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Sorption of hexavalent chromium from synthetic waste water using dolochar

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Abstract

The adsorption characteristics of hexavalent chromium on dolochar, a low cost natural adsorbent, were studied in the laboratory. Dolochar was found to be an efficient adsorbent for chromium removal from synthetic waste water. Dolochar which is a solid waste generated by the sponge iron industry, is processed and put to test as an adsorbent for removal of Cr (VI) ions from aqueous solution. 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 shaking has been studied to remove hexavalent chromium from synthetic waste water. The physical properties of dolochar such as specific gravity, void ratio, porosity, 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 94% of the removal was achieved under optimal condition.

Keywords: chromium removal; dolochar; adsorption; solid wastes; specific gravity.

INTRODUCTION

Hexavalent chromium is recognized as a carcinogenic and mutagenic agent [1]. 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. Chromium is toxic metals found in different industrial discharges and effluents [2]. 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].

The permissible limit of hexavalent chromium in industrial effluents is 0.5 mg/l by the Ministry of Environment and Forests (MoEF), Government of India. But in most of the mining and industrial effluents it is present in much higher concentration than the permissible limit several efforts have been made for its removal from industrial waste water involving textile dyeing, leather tanning, electroplating, mining, etc. [5]. Adsorption is a versatile treatment technique practiced widely in fine chemical and process industries for wastewater.

In recent years there has been huge demand of sponge iron as raw material for steel production in steel industries due to added advantage of non dependence on coking coal and stability of steel quality because of uniform chemistry of sponge iron. The principal raw materials required for sponge iron production are iron ore, non-coking coal and dolomite. 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. But due to non availability of good grade coal, the present practice is due to use poor quality (F grade) coal. Therefore the amount of raw material required is higher than the ideal values which in fact catalyst for the generation of more solid waste product. It has been estimated that the dolochar generated from 146 rotary kilns having capacity of about 16000 TPD (Tonnes Per Day) is 3.8 million TPA (Tonnes Per Annum) and disposal of such a huge amount is major concern [6]. The dolochar invariably contains 15-30 % unburned carbon. This means a large proportion of carbon values are going to be wasted and its commercial recovery by any suitable physical process will give added advantage to the economy and efficient utilization of resources as well as environmental pollution control [7]. Chromium compounds mainly occur in the environment as trivalent, Cr(III), and hexavalent, Cr(VI). Trivalent chromium is an essential element in humans and is much less toxic than the hexavalent [8].

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.

EXPERIMENTAL TECHNIQUE

Adsorbate

A stock solution of chromium (VI) was prepared (1000 mg/L) by dissolving required amount of, potassium dichromate ($K_2Cr_2O_7$) in

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distilled water. Potassium dichromate ($K_2Cr_2O_7$) was used without any purification. The stock solution was diluted with distilled water to obtain desired concentration ranging 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.

Preparation of Adsorbent

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

Method of experiment

Batch adsorption experiments were performed by contacting 0.1 g of the selected activated samples with 50ml of the aqueous solution of different initial 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 45mins 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 (VI) in each sample after adsorption at different time intervals was determined by atomic-absorption spectroscopy after filtering the adsorbent with Whatmen filter paper to make it carbon free. 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.

The effect of adsorbent dosages (5-30g/L) on the equilibrium adsorption of chromium (VI) on the selected dolochar was investigated by employing different initial concentrations (10-50mg/L) at different temperature (10–50 ◦C). For these experiments, the flasks were shaken, keeping the pH (2±0.5) and agitation speed (150 rpm) for the minimum contact time required to attain equilibrium. Further, experiments were carried out by different variables such as adsorbent dose, adsorbate concentration, pH, particle size, time, and speed, etc.

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 [9]. 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 [10].

Atomic-absorption spectrophotometer consists of four basic structural elements; a light source (hollow cathode lamp), an atomizer section for atomizing the sample (burner for flame, graphite furnace for electro thermal atomization), a monochrometer for selecting the analysis wavelength of the target element, and a detector for converting the light into an electrical signal. It detects concentration of chromium (VI) in parts per million (ppm) level in the solution and volume of sample required is only 1 ml for one analysis.

RESULTS AND DISCUSSIONS

Physical and chemical properties of the adsorbent

Physical properties

The smaller the particle sizes of dolochar, the greater the rate of diffusion and adsorption. Intraparticle diffusion is reduced as the particle size reduces, because of the shorter mass transfer zone, causing a faster rate of adsorption. Since we have prepared our dolochar in a powdered form so it has a great efficiency of removal.

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. 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.

Chemical properties

Adsorbent pH may influence the removal efficiency. The pH of the dolochar was measured by using the method by Al-Ghouti et al. [11] 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 sample

Major Constituents	Values (%)
Fe_2O_3	51.10
SiO_2	20.35
Al_2O_3	12.37
Loss of ignition	11.80

Washability study

The washability studies were carried out for each size fraction of fine dolochar samples by sink and float method by using a mixture of acetone and bromoform, a medium at different specific gravities ranging from 1.4 to 2.3. The sink and float products were washed thoroughly by acetone, dried and analyzed for ash by following standard American Society for Testing and Materials (ASTM) method.

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 58 to 100% at 10mg/l initial feed concentration with the increase in the adsorbent dosages varies from (5 to 30g/L) at constant temperature (25±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.

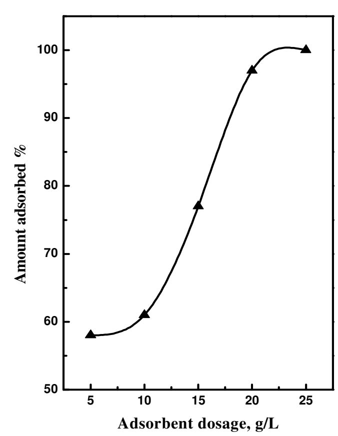

Fig 1. Effect of amount of adsorbent on Cr(VI) (contact time 45 min, metal concentration 10mg/L, pH 2, speed 150rpm, temp 25ºC, particle size 75μm).

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 41to 85% with the chromium concentration of 10mg/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. The initial concentration of metal ions of 10mg/L was taken using 1gm of adsorbent at 25ºC.

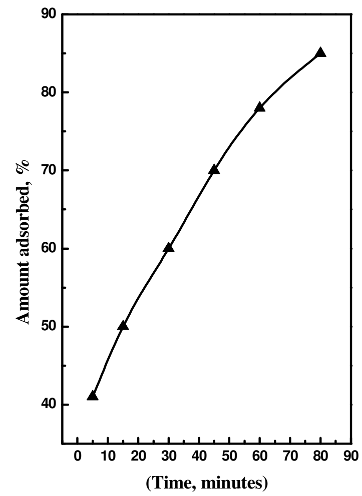

Fig 2. Effect of contact time on Cr(VI) (pH 2.5, metal concentration 10mg/L, dolochar 1gm, temp 25ºC, speed 150rpm, particle size 75μm).

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 91 to 60% at adsorbent doses 20g/L with the increase in the initial feed concentration from 2 to 15 mg/L at constant temperature 25 ºC and pH 2.5.

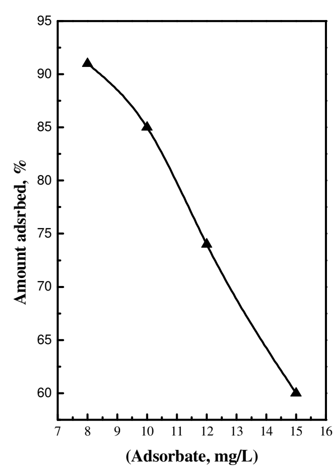

Fig 3. Effect of concentration on Cr(VI) (pH 2.5, dolochar 1gm, temp 25ºC, time 45 min, speed 150rpm, particle size 75μm).

Effect of particle size

The influence of particle size was studied on 10mg/L concentration of chromium (VI) at constant temperature 25ºC and pH2.3. In 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 90 to 60% at 10 mg/l initial feed concentration 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.

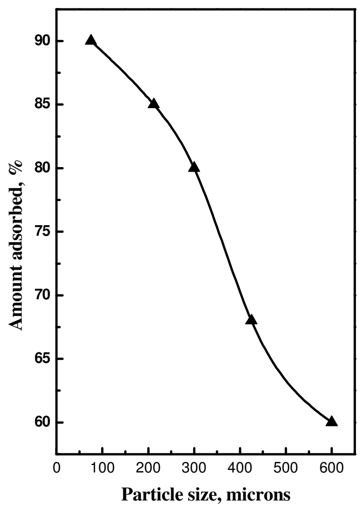

Fig 4. Effect of particle size on sorption of Cr(VI) (pH 2.5, initial concentration 10mg/L, temp 25ºC, time 45 min, speed 150rpm, adsorbate 1gm).

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 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 30 to 94% as the pH decreases from 9.0 to 1.5. It is important that the maximum adsorption was found at pH 1.5. This behaviour can be explained considering the nature of the adsorbent at different pH in metal adsorption. The pH dependence of metal adsorption can largely be related to the type and ionic state of the functional groups and also on the metal chemistry in solution. Adsorption of chromium (VI) below pH 2.5 suggests that the negatively charged species (chromate/dichromate in the sample solution) bind through electrostatic attraction to positively charged functional groups on the surface of activated carbon because at this pH more functional groups carrying positive charge would be exposed. But at above pH 2.5, it seems that activated carbon possesses more functional groups carrying a net negative charge, which tends to repulse the anions. However, there is also the removal above pH 2.5, as indicated by Fig.5, but the rate of removal is considerably reduced. Hence, it could be said that above pH 2.5, other mechanism like physical adsorption on the surface of adsorbent could have taken an important role in the adsorption of chromium (VI) and exchange mechanism might have reduced. In addition adjustment of pH is very important. The possibilities of other subsidiary substances and hydrogen bonding may affect the adsorption process and need careful analysis.

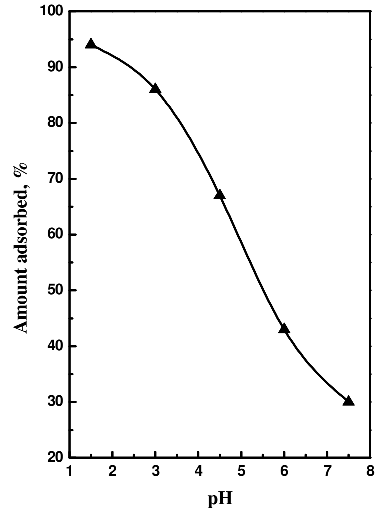

Fig 5. Effect of pH on removal of Cr(VI) (adsorbate 1gm, initial concentration 10mg/L, temp 25ºC, time 45 min, speed 150rpm, particle size 75μm).

CONCLUSIONS

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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