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Removal of Heavymetals (Cr^{6+}) From Aqueous Solution Using Industrial Waste

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***Abstract*— Dolochar which is a solid waste generated by the sponge iron industries is a major concern worldwide. In this paper an attempt has been made to investigate the properties (i.e. physical and chemical) so as to reutilize it as absorbent to absorb the pollutants present in water. The adsorption behavior of dolochar using batch process has been studied to remove hexavalent chromium from synthetic waste water. The physical properties of dolochar such as specific gravity, void ratio, porosity, grain size, density and chemical properties such as chemical composition have been analyzed. Batch adsorption experiment have been conducted by varying adsorbent dose, adsorbate concentration, pH, particle size, time on removal of chromium of these metal ions. It was found that more than 100% of the removal was achieved under optimal condition. The experimental results obtained at various concentration (27±1ºC) showed that the adsorption pattern on the dolochar have followed Langmuir and freundlich models. Kinetic of adsorption is found to follow pseudo-first order and second order reaction to perform the mechanism of adsorption.**

***Keywords*—Adsorption, Chromium removal, Dolochar, Density, specific gravity.**

I. Introduction

The presence of metal ions in the environment is of major concern due to their toxicity to many life forms. Unlike organic pollutants, the majority of which are susceptible to biological degradation, metal ions do not degrade into harmless end products. The metals of most immediate concern are Cr, Mn, Fe, Zn, and Cd. These metals are widely distributed in materials which make up the earth's surface [1]. Discharge as aqueous effluents from various industrial activities of chemical processing outfits may contain heavy metals which are non-biodegradable and toxic priority pollutants [2]. 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 sustainability of any human community hinges on adequate supply of potable water, which conforms to the acceptable standard. This makes removal of heavy metal species in wastewater an essential factor for environmental and human health protection. Cr^{+6} as representative of these heavy metals are chosen for this study as they are present in many industrial effluents. 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 [3,4].

Removal of heavy metals (Cr^{+6}) has been investigated by using phytoextraction, reverse osmosis, adsorption, chemical precipitation, ion-exchange, membrane separation and biological processes electro dialysis [5]. 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 [5,6]. To increase the adsorption capacity and physical and chemical properties, dolochar has gain important consideration as an effective adsorbent.

The production of iron and steel generates several types of waste materials in large quantities, such as dolochar, electric-arc-furnace slag, scrap fines, mill scale, and basic oxygen furnace mud. So dolochar is a carbonaceous material and therefore, it is expected to have high surface area with requisite porosity which makes it ideal for adsorption. In this case an attempt has been made to remove hexavalent chromium from the aqueous solutions using dolochar and also analyzed the physical and chemical properties of dolochar. The influence of several operating parameters for adsorption of chromium(VI), such as contact time, speed, initial concentration, pH, particle size and adsorbent dose, etc. were investigated in batch process. The main objective is to find a suitable use of dolochar, which is produced in huge amounts as a by-product of sponge iron industry [8].

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Chromium is toxic metals found in different industrial discharges and effluents [7]. 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. Adsorption involves attracting molecules of adsorbate on surface of the adsorbent.

II. Experimental Technique

A. Adsorbate

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 10 to 50 mg/L. The pH of the solution was adjusted to the required value by adding either dilute H_2SO_4 or NaOH solutions.

B. 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 h. 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.

C. Adsorption method

Batch shaking experiment were carried out to evaluate the adsorption capacity of dolochar in the removal of chromium from aqueous solution. The batch adsorption experiments were carried out in 250mL conical flasks in a solution of Cr (VI) in various concentration (10 -50 mg/L) with pH (1.5-2.5). The experiments were performed in a mechanical shaker at controlled temperature (25±1ºC) for a period of 60mins at 150rpm using 150 ml conical flasks containing 50ml 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 to make it carbon free. The pH of the final solution was measured at the end of the experiment. 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

$$q_e = \frac{(Ci - Ce)\ V}{W}$$

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

D. 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 [10]. 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 [9].

III. Results Discussions

A. Physical and chemical properties of the adsorbent

Collected dolochar samples are examined under different processes to know the major physical properties and some are related to engineering properties. The properties analyzed are specific gravity, void ratio, porosity, and density.

The specific gravity of dolochar was determined by using pycnometer method. The pycnometer method is more accurate and suitable for all types of materials. So the specific gravity of dolochar was found 2.25. By using specific gravity also analyzed void ratio and porosity. The void ratio and porosity of dolochar was found to be 0.27 and 0.21 respectively. Generally both void ratio and porosity were measured the denseness or looseness of any materials.

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As the material becomes more and more dense, their values decrease. Density is particularly important in removal. If two dolochar differing in bulk density are used at the same weight per liter, the dolochar having higher bulk density will be able to remove more efficiently. Average bulk density can be calculated by water displacement method. In this method, volume of water displaced is observed by a particular amount of dolochar. The average bulk density was found to be 1203 kg/m^3.

Adsorbent pH may influence the removal efficiency. The pH of the dolochar was measured by using the method by Al-Ghouti et al. [14] as follows: 1 g of dolochar was mixed with 50 ml of distilled water and agitated for 24 h. Then the pH value of the mixture was recorded with a pH meter. For our experiment the pH of dolochar was found (2±0.5).

The dolochar consists mainly of minerals such as silica, aluminum, iron, etc. The Table 1 shows the chemical analysis of dolochar.

TABLE 1
CHEMICAL ANALYSIS OF DOLOCHAR

MAJOR CONSTITUENTS	VALUES (%)
Fe_2O_3	51.10
SiO_2	20.35
Al_2O_3	12.37
LOSS OF IGNITION	11.80

B. Chromium Adsorption

Adsorbent Dose Study: The effect of adsorbent dosage on the percentage removal chromium (VI) has been shown in Fig. 1. 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 60 to 98, 58 to 100, 50 to 90% at 5, 10, 20mg/l initial feed concentration respectively with the increase in the adsorbent dosages varies from (5 to 30g/L) at constant temperature (27±1ºC) and pH (2±0.5). 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.

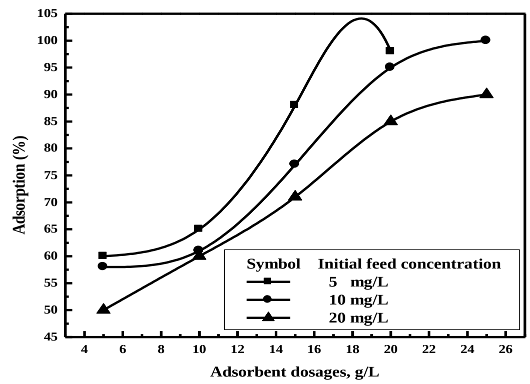

Fig.1. Effect of amount of adsorbent on Cr(VI) (contact time 60 min, initial concentration 5, 10, 20mg/L, pH 2, speed 150rpm, temp 27ºC, particle size 75µm)

Contact Time Study: The relationship between contact time and chromium adsorption on dolochar at different initial chromium concentrations is shown in Fig.2. The adsorption capacities increased from 50 to 91, 41 to 90, 32 to 71% with the chromium concentration of 5, 10, 20mg/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.

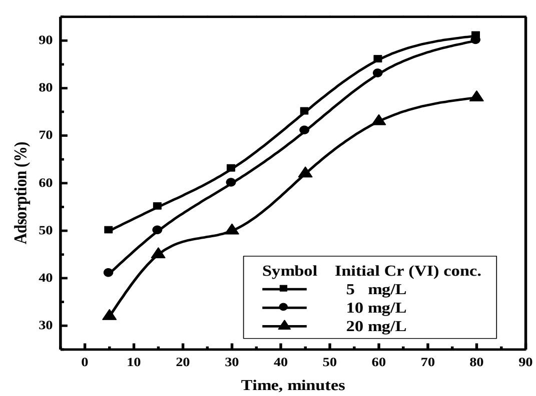

Fig.2. Effect of contact time on Cr(VI) (pH 2.5, metal concentration 5, 10, 20mg/L, dolochar 20g/L, temp 27ºC, speed 150rpm, particle size 75µm)

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Adsorbate Study: The effect of chromium concentration in the solution on the adsorption has been shown in Fig.3. 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, 98 to 68, 98 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 25 ºC and pH 2.5. Therefore the use of adsorbate dose 10mg/L is justified for economical purposes.

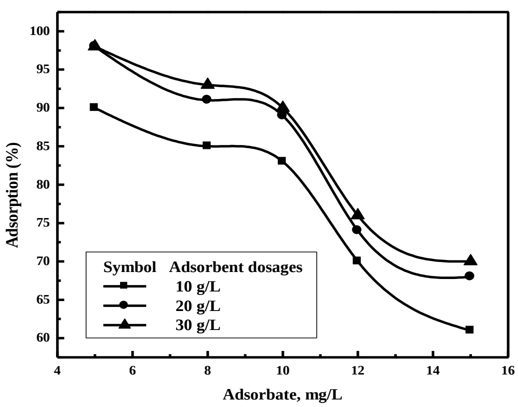

Fig.3. Effect of concentration on Cr(VI) (pH 2.5, dolochar 20g/L, contact time 60 min, temp 27ºC, speed 150rpm, particle size 75µm)

Effect of Particle Size: The influence of particle size was studied for different initial feed concentration of Cr (VI) at constant temperature 27ºC and pH 2. Fig.4 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 91 to 61, 90 to 60 and 88 to 57% at 5, 10, 20mg/L initial feed concentration respectively with the increase in the particle size from 45 to 600µm 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.

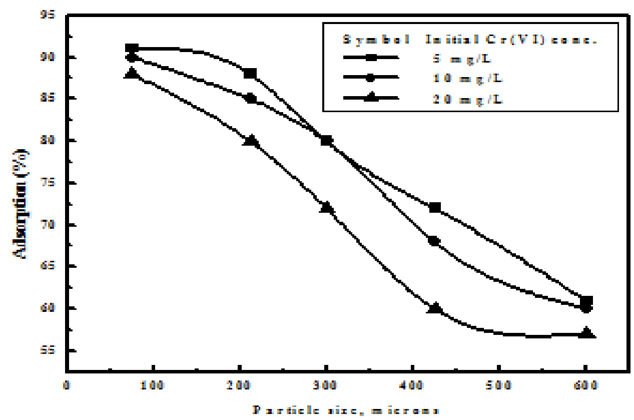

Fig.4. Effect of particle size on Cr(VI) (pH 2.5, dolochar 20g/L, contact time 60 min, temp 27ºC, speed 150rpm, concentration 5, 10, 20mg/L)

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.5. It is clear from this figure that the percent adsorption of chromium (VI) decreases with increase in pH from pH 1.5 to 9.0. Removal of hexavalent chromium by dolochar at different pH values indicated that the amount of adsorbed Cr (VI) increases from 32 to 94, 30 to 94, 28 to 92% at 5, 10, 20mg/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.

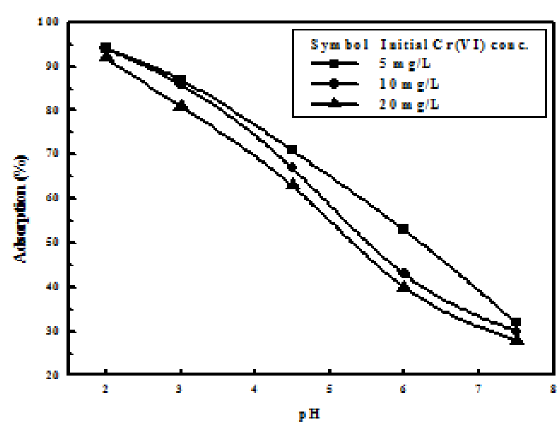

Fig.5. Effect of pH on Cr(VI) (dolochar 20g/L, contact time 60 min, temp 27ºC, speed 150rpm, concentration 5, 10, 20mg/L, particle size 75µm)

C. Adsorption Kinetics Models

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 to model the kinetics of chromium adsorption onto dolochar.

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

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

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 Kad is the equilibrium rate constant of pseudo first-order adsorption (min^{-1}). This model was successfully applied to describe many adsorption systems.

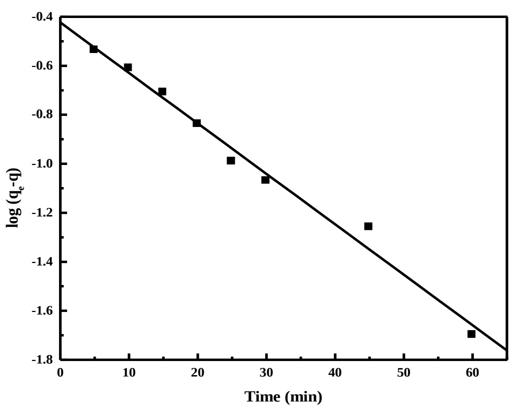

Fig.6. pseudo-first-order model

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

$$\frac{t}{q} = \frac{1}{K_2 q_e{}^2} + \frac{1}{q_e}t$$

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.6 and 7. 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 is in the range of 0.996) than the pseudo-first-order model (R^2 is in the range of 0.985) so the kinetics of adsorption is found to better fit to pseudo-second-order reaction.

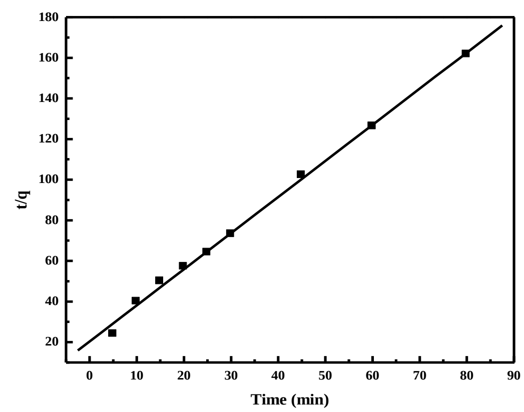

Fig.7. pseudo-second-order model

D. 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.8. 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

$$\ln q_e = \ln k + \frac{1}{n} \ln C_e$$

Where the intercept ln k is a measure of adsorbent capacity, and the slope 1/n is the adsorption intensity. The isotherm data fit the Freundlich model well (R^2 = 0.9714). The Langmuir equation relates solid phase adsorbate concentration (q_e), the uptake, to the equilibrium liquid concentration (C_e) as follows:

$$q_e = \left(\frac{K_L b C_e}{1+bC_e}\right)$$

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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.9 that the isotherm data fits the Langmuir equation well (R^2 = 0.9812).

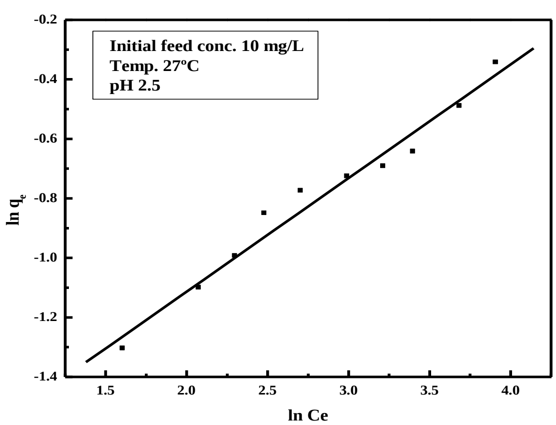

Fig.8. Freundlich adsorption isotherm

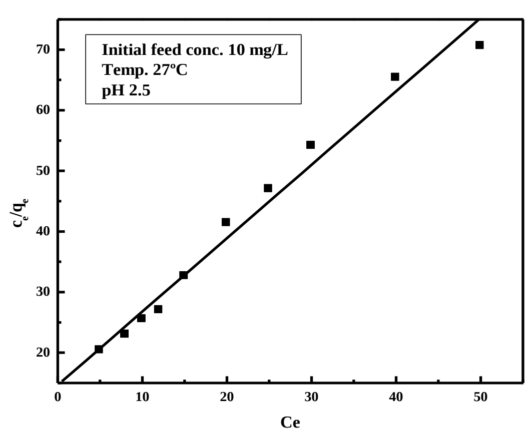

Fig.9. Langmuir adsorption isotherm

IV. CONCLUSION

Removal of chromium (VI) from aqueous solutions 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. 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.

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