was a gradual decrease of adsorption with the increase in particle size. Therefore the use of 75micron particle size is decided for economical purposes.

B.5 Effect of pH on chromium adsorption

Earlier studies have indicated that solution pH is an important parameter affecting adsorption of heavy metals. Chromium (VI) removal was studied as a function of pH for three initial concentrations for a fixed adsorbent dose (20g/l) and the results are shown in Fig.6. It is clear from this figure that the percent adsorption of chromium (VI) decreases with increase in pH from pH 2 to 9. Removal of hexavalent chromium by dolochar at different pH values indicated that the amount of adsorbed Cr (VI) increases from 43 to 95, 35 to 90, 24 to 85% at 10, 30, 50mg/L initial concentration respectively with the decrease pH from 9.0 to 2. It is important that the maximum adsorption was found at pH 2. Therefore the use of pH is 2±0.5.

B.6 Effect of temperature

Experiments were performed at different temperatures 20, 30 and 40ºC at a concentration of 20 mg/l and pH 2. The adsorption increased from 72 to 98, 68 to 93, 65 to 91 and 55 to 83% for different initial feed concentration 10, 20, 30,50mg/l respectively with the rise in temperature from 20 to 40ºC (Fig.8). Equilibrium time for 20, 30and 40ºC was found to be 60 min indicating that the equilibrium time was independent of temperature, also (Fig.7) shows the effect of temperature for different initial feed concentration at constant adsorbent dose 20 g/l and pH 2.5. It can be seen from the figure that initially the percentage removal increases very sharply with the increase in temperature. The figs.7 and 8 showed that, the adsorption was endothermic in nature

B.7 Adsorption kinetics models

The kinetic study of adsorption process is important as it gives insight into the rate of adsorption process, which is helpful in finding out contact time required for adsorption to take place and also facilitates evaluation of reaction coefficients. To investigate the mechanism of adsorption kinetics of chromium onto dolochar, two kinetic models, namely pseudo-first- order and pseudo-second-order models were analyzed. Basically, the adsorption process is controlled by the slowest steps of the reaction, i.e. either external mass transfer (film diffusion) or intra-particle diffusion (pore diffusion) or by both [35-37].

In order to investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, the pseudo-first-order and pseudo-second-order equations are applied [31].

B.8 Pseudo-first-order model

Lagergren proposed a pseudo-first-order kinetic model. The integral form of the model is

$$\log(q_e - q) = \log q_e - \frac{Kad}{2.303} t \quad \text{..... (2)}$$

where q is the amount of chromium (VI) sorbed (mg/g) at time t (min), q_e is the amount of chromium (VI) sorbed at equilibrium (mg/g), and *K*ad is the equilibrium rate constant of pseudo first-order adsorption (min^{-1}). This model was successfully applied to describe many adsorption systems.

B.9 Pseudo-second-order model

The adsorption kinetics may also be described by a pseudo-second-order reaction. The linearized-integral form of the model is

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t \quad \text{.....(3)}$$

Where K_2 is the pseudo-second-order rate constant of adsorption.

The applicability of the above two models can be examined by each linear plot of log (q_e-q) versus t, and (t/q) versus t, respectively, and are presented in Fig.9 and Fig.10. To quantify the applicability of each model, the correlation coefficient, R^2, was calculated from these plots. The linearity of these plots indicates the applicability of the two models. However, the correlation coefficients, R^2, showed that the pseudo-second-order model, an indication of a chemisorptions mechanism, fits better the experimental data ($R^2 > 0.998$) than the pseudo-first-order model (R^2 is in the range of 0.991-0.994) so the kinetics of adsorption is found to better fit to pseudo-second-order reaction.

The outcome values of parameters q_e, K_{ad}, K_2, and R^2 for all the experiments with pH of solution equal to 2 for maximum removal of chromium (VI) are presented in Table 4.

B.10 *Adsorption isotherms*

Several models have been used to describe the experimental data of adsorption isotherms. The Freundlich and Langmuir models are the most frequently employed models. In the present work both models were used. The chromium (VI) adsorption isotherm followed the linearized Freundlich model as shown in Fig.11. The Freundlich isotherm model explains about the adsorption process wherein a heterogeneous adsorbent surface involves in the multilayer distribution of the adsorbate with interaction amongst adsorbed molecules [32]. The relation between the metal uptake capacity q_e (mg/g) of adsorbent and the residual metal ion concentration C_e (mg/l) at equilibrium is given by

$$\ln q_e = \ln k + \frac{1}{n} \ln C_e \quad \text{..... (4)}$$

where the intercept ln *k* is a measure of adsorbent capacity, and the slope 1/*n* is the adsorption intensity. *k* is related to temperature and the chemical or physical characteristics of adsorbents, where as "n" is an indicator of the change of intensity of adsorption process and also a measure of the deviation from linearity of the adsorption. A higher value of n (n > 1) indicates favorable adsorption; where as n < 1 represents poor adsorption characteristics [33]. The value of n = 3.66 suggests favorable adsorption. The isotherm data fit the Freundlich model well ($R^2 = 0.997$).

The Langmuir isotherm suggests monolayer adsorption on a homogeneous surface with a finite number of adsorption sites and without any interaction between the adsorbed molecules [33].The Langmuir equation relates solid phase adsorbate concentration (q_e), the uptake, to the equilibrium liquid concentration (C_e) as follows:

$$q_e = \left(\frac{K_L b C_e}{1 + b C_e}\right) \quad \text{.....(5)}$$

where K_L and b are the Langmuir constants, representing the maximum adsorption capacity for the solid phase loading and the energy constant related to the heat of adsorption, respectively. It can be seen from Fig.12 that the isotherm data fits the Langmuir equation well ($R^2 = 0.999$).

The outcome values of parameters *k*, *n*, K_L, *b*, R^2 for all the experiments with pH of solution equal to 2 for maximum removal of chromium (VI) are presented in Table 2.

Langmuir equation can also be used to calculate a dimensionless equilibrium parameter, R_L also known as the separation factor [34] and can be expressed as:

$$R_L = 1/ (1+bC_0) \quad \text{.....(6)}$$

where, C_0 is the initial concentration of chromium (mg/l).

R_L = 1 represents linear adsorption, while R_L= 0 stands for the irreversible adsorption process. R_L< 1 is for favorable adsorption, while R_L> 1 represents unfavorable adsorption. In this case, the value of R_L was found to be 0.975, suggesting that the adsorption process was less than 1 but it was nearly equal to 1 so it was linear adsorption.

C. Scanning Electron Microscopy (SEM) analysis

Scanning electron microscopy (SEM) analysis was carried out on the distilled water washed dolochar and metal adsorbed dolochar under optimum conditions, to study its surface texture and the development of porosity. In this study, the images of SEM were recorded by using JEOL JSM-6300F field emission of SEM. A thin layer of platinum was sputter-coated on the samples for charge dissipation during SEM imaging. The sputter-coated was operated in an argon atmosphere by using a current of 6 mA. The coated were then transferred to the SEM specimen chamber and observed at an accelerating voltage of 20 kV for dolochar.

The SEM enables the direct observation of the surface microstructures of different adsorbents. The studies are available which have reported the utilization of the scanning electron microscopy analysis for showing morphology of different adsorbents. The SEM micrographs were obtained for three magnifications (x200, x1000 and x3500). The SEM micrographs for distilled water washed dolochar is shown in Fig.1,2 and3. The SEM micrographs for treated dolochar are shown in Fig.4,5 and 6.

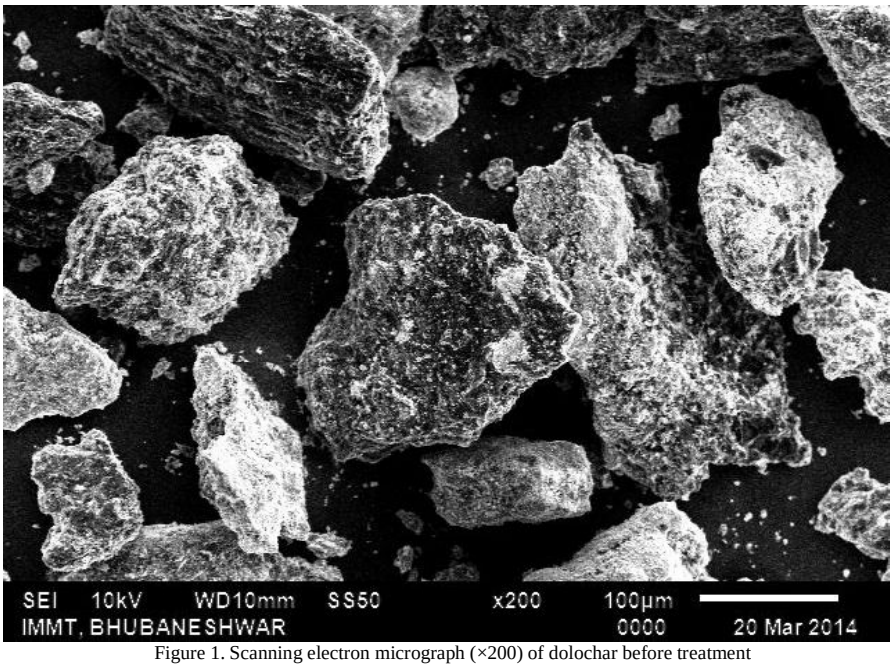

Figure 1. Scanning electron micrograph (×200) of dolochar before treatment

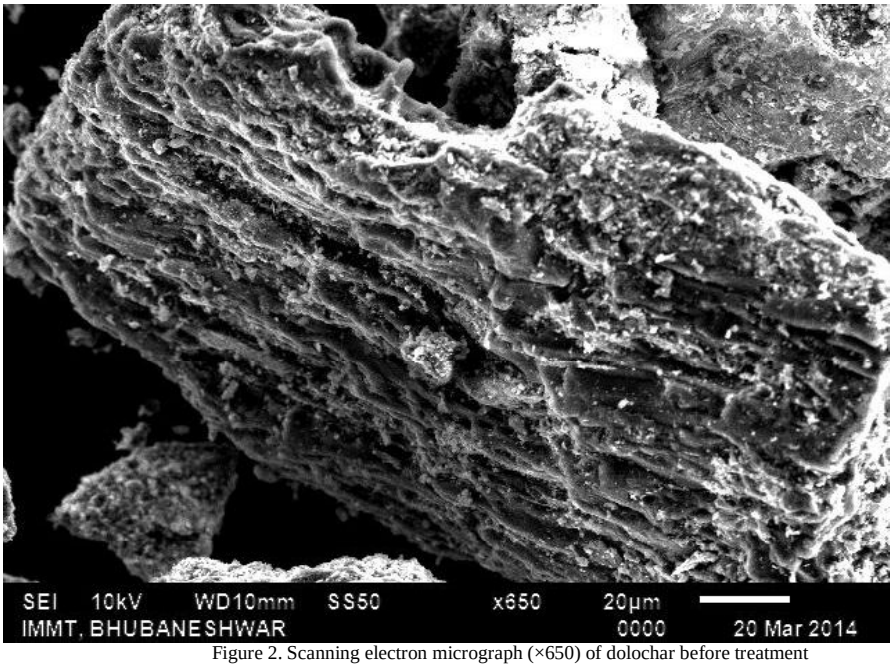

Figure 2. Scanning electron micrograph (×650) of dolochar before treatment

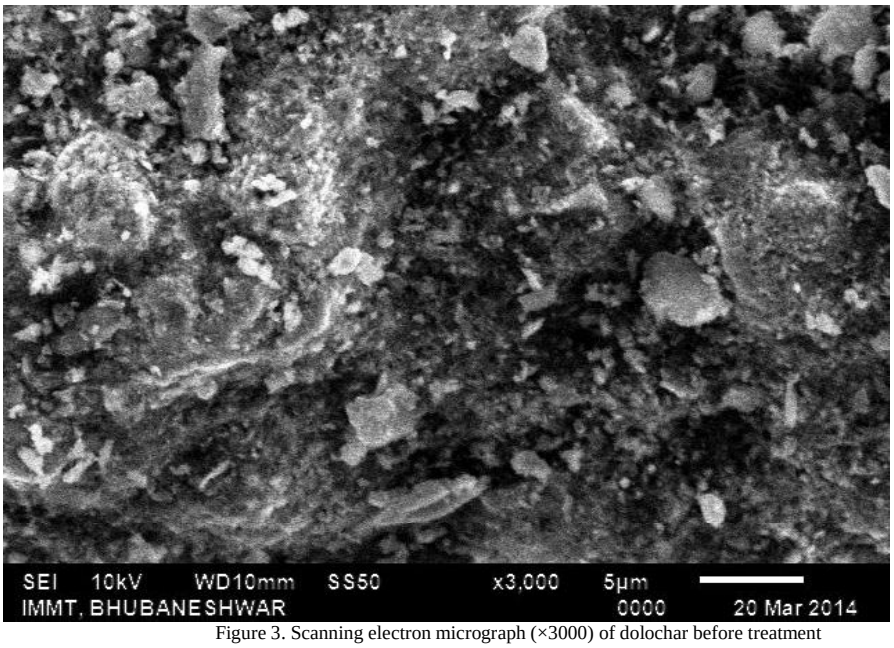

Figure 3. Scanning electron micrograph (×3000) of dolochar before treatment

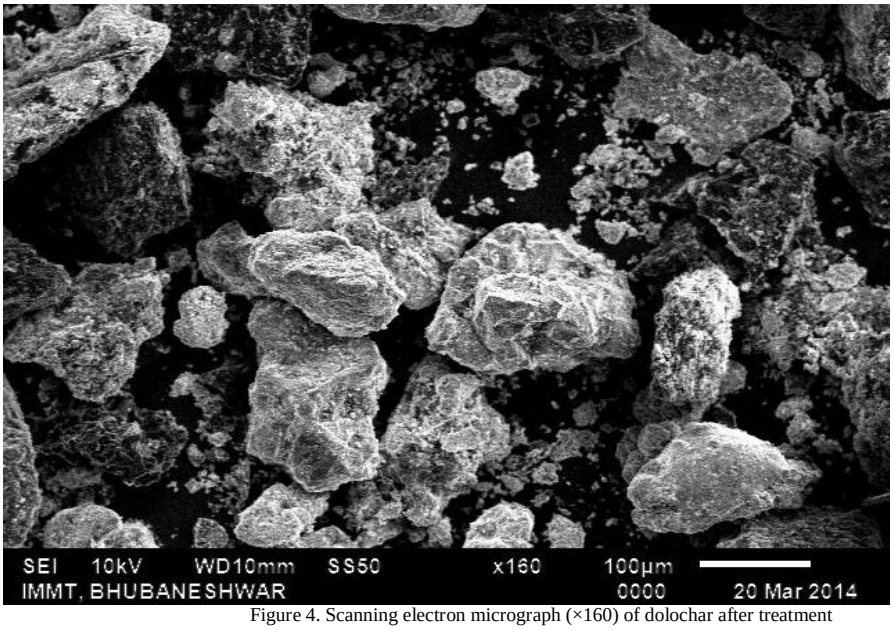

Figure 4. Scanning electron micrograph (×160) of dolochar after treatment

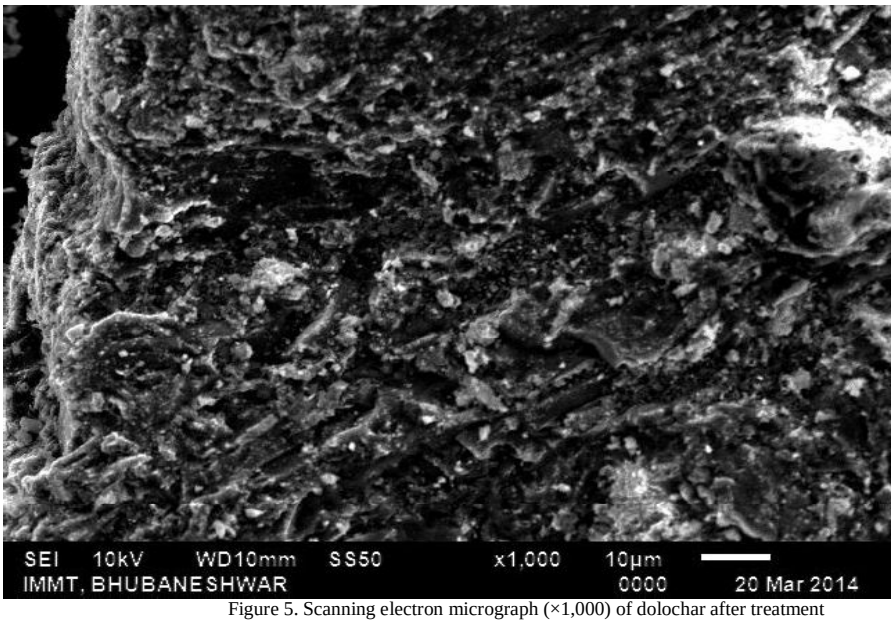

Figure 5. Scanning electron micrograph (×1,000) of dolochar after treatment

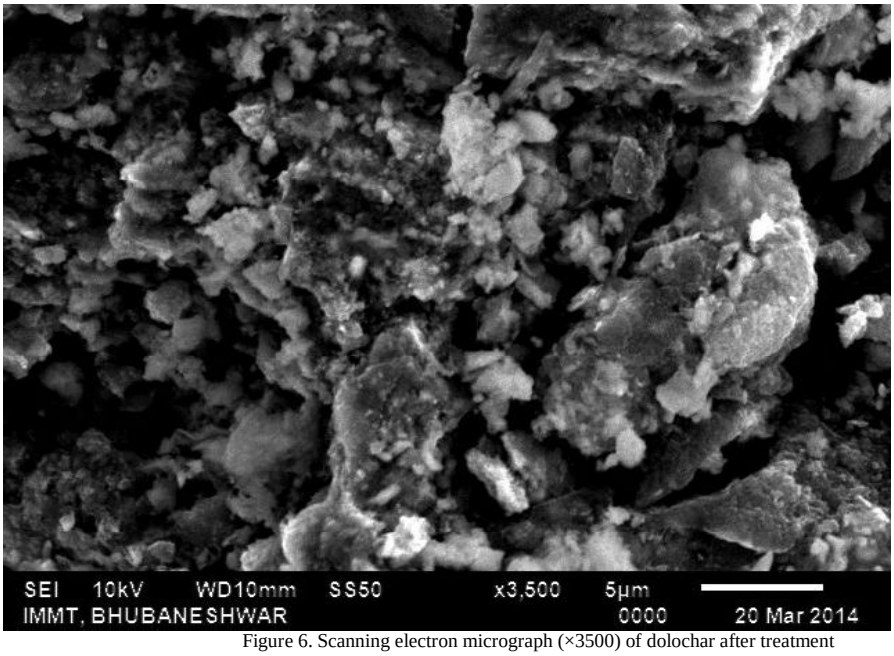

Figure 6. Scanning electron micrograph (×3500) of dolochar after treatment

Scanning electron micrograph of dolochar before and after treatment was obtained for different magnifications as shown in Fig. 1 to 6. The morphology of these materials can facilitate the sorption of metal ions, due to the irregular surface of dolochar, thus it makes the sorption possible in different parts of the material. Based on the morphology, as well as on the fact that high amount of iron is concentrated on the external epidermis of the dolochar. It can be concluded that this material presents adequate morphological profile to retain metal ions. The treatment with chromium was able to expose more surfaces for sorption, as can be seen in SEM of after treated dolochar as compared with before treated dolochar. Some modification can be observed on the after treated dolochar after sorption of metal ions and SEM results showed the increase of Cr count after adsorption, which unequivocally proved the adsorption of the said ion on the adsorbent. The results shows the considerable changes in morphology of sorbents after chromium treated dolochar with increased the number of cavities on surface responsible for more sorption potential of heavy metal adsorption. The SEMs at different magnifications of ×160, ×200, ×1000, ×1500, ×3000, and ×3500 do not reveal any apparent surface deformations due to the partial acidic treatment. This shows the physical integrity of the bio-matrix.

D. Fourier Transform Infrared Radiation (FTIR) spectroscopy

The FTIR technique is an important tool to identify some characteristics of functional groups, which are capable of adsorbing metal ions. The spectra were plotted by using the same scale on the transmittance axis for all the adsorbents before and after adsorption. FTIR analysis of the adsorbents was carried out using JASCO make FTIR-3500 spectrophotometer. Pellets (press disk) were used for measuring absorption spectra. The samples were ground with 200 mg of KBr (spectroscopic grade) in a mortar and pressed into 10 mm diameter disks less than 10 tons of pressure and high vacuum for FT-IR analysis. The conditions used were 16 scans at a resolution of 4 cm-1 measured between 600 and 4000 cm-1. The results are shown in Fig.7.

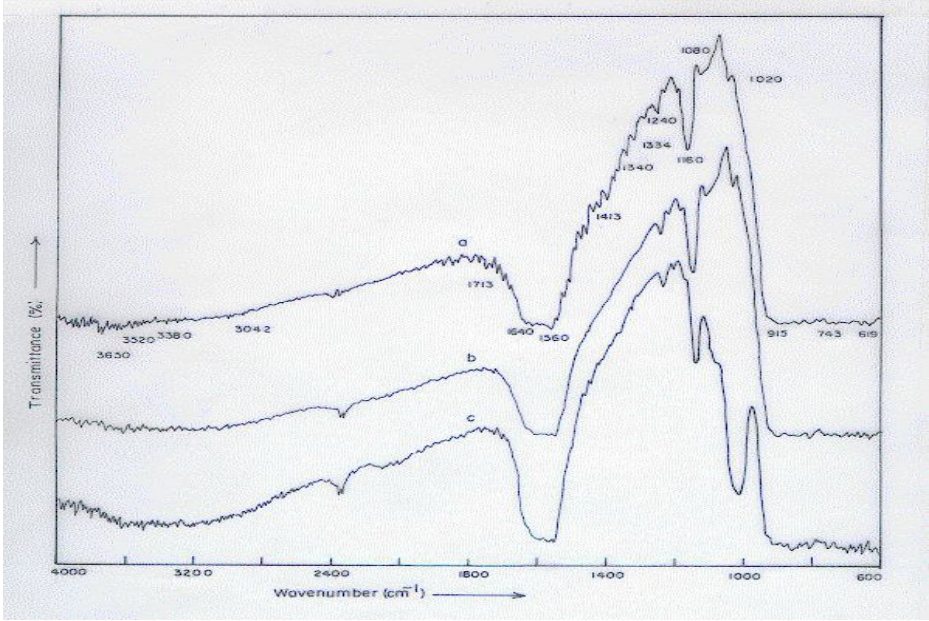

Figure 7. FTIR microscopic spectra of (a) Unwashed dolochar before adsorption (b) Washed dolochar before adsorption (c) Washed Dolochar after adsorption

B. Conclusion

Removal of chromium (VI) from mine drainage is possible using several abundantly available low-cost adsorbents. The present investigation shows that the dolochar is an effective adsorbent for the removal of chromium (VI) from aqueous solutions. Dolochar was found to be effective, as the removal of Cr (VI) reached 100% at normal temperature. It was also observed that the process of adsorption is strongly affected by the experimental parameters such as adsorbent dose, adsorbate concentration, pH, particle size, time and temperature. Adsorption of chromium is highly pH dependent.

However, more investigations are needed on different types of industrial wastewaters and different operating conditions before such conclusions can be generalized.

Nomenclature

$1/n$	adsorption intensity (dimensionless)
b	Langmuir constant (l/g)
Ce	equilibrium chromium (VI) concentration (mg/l)
Ci	initial chromium (VI) concentration (mg/l)
k	measure of adsorbent capacity (l/g)
K_2	equilibrium rate constant of pseudo-second-order adsorption (min^{-1})
K_{ad}	equilibrium rate constant of pseudo-first-order adsorption (min^{-1})
K_L	Langmuir constant (mg/g)
q_e	amount of chromium(VI) adsorbed at equilibrium (mg/g)
T	temperature (◦C)
t	time (min)
V	volume of the solution (l)
W	weight of adsorbent (g)
q	amount of chromium (VI) sorbed (mg/g)
Cr(VI)	hexavalent chromium

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