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Cadmium Removal from Aqueous Solutions by adsorption on Sawdust

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Abstract : The presence of highly toxic Cadmium in effluent streams is a major environmental issue. Electroplating, mining and metallurgical operations and refineries are the major source of Cd present in wastewater streams. The present work deals with the determination of Cd removal capacity using sawdust which is a low cost adsorbent. The studies on adsorption of Cadmium were conducted by varying various parameters such as contact time, amount of adsorbent, and pH. Batch experiments and column studies were conducted to find out the adsorption capacity of sawdust. By batch adsorption studies, it has been found that the percentage of adsorption increased with contact time up to a specific time and increased with the adsorbent dosage reaching almost a constant value at a particular dosage. The percentage removal also increased with pH up to pH of 6-7 and then decreased. It has been found that the amount of adsorbate per unit weight of adsorbent increased with increasing contact time at all initial concentrations and equilibrium was attained within 3 hours for cadmium sawdust system. The equilibrium adsorption results were analyzed by Langmuir and Freundlich models to determine the mechanistic parameters associated with the adsorption process. The results showed that sawdust shows potential to be applied in waste water technology for heavy metal remediation.

Keywords: Adsorption, heavy metals, cadmium, adsorbent.

INTRODUCTION

Heavy metals are very toxic in nature and harmful to the environment. Toxic metal compounds coming to the earth's surface not only reach the earth's waters (seas, lakes, ponds and reservoirs) but can also contaminate ground water in trace amounts by leaching from the soil [Arivoli et al.,2008]. Cadmium enters the environment from mining and metallurgical operations, electroplating industries, zinc smelters, sewage sludge etc. [Hutchinson & Meema, 1987]. Cadmium is a serious cause of environmental degradation. Therefore, it is necessary to alleviate this metal ion from industrial effluents [Saikaew et al., 2009]. At present, there exist a number of different technologies for treating heavy metals-bearing waste streams. These include chemical precipitation, filtration, ion exchange, adsorption using activated carbon and membrane processes. Chemical precipitation processes have several disadvantages, which include incomplete metal removal and sludge generation. Other technologies are generally expensive when metals are present in the wastewater at low concentration. Among these processes, the adsorption with the selection of a suitable adsorbent can be an effective technique for the removal of heavy metal ions from waste waters [Sen, 2009]. The main advantage of adsorption process are low operating cost, easily available sources, minimization of volume of sludge to be disposed off, regeneration of metals from the adsorbents. A number of natural and synthetic adsorbents like agricultural wastes, clay [Saha et al, 2010], neem leaves, cooked tea dust [Dhanakumar et al, 2007], zeolites [Erdem et al., 2004], fly ash [Alinnor 2007] etc have been studied by various researchers for the removal of heavy metals. Commercial adsorbents are very costly which make the adsorption process costly which led to the search for any natural or waste material which can be used as an adsorbent. Sawdust is an inexpensive, easily available waste material from timber industry which can be disposed of without expensive regeneration. The objective of this study was to find out the potential of Sawdust as an adsorbent for the removal of Cadmium from wastewater.

MATERIALS AND METHODS

Preparation of Adsorbent

The sawdust of teak was collected from a sawmill and dried and all impurities present were removed. The sawdust was sieved to 150-250 micron size. Sawdust contained water soluble compounds like tannin, which gave brown color to the effluents during the treatment.

Preparation of Cadmium Solution

All chemicals used were of analytical grade. Stock standard solution of Cadmium was prepared by using reagent grade cadmium nitrate. ($Cd(NO_3)_2 4H_2O$). A stock solution of 1000 ppm was prepared by dissolving the required amount of Cadmium nitrate in distilled water in a one liter volumetric flask. By diluting this stock solution, different concentrations of experimental solutions were prepared. The pH of the system was adjusted using NaOH and HNO_3.

Adsorption

Adsorption is a process in which certain adsorbates are selectively transferred from the fluid phase to the surface of insoluble, rigid particles suspended in a vessel or packed in a column. It is actually the accumulation of atoms or molecules on the surface of a material. This process creates a film of the adsorbate (the molecules or atoms being accumulated) on the adsorbent's surface. Adsorption is present in many natural, physical, biological, and chemical systems, and is widely used in industrial applications. Similar to surface tension, adsorption is a consequence of surface energy.

Instrumentation

Cadmium in solution was estimated using "ORION 960 Autochemistry system". ORION 960 Autochemistry system offers a wide range of analytical techniques. It consists of ORION 960 module and an EA 940 pH/ISE meter which is placed on top of module base. Module consists of a microprocessor, which controls the systems, an auto dispenser and an electrode tower. EA 940 provides the display and key for entry of information. When the cadmium electrode is in contact with a cadmium solution, an electrode potential develops across the sensing element and is measured against a constant reference potential.

Batch Experiments

The apparatus used for batch adsorption studies was Jar Test Apparatus. By diluting the stock solution, experimental solution was prepared having same initial concentrations. One liter each of this solution was taken in 6 different jars and different quantities of sawdust varying from 1g/l to 40 g/l was added in the different jars. Paddles were allowed to rotate at 60 rpm continuously for six hours. Samples of solutions were taken after 5 minutes, 30 minutes, 1 hour, 2 hour, 3 hour, 4 hour, 5 hour and 6 hours. Final concentrations of cadmium were measured in ORION 960 Autochemistry system after filtration. The percentage removal of Cadmium at various time intervals and for varying adsorbent dosages were determined. The experiment was repeated with cadmium solutions of varying initial concentrations.

For pH studies, pH was adjusted to vary between 2 and 8 in different jars for various initial concentrations. NaOH was added for making the solution alkaline and nitric acid was added to make the solution acidic. Same quantity of sawdust was added in each of the jars and paddles were rotated for 2 hours. Final concentration of cadmium was measured.

Column Experiments

Continuous flow experiments were conducted in a glass column.. A series of experiments were conducted with various concentrations of cadmium solutions. Glass columns were packed with sawdust. Cadmium solution having a particular initial concentration was taken in an overhead tank having a float apparatus. Solution was allowed to pass through the glass column containing sawdust. Discharge through the column was collected and concentrations were measured. Column experiments were conducted using solutions with different pH. The pH of cadmium solution was varied by adding NaOH and HNO_3.

RESULTS AND DISCUSSIONS

Effect of Contact Time

The effect of contact time on Cd adsorption on sawdust was investigated to study the rate of Cd removal. A plot of percentage removal of Cadmium versus adsorption time for initial concentration of 10 ppm of Cadmium and various adsorbent dosages is shown in Figure 1. It is evident from the figure that the equilibrium time is varying from 2-3 hours for varying quantity of adsorbents. The time of contact was varied from 5 minutes to 6 hour at same initial concentration of 10 ppm of cadmium. It revealed that the rate of uptake was rapid in the early stages but gradually decreased and became constant when equilibrium was reached.

The percentage removal of Cadmium for various contact times using column studies for an initial cadmium concentration of 10ppm is shown in Figure 2. The percentage removal of Cadmium is almost 100% in the beginning and then decreased. . The rate of removal is constant after contact time of about 3 hours. The rate of Cd removal using sawdust is increased rapidly till 2 hours. A further increase in the contact time had a negligible effect on the rate of adsorption of Cd. The nature of adsorbent and available adsorption sites affects the rate of adsorption of Cd. The mechanism of solute transfer to the solid includes diffusion through the fluid film around the adsorbent particle and diffusion through the pores to the internal adsorption sites. In the initial stage of adsorption of Cd, the concentration gradient between the film and the available pore sites is large, and hence the rate of adsorption of Cd is faster. The rate of adsorption decreases in later stage may probably be due to the slow pore diffusion of the solute ion into the bulk of the adsorbent. Similar trend has also been reported by other investigators for different heavy metal adsorptions [Sen & Sarzali., 2008, Gupta & Babu].

Effect of Adsorbent Dosage

Study on the effect of sawdust amount for Cd removal is important to get the trade-off between the adsorbent capacity and percentage removal of Cd resulting in optimum sawdust amount. The influence of sawdust amount, varying from 1-40 mg/l onto the Cd adsorption is shown in Fig. 3 for a constant initial Cd concentration of 10 ppm. The percentage adsorption increased with increase in adsorbent dose. The percentage adsorption increased from 40 at lower adsorbent dose (1 g per liter) to 97.2 at higher adsorbent dose (40 g per liter) for contact time 5 minutes. For 6 hours contact time, the percentage removal of Cd varied from 60.3% for lower adsorbent dosage (1 mg/l) to 97.28 % for higher adsorbent dosage (40 mg/l). However, the adsorption capacity almost remains constant when the adsorbent dosage reaches around 20 g per liter. As weight of adsorbent increases, more surface area becomes available for adsorption of cadmium, and hence more percentage removal. In the initial stages, film transport controls the rate of adsorption when solute from solution, through the stagnant layer of fluid, adheres on the external surface of the adsorbent and the mono molecular is formed as such, at the initial stage, there is a

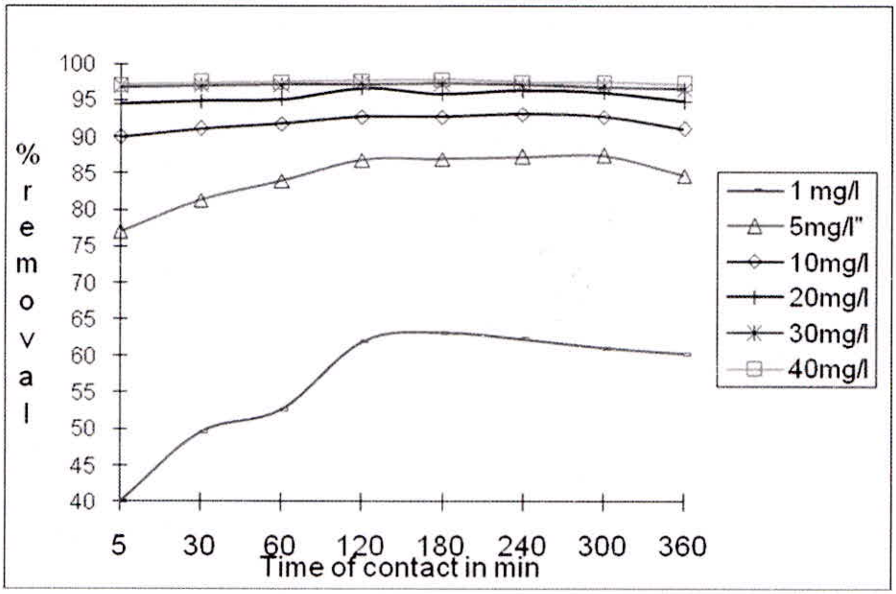

Fig.1. Percentage removal of Cd for various contact time

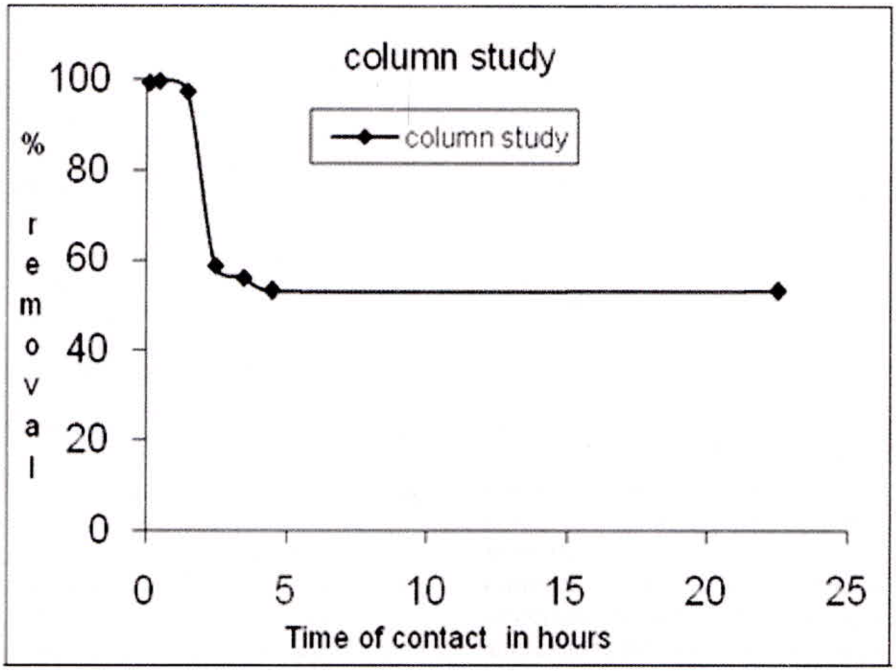

Fig.2. Percentage removal of Cd using Column Studies

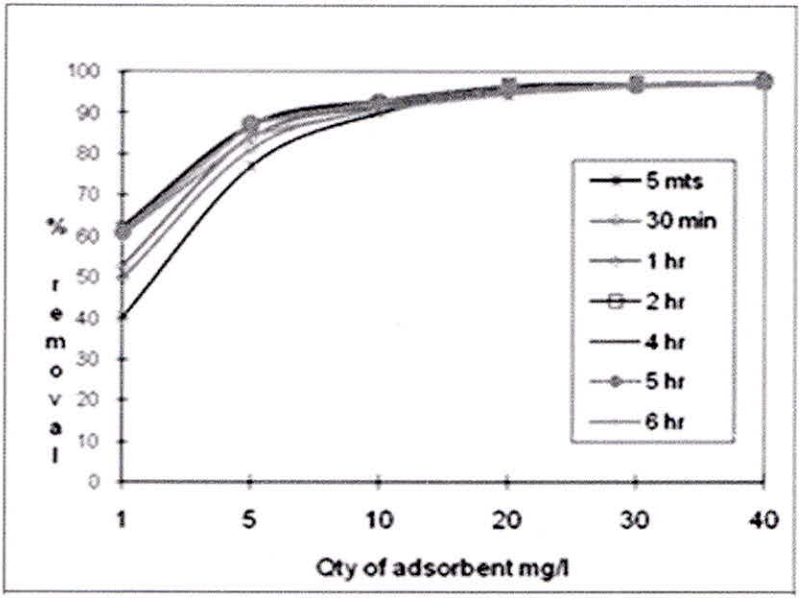

Fig. 3. Percentage removal of cadmium on various adsorbent dosages

greater percent removal. Large solute removal takes place immediately after mixing and agitation of sorbent. In the next instant, internal diffusion process controls the transfer of solute from the external porous surface to the internal sites, and the rate of adsorption decreases. Similar trend was reported on adsorption of various heavy metals during different adsorbents. [Kannan&Veemaraj., 2009, Yu et al, 2001]

Effect of pH

The pH of the solution is an important factor that controls the uptake of Cd. The experimental results revealed that the percentage removal of Cd increased with increase in pH up to pH 6 or 7 and then decreased. Maximum percentage removal occurred at pH 6 or7 for various initial concentrations. The binding of heavy metal ions is ph dependant, probably because tannins in the sawdust act as weak ion exchangers exchanging two hydrogen ions into solution for each divalent metal ion bound to the solid. The electrostatic attraction between the negative surface and the cationic Cd molecule increases with pH and reaches saturation at a pH of 7 [Gupta & Babu 2006]. The effect of pH on percentage removal for various initial concentrations is shown in the Figure 4. Similar trend was reported for the adsorption of Basic Red 29 by a non-conventional activated carbon [Sivakumar &.Palanisamy, 2009].

Effect of Initial Concentration

The effect of cadmium ion concentration was investigated by varying the metal ion concentration from 1mg/l to 20 mg/l. It was observed that the percentage metal ion removal of sawdust increased with increasing initial concentration. For higher initial concentration, more efficient utilization of sorption sites is expected due to a greater driving force by a higher concentration gradient.[Mohammed&. Fawwaz, 2010]

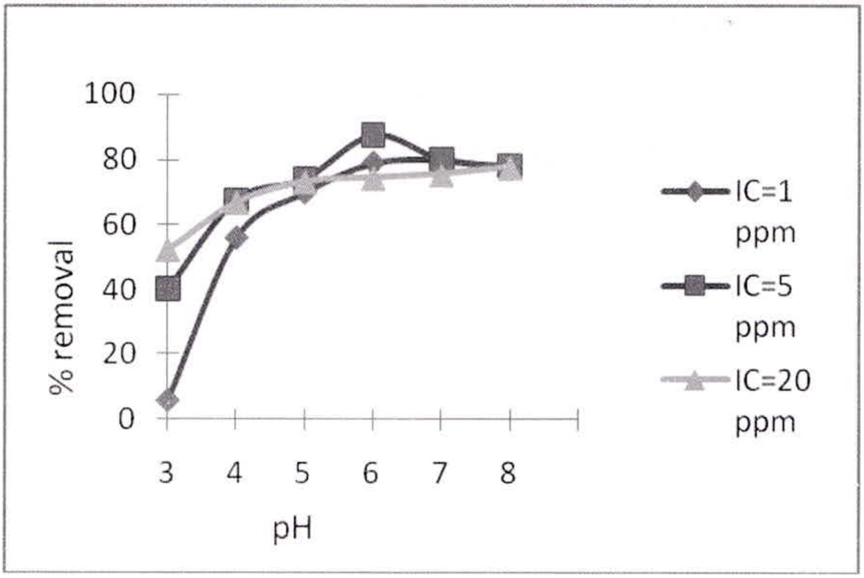

Fig. 4. Percentage removal of Cd for various pH

Langmuir Isotherms

The Langmuir isotherm was applied for adsorption equilibrium represented by the equation

$$(Ce / qe) = (1/Qmb) + (Ce / Qm) \quad (1)$$

where Ce is the equilibrium concentration (mg/l) and qe is the amount adsorbed (mg/g) at equilibrium and Qm and b are Langmuir constants related to adsorption capacity and energy of adsorption respectively. The plots of Ce / qe Vs Ce is shown in Figure 5. It is linear which show that the adsorption follows the Langmuir isotherm model for Cadmium ion adsorption. The Langmuir constant Qm, which is a measure of the monolayer adsorption capacity of sawdust, is obtained 'as 3.03 mg/g. The Langmuir constant b, which denotes adsorption energy, is found to be 0.52 l/mg. The values of Qm and b were calculated from the slope and intercept of the Langmuir plot.

Freundlich Isotherm

The Freundlich equation can be mathematically represented by

$$Qe = K_f Ce^{1/n} \quad (2)$$

where Qe is the amount of cadmium adsorbed at equilibrium time, Ce is the equilibrium concentration (mg/l) and Kf is a constant which is a function of energy of adsorption and temperature and *n is a* constant. The plot of log C_e versus log Q_{e-} is shown in Figure 6 which is showing that the adsorption is following Freudlich isotherm model. The Freundlich constants n and K_{f-} were found to be 1.25 and .316.

SUMMARY AND CONCLUSIONS

The experimental results show that sawdust is an excellent alternative for the removal of Cd from aqueous solutions. Based on the above experimental studies, the following conclusions have been drawn:

(a) The adsorption of Cadmium by Sawdust increased with contact time. The percentage removal of Cadmium increased from 40 % after 5 minutes of contact time to 60.3% after 6 hours for an initial concentration of 10 ppm and adsorbent dosage of 1 g per liter.

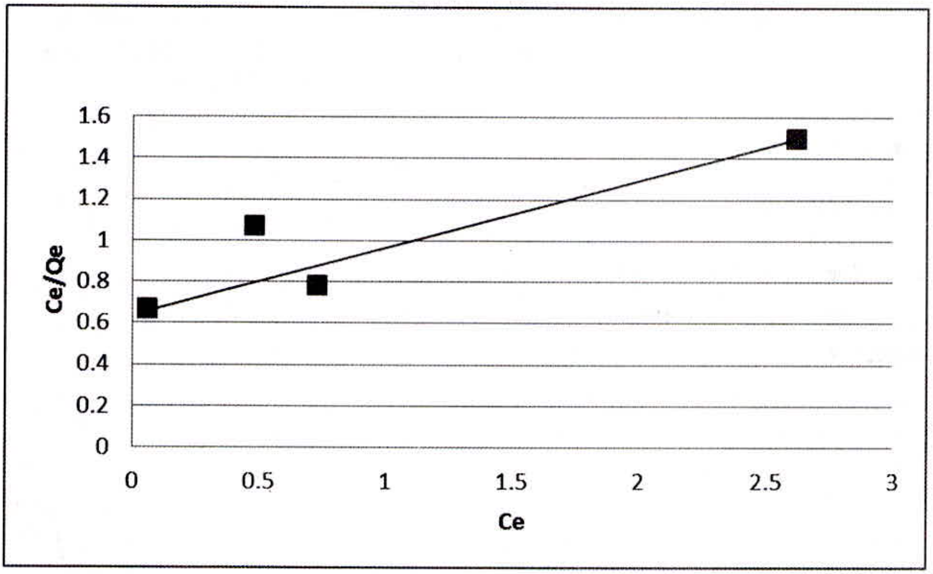

Fig. 5. Langmuir isotherm

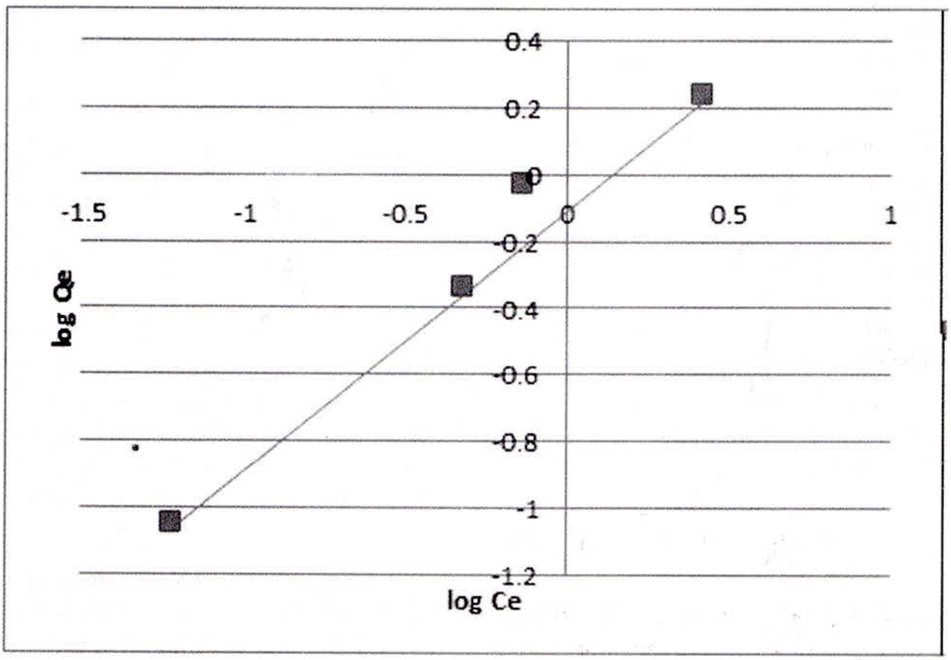

Fig. 6. Freundlich isotherm

(b) The adsorption capacity increased with adsorbent dosage reaching almost a fixed value after a particular dosage. The percentage removal varied from 62% for 1 g per liter of adsorbent to 97.2 % for 40 g per liter of adsorbent for an initial cadmium concentration of 1 ppm. However, the effectiveness for removal is more when the quantity of adsorbent is small.

(c) The adsorption was pH-dependent and the maximum adsorption occurs at pH 6-7.

(d) By conducting column studies, it was found that the adsorption rate was very high initially reaching almost constant values after 2-3 hours.

(d) These experimental studies on low-cost adsorbents would be quite useful in developing an appropriate technology for the removal of Cadmium from contaminated effluents.

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