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Removal of Hexavalent Chromium from Aqueous Solutions using Sawdust as a low Cost Adsorbent

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A B S T R A C T

In the present study, adsorbent is prepared from *Delbergia sissoo*, and used for Cr (VI) removal from aqueous solutions. Adsorbent is activated with the use of concentrated sulphuric acid. The adsorption of chromium (VI) from aqueous solutions by activated sawdust was studied under a batch and column mode and was demonstrated that the adsorbent prepared from sawdust has a significant capacity for adsorption of Cr (VI) from aqueous solution. The influence of pH, contact time, adsorbent dose and initial concentration of Cr (VI) on the chromium removal was investigated under the batch studies. Adsorption of Cr (VI) is highly pH-dependent and the results indicate that the optimum pH for the removal is 2. In column studies maximum removal was found at bed height 10 cm and flow rate of 1 ml/min. The capacity of chromium adsorption at equilibrium by these natural wastes increased with absorbent concentration. The suitability of adsorbents was tested with Langmuir and Freundlich isotherms and their constants were evaluated.

Introduction:

Environmental contamination by toxic metals is of great concern because of health risks on humans and animals. In recent years, there has been a growing concern with environmental protection. Removal of trace amounts of heavy metal ions from wastewater and drinking water is of great importance due to their high toxicity [1]. Among the toxic metal ions, chromium is one of the common contaminant which gains importance due to its high toxic nature even at very low concentrations [2, 3]. Although both trivalent and hexavalent forms of chromium exist in industrial wastewater, the toxicity caused by hexavalent chromium tends to be much higher than that by trivalent and; therefore, priority is given to the regulation of this pollutant at the point of discharge [4]. Chromium (VI) is a cancer-causing agent and can pose health risks such as liver damage, dermatitis and gastrointestinal ulcers. Wastewaters such as those generated during dyes and pigments production, film and photography, galvanometer, metal – cleaning, plating and electroplating, leather and mining may contain undesirable amounts of chromium (VI) anions [5,6,7]. It is necessary for risk assessment not only to determine the total chromium in different environments, but also to determine chromium in its different oxidation states [8, 9, and 10]. The commonly used procedures for removing metal ions from effluents include chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction [11, 12]. These techniques apart from being economically expensive have disadvantages like incomplete metal removal, high reagent and energy requirements, and generation of toxic sludge or other waste products that require disposal. Efficient and environment friendly methods are thus needed to be developed to reduce heavy metal content. Therefore, there is a need to produce low cost adsorbent for Cr (VI) removal from cheaper and readily available materials which can be used economically on large scale.

To solve these problems, in recent years, investigations have been carried out for the effective removal of large quantities of Cr (VI) from wastewaters using low cost, non-conventional adsorbents, including C*asurina* leaves [13], leaf mould [14], moss pea [15], green algae [16], and coconut waste [17] which are economically viable. Sawdust is a waste byproduct of the timber industry, which is either used as cooking fuel or a packing material, but can also be economically used for the removal of heavy metals in wastewaters.

In the present work, the Cr (VI) adsorption capacity of sawdust derived from *Delbergia sissoo* (Sheesham) was studied. Batch experiments and column experiments have been carried out for the removal of Cr (VI) from aqueous solution. The effect of various parameters such as pH, contact time, adsorbent dose and initial concentration under the batch mode and flow rate and bed height under the column mode were studied. Adsorption isotherms studies were also investigated with Langmuir and Freundlich isotherms and their constants were evaluated in order to understand the adsorption mechanism and efficiencies of activated sawdust.

Materials and Methods:

Adsorbent preparation:

The sawdust of *Delbergia sissoo* (Sheesham) used in this experiment was collected from a local sawmill. The sawdust was sieved and soaked overnight in distilled water and dried in sunlight until almost all the moisture evaporated. Sawdust was activated by treating one part of sawdust with 1.5 parts by weight of concentrated sulphuric acid and keeping it an air oven at 150 °C for 24 h. The treated sawdust are washed with distilled water to remove free acid and dried at 100 °C for 5 h then impregnation of sawdust with alum was done by digesting 250 g of sawdust carbon with 1 L of 2% sodium bicarbonate solution for some time followed by washing with distilled water till free from bicarbonate. Then the material was soaked in 2% aluminium sulphate solution for some time and washed until free from Al (III) ions. Finally, the adsorbent is dried at 100°C for 6 h.

Preparation of Chromium solution:

The stock solution of chromium (VI) (1000 mg/l) was prepared by dissolving 2.829 g of potassium dichromate ($K_2Cr_2O_7$) in 1000 ml of distilled water. Experimental solutions of the desired concentrations were obtained by successive dilutions and pH of the solution was adjusted using 0.1N HCl or NaOH. Fresh dilutions were used for each study.

Adsorption experiments:

The adsorption characteristics of Cr (VI) on activated sawdust were evaluated as a function of pH (2-8), adsorbent dosage (0.2g - 1.6g/100ml), contact time (15-120 min), initial concentration of Cr (VI) (10-100 mg/L), and stirring rate (120 rpm) in 250 ml borosil conical flasks on mechanical-cum-rotatory shaker.

The column experiments were conducted for removal of Cr (VI) by varying different parameters like flow rate(1ml/min , 2ml/min and 5 ml/min.), bed height (5 cm , 7 cm and 10 cm) with column diameter 2.5 cm. The pH was kept constant (2.0) in all experiments during optimization of flow rate and bed height. The adsorbent was separated through wattman No.2 filter paper.

The concentration of free Cr (VI) ions in the effluent is determined through spectrophotometer by developing a purple-violet colour with 1, 5 - diphenylcarbazide in acidic solution as a complexing agent [18]. The absorbance of the purple-violet colored solution is read at 540 nm after 20 min. The amount of chromium adsorbed by the activated Sawdust is calculated using the following equation: $q = (C0 - Ce) V/W$ where, q amount of Cr (VI) adsorbed by the adsorbent (mg/g), C0 initial concentration of Cr (VI) (mg/ml), Ce concentration of chromium at equilibrium (mg/ml), V initial volume of chromium solution (ml), W weight of the adsorbent (g).

Results and Discussion:

Effect of pH

Earlier studies on heavy metal adsorption have shown that solution pH is the single most important parameter affecting the adsorption process [19]. In order to establish the effect of pH on the adsorption of chromium (VI) ions, batch sorption studies at different pH values were conducted in the range of 2.0 to 8.0. Fig.1. reveals that adsorption capacity of Cr (VI) ions is maximum at pH 2.0 and significantly decreases with increase in pH values upto 8.0.

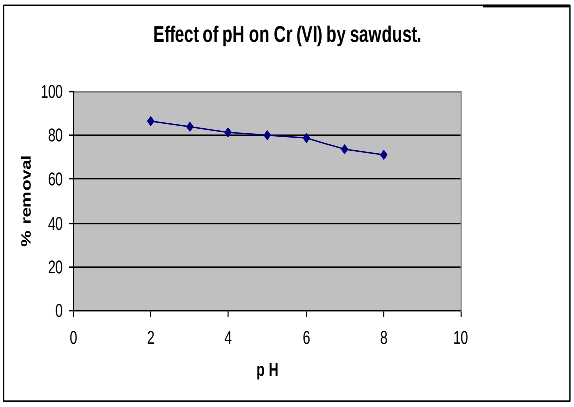

Fig: 1. Effect of pH on the removal of Cr (V1) by activated sawdust: initial Cr (V1) concentration=20mg/L, adsorbent dose= 1g/100mL, contact time=120 min., stirring rate=120 rpm

At pH 2 and 8 corresponding uptake yield values were found to be 1.71and 1.42, respectively. At lower pH, the biosorbent is positively charged due to prolongation and dichromate ion exists as anion leading to an electrostatic attraction between them [20]. Thus the uptake of chromium (VI) increased markedly with decreasing pH. A sharp decrease in adsorption above pH 4 may be due to occupation of the adsorption sites by anionic species like $HCrO^-_4$; $Cr_2O_7^{2-}$; CrO^{2-}_4; etc. which retards the approach of such ions further towards the sorbent surface [21, 22]. [23] has reported that the decrease in adsorption at high pH values may be due to the competitiveness of the oxidation of chromium and OH^- ions in the bulk. These results suggest that pH affects the solubility of metals and the ionization state of the functional groups like carboxylate, phosphate and amino groups of the cell walls of the biosorbent.

Effect of adsorbent dose:

The effect of adsorbent dosage on the adsorption of Cr (VI) process is shown in Fig.2. Removal of Cr (VI) increases with an increase in the adsorbent dosage. The percentage removal increases from 57.7% to 82.3% by increasing the adsorbent dosage from 0.2gm to 1.6 gm/100ml. However, the adsorption capacity showed a decreasing trend with increasing adsorbent dosage. If the adsorbent amount is increased by keeping the Cr (VI) concentration constant, the amount of Cr (VI) adsorbed per unit mass showed a decrease due to availability of less number of Cr (VI) ions per unit mass of the adsorbent. The adsorption capacity dropped from 1.64 to 1.19 mg/g by increasing the adsorbent dosage from 0.2 to 1.6 gm/100ml. The drop in adsorption capacity is basically due to the sites remaining unsaturated during the adsorption process. For the 1 gm/l00ml of adsorbent dosage, the optimum values of Cr (VI) removal and adsorption capacity are found to be 74.4 and 1.58 mg/g, respectively.

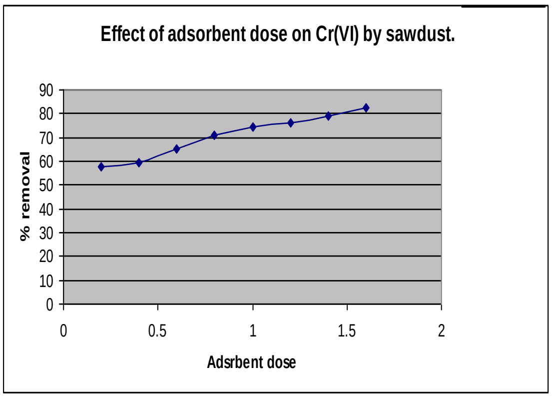

Fig: 2. Effect of adsorbent dose on the removal of Cr (V1) by activated sawdust: pH=2, initial Cr (V1) concentration=20mg/L, contact time=120min., stirring rate=120 rpm

Effect of contact time:

It is evident that time has a significant influence on the adsorption of Cr (VI). It is apparent from Fig.3 that till 90 min., the percentage removal of Cr (VI) from synthetic solution increases rapidly and reaches up to 77%. After that, the percentage removal of Cr (VI) increases slowly and reaches up to 84%. A further increase in contact time has a negligible effect on the percentage removal. Therefore, the contact time of 90 min. could be considered for adsorption of Cr (VI) on sawdust.

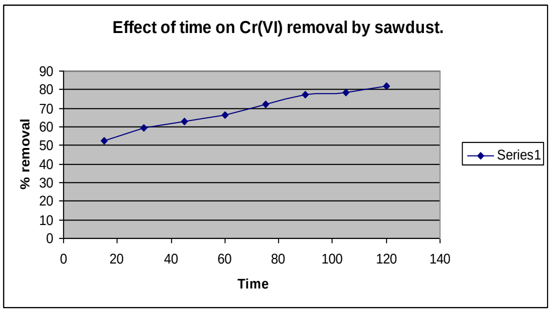

Fig: 3. Effect of time on the removal of Cr (V1) by activated sawdust: pH=2, initial Cr (V1) concentration=20mg/L, adsorbent dose= 1g/100mL., stirring rate=120 rpm

Effect of initial concentration:

Cr (VI) adsorption is significantly influenced by the initial concentration of Cr (VI) in aqueous solutions. In the present study, the initial Cr (VI) concentration is varied from 10 to 100ppm, while maintaining the adsorbent dosage at 1 g/100ml. Fig.4 showed the effect of initial concentration on percentage removal of Cr (VI) and adsorption capacity of activated sawdust. The percentage removal decreases from 86.1% to 60.4% and adsorption capacity increases from 0.88 to 6.05 mg/g when Cr (VI) concentration increases from 10 to 100 mg/l with the same contact time. The percentage removal of Cr (VI) decreases with an increase in initial Cr (VI) concentration. It may be due to an increase in the number of Cr (VI) ions for the fixed amount of adsorbent. The amount of Cr (VI) adsorbed per unit mass of activated sawdust increases with increase in Cr (VI) concentration, may be due to the complete utilization of adsorption surface and active sites available which is not possible in lower concentration.

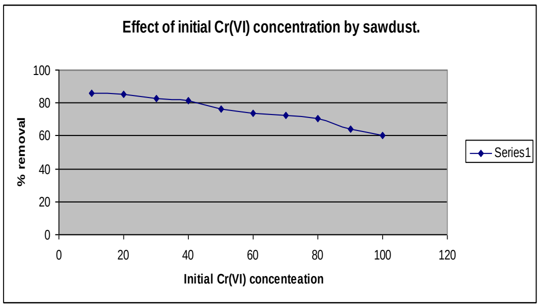

Fig: 4. Effect of initial Cr (V1) concentration on the removal of Cr (V1) by activated sawdust: pH=2, adsorbent dose= 1g/100mL., contact time=90 min., stirring rate=120 rpm

Column experiments:

Effect of Flow rate:

The column experiments were conducted to study the effect of flow rate on Cr (VI) removal by sawdust by varying flow rate i.e. 1ml/min, 2ml/min and 5 ml/min. at optimized bed height of 7 cm, while the column diameter 2.5 cm and initial Cr concentration 20 mg/L were kept constant. The Cr (VI) concentration was observed to be 2.78 mg/L after 1 hr and 7.98 mg/L after 6 hrs at 1 ml/min flow rate (Fig.5), 3.92 mg/L after 1 hr and 9.94 mg/L after 6 hrs at 2 ml/min flow rate (Fig.6) and 5.56 mg/L after 1 hr and 9.98 mg/L after 6 hrs at 5 ml/min flow rate (Fig.7), The Cr (VI) adsorption capacity of the adsorbent was found to be maximum at flow rate of 1ml/min. This was selected as the optimum flow rate for further studies. The probable reason behind the decreasing rate of adsorption and hence decreasing percentage removal with increasing flow rate is the decreasing contact time for the adsorbent and adsorbate as the flow rate increases.

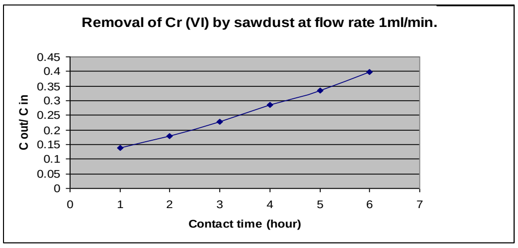

Fig: 5. Effect of flow rate (1ml/min.) on the removal of Cr (V1) by activated sawdust: (Flow rate – 1ml/min; column bed height– 7 cm; column diameter – 2.5 cm; Cr concentration–20 mg/L and pH- 2.0)

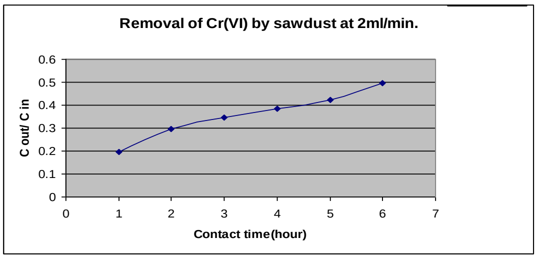

Fig: 6. Effect of flow rate (2ml/min.) on the removal of Cr (V1) by activated sawdust: (Flow rate – 2ml/min; column bed height– 7 cm; column diameter – 2.5 cm; Cr concentration–20 mg/L and pH- 2.0)

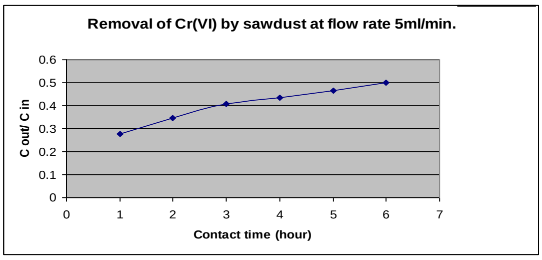

Fig: 7. Effect of flow rate (5ml/min.) on the removal of Cr (V1) by activated sawdust: (Flow rate 5ml/min; column bed height– 7 cm; column diameter – 2.5 cm; Cr concentration–20 mg/L and pH- 2.0)

Effect of Bed Height:

The experiments were conducted to study the effect of bed height at initial concentration of 20 mg/L, pH 2.0 for Cr (VI) and constant flow rate 1 ml/min. Three bed heights i.e. 5 cm, 7 cm and 10 cm were selected with column diameter 2.5 cm. As evident from the results, the residual Cr (VI) ions concentration was found to be 3.62 mg/L after 1 hr and 7.78 mg/L after 6 hrs 2.68 mg/L after 1 hr and 6.32 mg/L after 6 hrs and 2.48 mg/L after 1 hr and 5.12 mg/L after 6 hrs from column of (5, 7 and 10cm bed height). The Cr (VI) adsorption capacity of the adsorbent was also increased with increase in bed height and was found to be maximum at 10 cm, which was selected as the optimized bed height for further experiments. From the results it was observed that with increase in bed height, the percentage removal of Cr (VI) increased. This was due to increase in available surface area for adsorption. The percentage removal of Cr (VI) increased with increase in bed height due to availability of binding sites in the column.

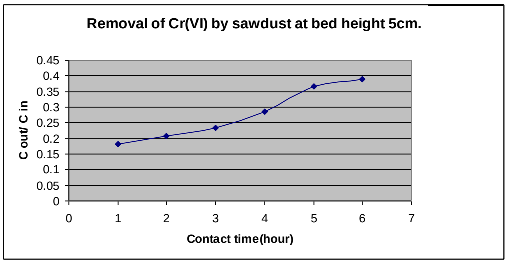

Fig: 8. Effect of column bed height (5cm) on the removal of Cr (V1) by activated sawdust: (Flow rate 1ml/min; column bed height– 5 cm; column diameter – 2.5 cm; Cr concentration–20 mg/L and pH- 2.0)

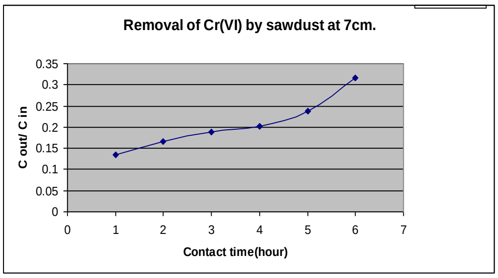

Fig: 9. Effect of column bed height (7cm) on the removal of Cr (V1) by activated sawdust: (Flow rate 1ml/min; column bed height– 7cm; column diameter – 2.5 cm; Cr concentration–20 mg/L and pH- 2.0)

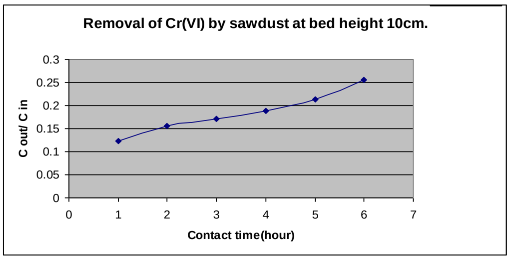

Fig: 10. Effect of column bed height (10cm) on the removal of Cr (V1) by activated sawdust: (Flow rate 1ml/min; column bed height– 10cm; column diameter – 2.5 cm; Cr concentration–20 mg/L and pH- 2.0)

Scanning electron microscope

SEM of raw sawdust, activated sawdust and treated sawdust was carried out with Scanning Electron

Microscope JSM-6100, at Punjab University, Chandigarh.

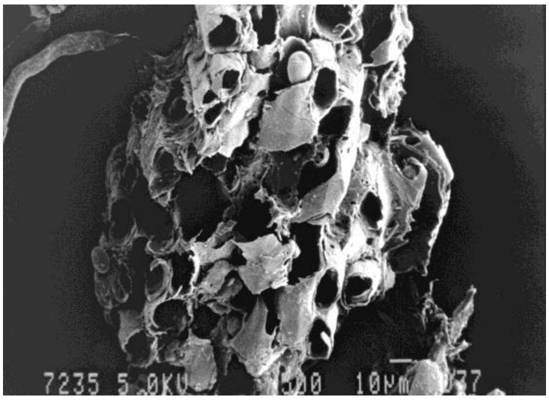

Fig: 11(a). SEM image of raw sawdust of *Delbergia sisso*

Fig: 11(b). SEM image of activated sawdust

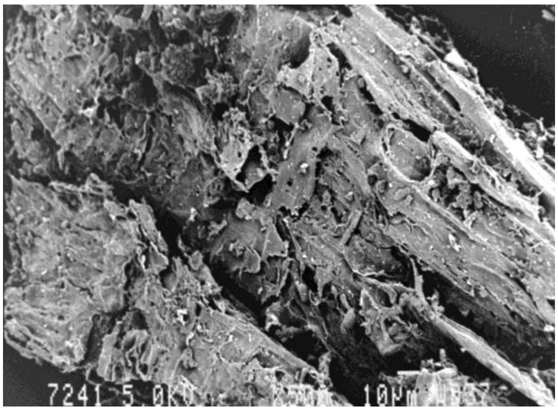

Fig: 11(c). SEM image of treated sawdust with chromium

X-ray Diffraction Analysis:

XRD pattern of the adsorbents (sawdust activated sawdust and treated sawdust) shows significant changes. Different peaks indicate the presence of different type of elements and sharp peaks shows the crystalline nature of elements. XRD data gives evidences of decrease in the peak intensity of treated sawdust which shows that adsorption of Cr (VI) on the surface of the adsorbent. Fig. 12-A, 12-B.and 12-C.shows XRD of sawdust, activated sawdust and treated sawdust and Fig. 12-B. and 12-C.indicate the decrease in the peak intensity.

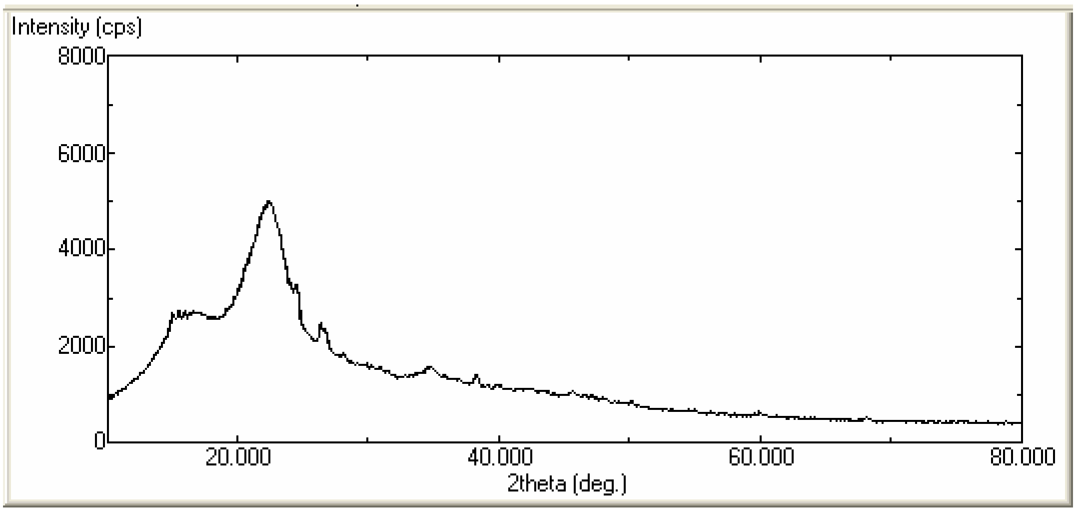

Fig: 12.A. X-ray Diffraction of Sawdust.

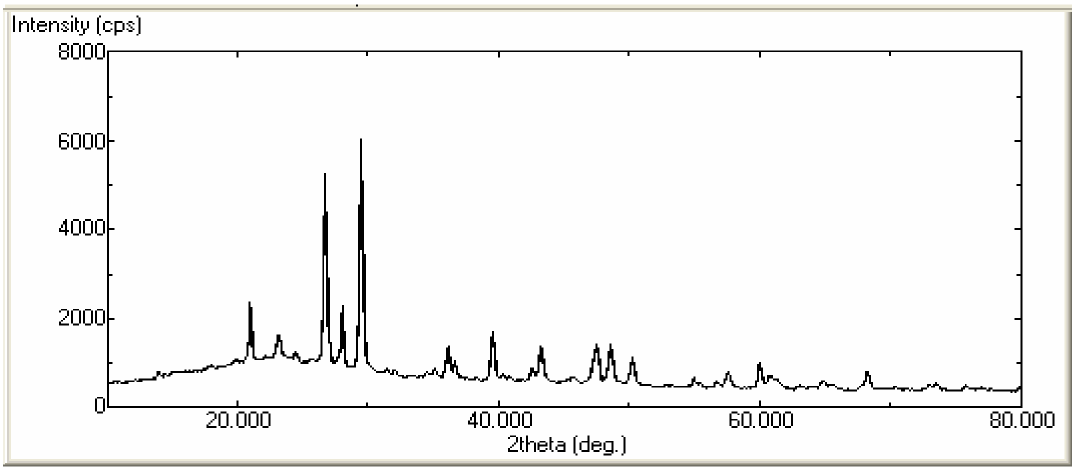

Fig: 12. B. X-ray Diffraction of Activated sawdust.

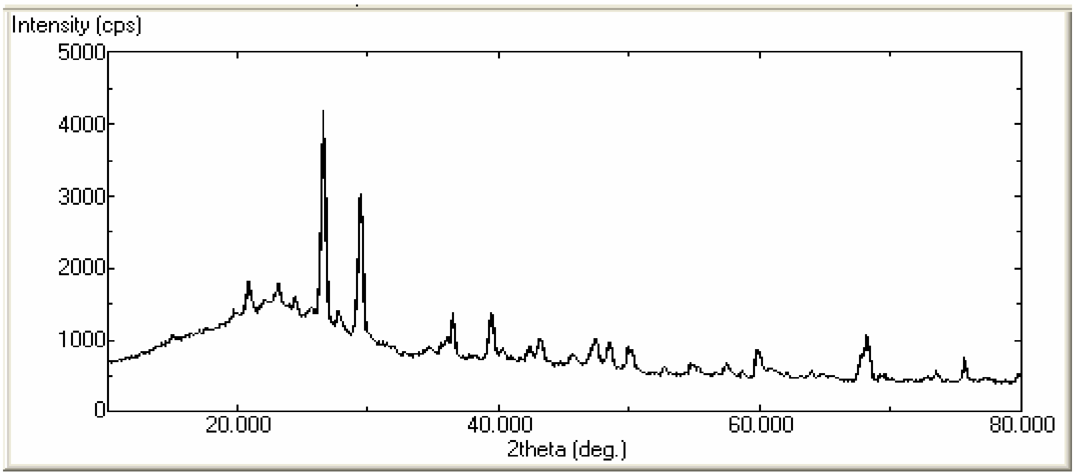

Fig: 12. C. X-ray Diffraction of Treated sawdust.

Adsorption Isotherm:

The adsorption isotherm studies were conducted on data obtained by varying the initial metal concentration of Cr (VI) solutions from 10 to 100 mg/L. After equilibration, the samples were separated and analyzed for their residual Cr (VI) concentrations. The equilibrium adsorption capacity was calculated using the following equation

$$q_e = (C0\text{-}Ce).V/M$$

Where as qe (mg/g) is the equilibrium adsorption capacity C0 and Cethe initial and equilibrium concentrations (mg/L) of Cr (VI), respectively. V (L) is the volume of solution and M (g) the weight of the adsorbent.

For modeling of the equilibrium data, both the Langmuir and Freundlich isotherms were applied. Cr (VI) adsorption by sawdust was evaluated using the Langmuir and Frendulich isotherm. In view of higher value of correlation coefficients R^2> 0.90 indicated that the adsorption data of Cr (VI) for adsorbent is fitted well in both Langmuir and Freundlich isotherm models. A plot between Ce and C_e/q_e yields a linearized form of Langmuir isotherm. (Fig.13). The value of the correlation coefficient (R^2 = 0.9927) indicated good agreement between the experimental equilibrium data and the Langmuir isotherm.

A plot between Log q_e and Log C_e yields a linearized form of Freundlich isotherm. (Fig.14). The value of the correlation coefficient (R^2 = 0.9565) was found in case of Freundlich isotherm. From the result, it was concluded that Cr (VI)) adsorption by sawdust followed Langmuir and Freundlich isotherm.

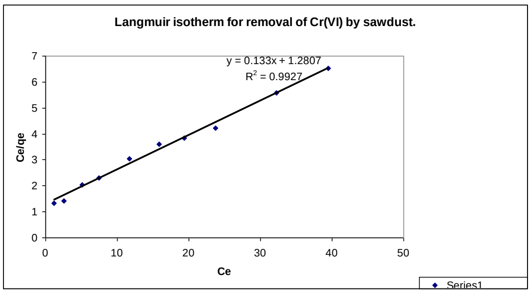

Fig: 13. Langmuir isotherm for removal of Cr (VI) by sawdust

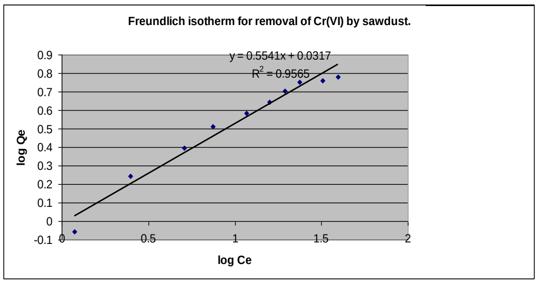

Fig: 14. Freundlich isotherm for removal of Cr (VI) by sawdust

Conclusion:

Based on the present study, the following conclusion can be drawn:

The results showed that the removal of hexavalent chromium from aqueous solutions by activated sawdust was effective for solution at lower pH and increased with increasing adsorbent dosage and contact time. In column process removal was high at greater bed height, column diameter and lesser flow rate. The adsorption pattern concluded that Cr (VI) adsorption by activated sawdust followed Langmuir and Freundlich isotherm. Finally, the results showed that the activated sawdust can be used as a low cost adsorbent for the treatment of aqueous solutions containing hexavalent chromium.

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