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Treatment of effluent from fertilizer industry by adsorption on willow sawdust-removal of Ni(II) and Cd(II) from the effluent

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ABSTRACT

Sawdust of willow has been investigated as an adsorbent for the removal of Ni(II), and Cd(II) ions from aqueous solution. Since willow tree is widely grown in almost all parts of Kashmir, it can be a common most easily available, sustainable, low cost adsorbent for the treatment of wastewaters in this part of the world where growing industrialization is affecting water quality like elsewhere in the world. Therefore, it is worthwhile to investigate the potential of sawdust of willow tree as an adsorbent for the removal of Ni(II) and Cd(II) ions from aqueous solution as a first step. Batch experiments were conducted to study the effect of some parameters such as contact time, initial concentration of metal ions, solution pH and temperature. Langmuir and Freundlich models were employed for the mechanistic analysis of experimental data obtained. Results reveal that in our system adsorption follows the Langmuir isotherm. The maximum adsorption capacity of Ni(II) and Cd(II) were found to be 7.98 and 7.11 mg/g respectively at optimum conditions. The pseudo-first-order and pseudo-second-order models were employed for kinetic analysis of adsorption process. The adsorption process follows pseudo-second-order kinetics. The efficacy of the adsorbent in the treatment of effluent from fertilizer factory has been investigated and the results have been found encouraging.

Keywords: water treatment; sawdust; fertilizer; nickel; cadmium

1. INTRODUCTION

Excessive release of toxic heavy metals into aquatic systems due to industrialization can be detrimental to a variety of living organisms. They are important contaminants of liquid wastes discharged from a number of industries such as electroplating, dyes and dye intermediates, textiles, tanneries, oil refineries, electroplating mining, smelters, and so forth [1]. Unlike organic wastes, heavy metals are non-biodegradable and they tend to accumulate in living tissues, causing various diseases and disorders [2]. Cadmium is toxic heavy metal discharged into the environment as industrial waste from metallurgical industries, metalliferous mining, fertilizers, mannures, sewage sludge, land fill leachate and batteries [3]. Long term effects of Cd(II) poisoning include kidney damage and changes to the constitution of the bones, liver and blood. Short term effects include nausea, vomiting, diarrhea and cramps [4]. Nickel is used in stainless steel, electroplating, jewelry, coins, magnetic tapes, welding rods, as a catalyst in hydrogenation of oils and coal gasification, dental procedures, electric storage batteries, and pigments [5]. Nickel enters human body

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through inhalation and ingestion, causing cough, dyspnea, insomnia and carcinoma of lungs, nasal cavities, kidneys, stomach and prostrate [6].

Numerous methods are reported for the removal of heavy metal ions from water sources, including chemical precipitation, reverse osmosis, ion exchange, membrane separation adsorption, membrane filtration and electrochemical technologies [6]. However, most of these methods are either economically prohibitive or too complicated for the treatment of metals [7]. Among these techniques, adsorption offers flexibility in design and operation and, in many cases it generates high-quality treated effluents [8]. The removal of heavy metal pollutants, present in very low concentration, from aqueous solution can be readily accomplished by adsorption.

Adsorbent materials derived from low-cost agricultural wastes can be used for the effective removal and recovery of heavy metal ions from wastewater streams. Several biosorbents such as micro-algae [9], fungi [10], fungal biomass [11-13], walnut shell [14], *Helianthus annuus*stem waste [15], banana skin, green tea waste, oak leaf, peanut shell and rice husk[16], *Ocimumamericanum*L. seed pods[17], chemically modified coir pith [18], groundnut shell [19], activated carbon from tamarind wood activated with zinc chloride [20], olive stone [21], grape waste [22], hazelnut [23], walnut, almond shell [24], pistachio hull waste [25], agriculture wastes, carbons [26], rice husk-based carbon [27], fruit shell of gulmohar [28], coconut husk [29], husk of bengal gram [30], eucalyptus bark [31], agricultural waste biomass [32], pine needles [33], sugar cane bagasse [34], leaf mould[35], waste pomace of olive factory [36] and poplar sawdust [37] etc. have been investigated. The adsorption of heavy metals by these materials might be attributed to their proteins, carbohydrates and phenolic compounds which have carboxyl, hydroxyl, sulphate, phosphate and amino groups that can bind metal ions.

The objective of this study is to investigate the adsorption potential of Willow sawdust for the removal of heavy metal ions from aqueous solution. Willow is widely grown in Kashmir valley and therefore, sawdust of willow can be widely available, sustainable, low cost adsorbent for the treatment of industrial waste waters in the valley. Therefore, it was considered worthwhile to investigate the potential of sawdust of willow tree as an adsorbent for the removal of some toxic metal ions from the effluent of local industry. The effects of various parameters such as pH, contact time, initial metal ion concentration and temperature on adsorption of metal ions on Willow sawdust were investigated. Adsorption isotherms and kinetic studies were also investigated in order to understand the adsorption mechanism and efficiency of willow sawdust. The efficacy of the adsorbent in the treatment of effluent from fertilizer factory has been investigated and encouraging results were obtained.

2. MATERIALS AND METHODS

2.1 Adsorbent

The sawdust of willow tree was collected from a local saw mill and was washed with double-distilled water several times to ensure that all dust particles were removed. The cleaned material was dried in an oven at 100˚C for 24 hrs. The dried material was sieved to 100-300 μm particle size and used as such.

2.2 Chemicals

All the chemicals used in this study were Analytical Grade reagents from E. Merck India Limited and were used as received. The 1000 mg/L stock solutions of Ni(II) and Cd(II) were prepared by dissolving accurately weighed quantity of their respective nitrate salts in double-distilled water. The stock solutions were further diluted with double-distilled water to obtain solutions of various concentrations.

2.3 Adsorption Experiments

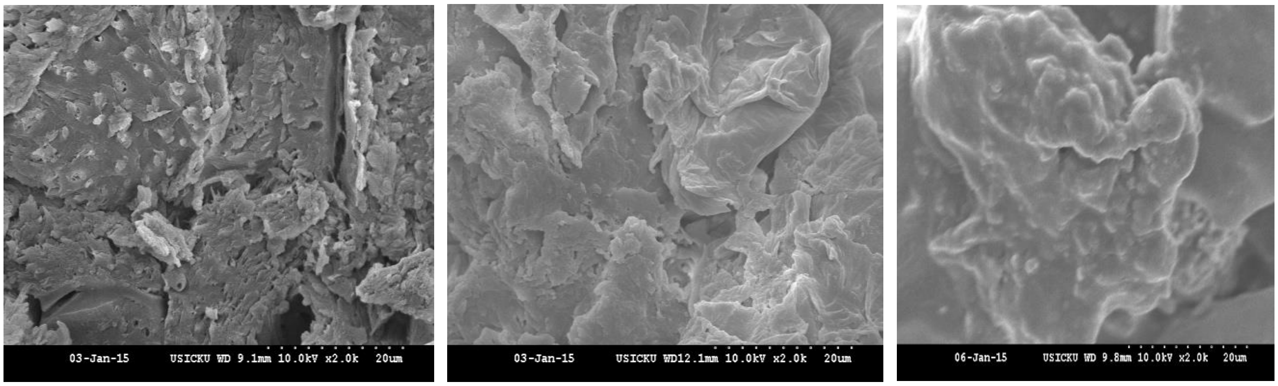
The sorption of Ni(II) and Cd(II) on Willow sawdust was studied by the batch equilibrium technique. The batch equilibrium technique provides the advantage of studying the effect of one experimental factor like pH, temperature, time, concentration, etc. by varying that factor and keeping the rest constant [38]. 1g of sawdust was shaken with 100 mL aliquot of the metal ion solution of a desired concentration on a flask shaker for a given time period. After equilibration for the required time interval, the solution was filtered and the filtrate analyzed for the metal ion concentration. The concentration of the adsorbed metal ion was calculated by subtracting the concentration of the metal ion in the filtrate from the initial metal ion concentration. Metal ion concentration was determined on Atomic Absorption Spectrometer (PerkinElmer Model Analyst-800). The amount of ions adsorbed per unit mass of sawdust (mg/g) was evaluated using the following equation

$$q_e = (C_o - C_e)\,\frac{V}{m} \qquad (1)$$

where q_e is the amount of the metal ion adsorbed at equilibrium (mg/g), C_o is the initial metal ion concentration (mg/L), C_e is the equilibrium metal ion concentration (mg/L), *V* is the volume of the aqueous phase (L), and m is the amount of the sawdust used (g).

2.4 SEM analysis of adsorbent

The surface morphological analysis of Willow sawdust was carried out using Scanning Electron Microscope, Model Hitachi S3000H. SEM images of dried Willow sawdust were taken before and after metal ion adsorption. The SEM images of surface of sawdust before and after adsorption of metal ions, presented in Fig.1, exhibit irregularities with cavities of various sizes. Upon adsorption the surface morphology seems to undergo changes due to interaction of the metal ions with the adsorption sites on the sawdust.



(a) (b) (c)

Fig. 1 SEM images of (a) Willow sawdust (b) Ni(II) loaded Willow sawdust and (c) Cd(II) loaded Willow sawdust

2.5 Effect of Contact Time

The effect of contact time on the efficiency of metal ion adsorption of Willow sawdust was studied by shaking 100mL aliquots of a given metal ion solution (100mg/L) in a number of conical flasks with 1g of sawdust for different time intervals e.g. 10, 20, 30, 40, 50, 60, 70, 80 minutes. After shaking for the given time interval, the solution was filtered and the final metal ion concentration in the filtrate determined.

2.6 Effect of pH

The effect of pH on the amount of metal ion adsorbed was studied over the pH range 2-7. Below pH 2, the adsorption of Ni(II) and Cd(II) is hindered by competing hydrogen ions for the sorption sites, hence not studied. The experiments were not conducted above pH 7 to avoid possible precipitation of the metal ions as their corresponding hydroxide. This is in agreement with the suggestions of many worker [39-42]. However, experiments were carried out upto pH 7 keeping in view the fact that in treating real samples we may be dealing with neutral solutions. In this study, 100mL aliquots of metal ion solution of different pH values were shaken with 1g of sawdust for 80 minutes. The pH of the solutions was adjusted to the desired pH value by 0.1N HNO_3 or 0.1N NaOH solutions. After equilibration the solutions were filtered and analyzed for metal ion concentration.

2.7 Effect of Initial Metal ion Concentration (Adsorption Equilibrium)

The effect of metal ion concentration on the adsorption of metal ion adsorption on Willow sawdust was studied by shaking 1g of sawdust with 100mL aliquots of metal ion solutions of different initial concentrations (20-200mg/L) for 80 minutes. After equilibration for 80 minutes, the solutions were analysed for the final metal ion concentration after filtration.

2.8 Effect of temperature

The effect of temperature on the adsorption of metal ion adsorption on Willow sawdust was studied at three different temperatures of 20°, 30° and 40°C. 1g of sawdust was treated with 100 mL aliquot of 100mg/L metal ion solution. The mixture was heated to the given temperature and shaken in a temperature controlled flask shaker. At a given temperature, the solutions was filtered analyzed for the final metal ion concentration.

3. RESULTS AND DISCUSSION

3.1 Effect of pH

The pH of an aqueous solution is the most important factor that affects the adsorption of metal ions on sawdust because it controls the solubility of the metal ions and availability of adsorption sites on sawdust etc. Fig. 2 depicts the effect of pH on the adsorption of Ni(II) and Cd(II) on Willow sawdust. The results reveal that the adsorption is low at a more acidic pH, increases gradually with increase in pH attaining a maximum at pH 4 and 7 for Cd(II) and Ni(II) respectively. It is now a known fact that the adsorption of the metal ions on the sawdust is because of the functional groups on proteins, carbohydrates, lignin and tannins present in it. At high H^+ concentration (low pH) the polar functional groups like aldehyde, ketone, amine, alcohol, phenol and carboxyl functional groups are protonated and hence rendered unavailable for ion exchange and incapable for complexation with the metal ions. Therefore, at low pH uptake of metal ions is low. At higher pH these polar functional groups are deprotonated and hence are available for complexation with the metal ions, resulting in increase in the metal uptake. The results conform to the ion-exchange and complexation mechanism of the adsorption of the metal ions on the sawdust. At more basic pH, the metal ions start precipitating, which defeats the very purpose of employing adsorption for removal of toxic metal ions and precludes further investigation. **In the adsorption equilibrium experiments, pH of 7 was maintained in all the solutions.**

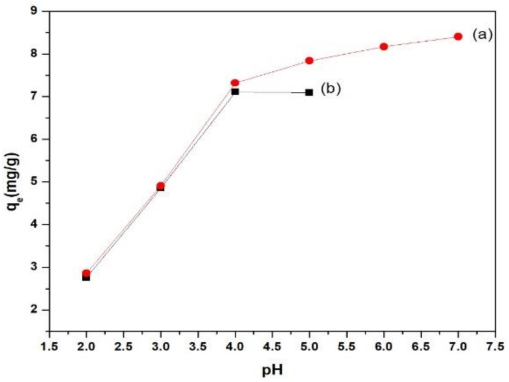


Fig. 2 Effect of pH on the adsorption of (a) Ni(II) and (b) Cd(II) on Willow sawdust

3.2 Effect of Initial Metal ion Concentration (Adsorption Equilibrium)

The effect of initial concentration of Ni(II) and Cd(II) on their adsorption on sawdust of willow from aqueous solution was investigated over a concentration range of 20-200mg/L. The results, presented in Fig.3, show that adsorption starts at a low metal ion concentration and increases with the increase in the metal ion concentration till all the adsorption sites become occupied. At low metal ion concentration available binding

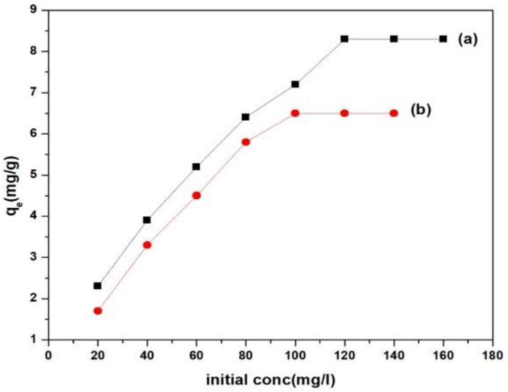


Fig. 3 Effect of initial metal ion concentration on the adsorption of (a) Ni(II) and (b) Cd(II) on Willow sawdust

sites is high; with increasing metal ion concentration the binding sites become exhausted quickly till no further uptake takes place in the given amount of sawdust.

The equilibrium data pertaining to the dependence of the adsorption on the initial metal ion concentration was studied by the Langmuir and the Freundlich isotherms. An adsorption isotherm is characterized by certain constants, which express the surface properties and affinity of the adsorbent and can also be used to compare the adsorption capacities of the adsorbent for different metal ions. The Langmuir isotherm is valid for monolayer adsorption onto a surface with homogeneous adsorption sites. The linear form of Langmuir equation is expressed as [43]:

$$\frac{1}{q_e} = \frac{1}{q_0} + \frac{1}{q_0 K_L}\frac{1}{C_e} \qquad (2)$$

where q_o and K_L are Langmuir constants related to maximum adsorption capacity (metal uptake per unit weight of adsorbent) and free energy of adsorption (which is an indicator of the affinity of the adsorbent for the metal ions), respectively. C_e is the equilibrium concentration of metal ions in the aqueous solution and q_e is the equilibrium adsorption capacity of adsorbent. Figure 4 represents the Langmuir isotherms of the metal ions.

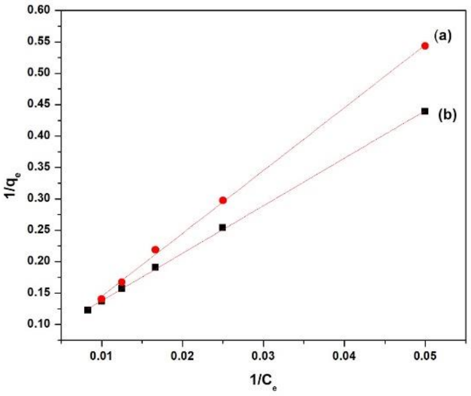


Fig. 4 Langmuir adsorption isotherm for the adsorption of (a) Cd(II) and (b) Ni(II) on Willow sawdust

The Freundlich model is an empirical equation based on adsorption on heterogeneous surface. The linearized form of the Freundlich isotherm is written as [44]:

$$lnq_e = \ln K_F + \frac{1}{n}\ln C_e \qquad (3)$$

where K_F and n are the Freundlich constants indicating adsorption capacity and adsorption intensity, respectively. The Freundlich constants, K_F and 1/n, can be determined from the intercept and slope of linear plot between $\ln q_e$ and $\ln C_e$, respectively (Fig 5).

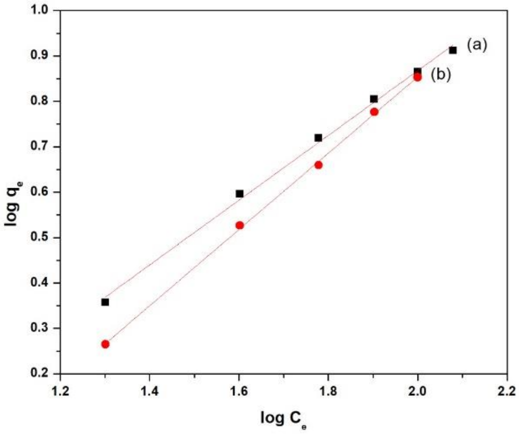


Fig. 5 Freundlich adsorption isotherm for the adsorption of (a) Ni(II) and Cd(II) on Willow sawdust.

The isotherm constants and correlation coefficients are given in Table 1. It is clear from the plots that the adsorption equilibrium data for Ni(II) and Cd(II) fitted well to the Langmuir equations with correlation coefficients above 0.99 in all the cases.

3.3 Effect of Contact Time (Adsorption kinetics)

Fig. 6 depicts the effect of contact time on the adsorption of Ni(II) and Cd(II) on Willow sawdust. The results show that adsorption increases with increase in contact time and reaches equilibrium after 50 minutes in case of both the metal ions Ni(II) and Cd(II). The high adsorption rate of the metal ions in the initial period of the process may be due to a higher number of adsorption sites available on the surface of the adsorbent and the higher concentration gradient between the metal ions in the solution and the metal ions on the surface of the adsorbent. As the surface adsorption sites are exhausted, the uptake rate is limited by the rate at which the metal ions are transported from the surface to the interior sites of the sawdust particles.

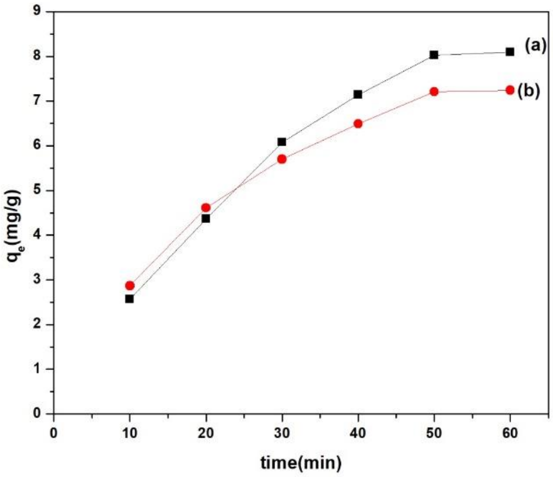


Fig. 6 Effect of time on the adsorption of (a) Ni(II) and (b) Cd(II) on Willow sawdust

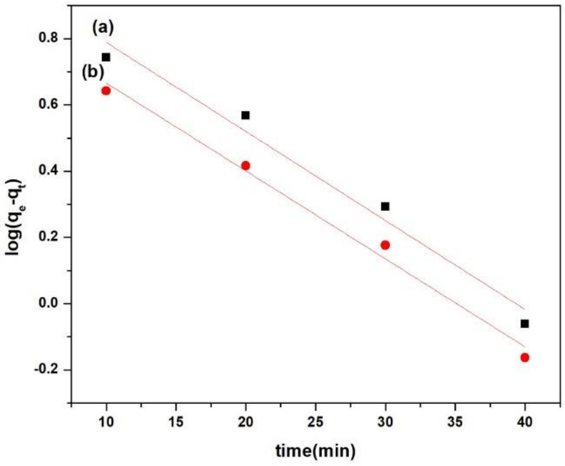


Fig. 7 Plot of log (q_e-q_t) versus time (min) for adsorption of (a) Ni(II) and (b) Cd(II) on Willow sawdust

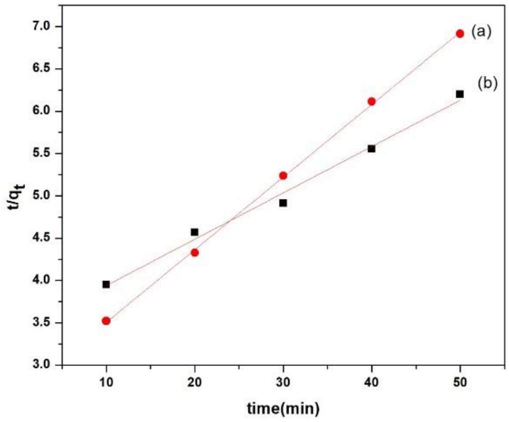


Fig. 8 Plot of t/q_t versus t(min) for adsorption of (a) Cd(II) and (b) Ni(II) on Willow sawdust

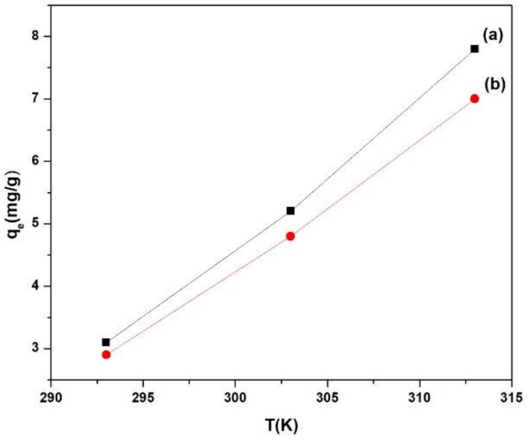


Fig. 9 Effect of temperature on the adsorption of (a) Ni(II) and (b) Cd(II) on Willow sawdust

Various adsorption kinetic models have been used to study the adsorption of metal ions. The first-order kinetic process has been used for reversible reaction with an equilibrium being established between liquid and solid phases. The linear form of pseudo-first-order kinetic equation is given as [45]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \qquad (4)$$

where q_t and q_e are the amounts of metal ions adsorbed at time *t* and at equilibrium (mgg^{-1}), respectively, and k_1 is the rate constant of pseudo-first-order adsorption process (min^{-1}). The first-order rate constant k_1 and equilibrium adsorption capacity q_e are determined from the slope and intercept of plots of log ($q_e - q_t$) versus t (Fig 7).

The pseudo-second order model is based on the assumption that the rate limiting step may be a chemical adsorption process involving sharing or exchange of electrons between adsorption sites and the metal ions. The pseudo-second-order kinetic model is given as [46]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \qquad (5)$$

where k_2 is the equilibrium rate constant of pseudo-second-order adsorption (gmg^{-1}min^{-1}). k_2 and q_e can be calculated from the slope and intercept of the linear plot between t/q_t and *t*. (Fig 8). The results are given in Table 2. The correlation coefficients (r^2) for the pseudo-second-order equation provided the best fit.

3.4 Adsorption thermodynamics

The variation of adsorption with temperature was studied at temperatures of 20^o, 30^o and 40^{o}C and the results are presented in Fig.9. The increase in adsorption capacity with temperature suggest that more adsorption sites become available for adsorption with increase in temperature. This could also be attributed to the opening up of channels and pores with increased pore size with temperature and increasing the rate of intraparticle diffusion of solute since diffusion is an endothermic process.

In order to understand the effect of temperature on the adsorption of Ni(II) and Cd(II) on Willow sawdust, thermodynamic parameters, Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) were obtained by using the following equations

$$\Delta G = -RT lnK \qquad (6)$$

where R is the ideal gas constant (kJmol^{-1}K^{-1}), T is the temperature (K) and *K* is the equilibrium constant which was calculated from the following relation:

$$K = C_A/C_E$$

where C_A and C_E are the equilibrium concentrations (mg/L) of metal ions on the adsorbent and in solution, respectively, at 100mg/L initial concentration of the metal ions.

The enthalpy and entropy of adsorption were determined from the Van't Hoff equation

$$\ln K = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \ldots\ldots\ldots\ldots\ldots\ldots(7)$$

where ΔH and ΔS were obtained from the slope and intercept of the Van't Hoff's plot of ln*K* verses 1/T (Figure 10).

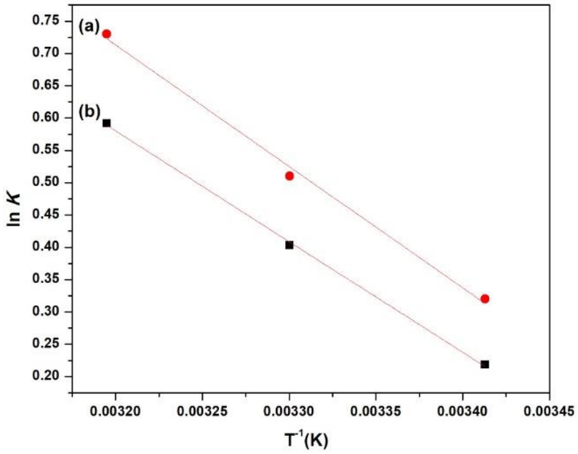


Fig.10 Plot of ln *K* versus T^{-1}(K) for adsorption of (a) Ni(II) and (b) Cd(II) on Willow sawdust

Table 1. Langmuir and Freundlich adsorption isotherm parameters of Ni(II) and Cd(II) on Willow sawdust

Metal	**Langmuir constant**			**Fruendlich constant**		
	q_o (mgg^{-1})	**K_L (mgL^{-1})**	**r^2**	**K_F**	**$1/n$**	**r^2**
Ni	7.98	0.0143	0.999	0.4020	0.588	0.996
Cd	7.11	0.0132	0.998	0.347	0.582	0.994

Table 2. Kinetic parameters for the adsorption of Ni(II) and Cd(II) on Willow sawdust

Metal ion	**q_e exp (mg g^{-1})**	**Pseudo-first order kinetics**			**Pseudo-second order kinetics**		
		$q_e$cal (mg g^{-1})	**K_1 (min^{-1})**	**r^2**	**$q_e$cal (mg g^{-1})**	**K_2 (g mg^{-1} min^{-1})**	**r^2**
Ni(II)	8.07	6.940	0.0833	0.984	7.32	0.0113	0.995
Cd(II)	7.23	4.119	0.0983	0.976	6.53	0.0359	0.997

Table 3. Values of thermodynamic parameters for the adsorption of Ni(II)and Cd(II) on Willow sawdust at various temperatures.

Metal ion	**T (K)**	**ΔG (kJmol^{-1})**	**ΔH (kJmol^{-1})**	**ΔS (kJmol$^{-1}K^{-1}$)**
Ni(II)	293 303 313	-1.3026 -1.7648 -2.292	12.709	0.0593
Cd(II)	293 303 313	-0.0393 -0.493 -0.950	11.548	0.0446

Table 4. Comparison of removal of Ni(II) and Cd(II) from synthetic metal ion solution and fertilizer industry effluent by adsorption on Willow sawdust by column method

Heavy metals	**Initial concentration (mg/L)**	**Final concentration (mg/L)**	
Ni(II)		**synthetic solution**	**industrial effluent**
	20	1.78	2.73
	40	3.28	7.46
	60	11.92	19.71
	80	27.76	34.8
	100	32.16	39.99
Cd(II)	20	2.17	4.25
	40	7.15	10.98
	60	15.97	20.93
	80	22.89	29.18
	100	34.3	41.1

Table 5. Removal of Cd(II) and Ni (II) from fertilizer industry effluent on Willow sawdust by using column method

Heavy metal	Initial conc (mg/L)	Final conc (mg/L)
Ni(II)	148	55.7
	55.7	13.17
	13.17	1.35
Cd(II)	112	37.06
	37.06	11.32
	11.32	0.84

The results of the thermodynamic calculations are presented in table 3. The negative value of ΔG indicated the spontaneous nature of the adsorption process. The increase in negative values obtained for ΔG with increasing temperature indicates that the adsorption process is more favourable at higher temperature. The positive value of ΔS shows the increased randomness at solid/solution interface during the adsorption process. A positive value of ΔH confirms the endothermic nature of the process. The enhancement of adsorption at higher temperature may be attributed to the enlargement of pore size, enhancement of the rate of intraparticle diffusion of the metal ions and/ or activation of adsorbent surface.

Treatment of fertilizer factory effluent using glass column

Fertilizer factory effluent was collected from Industrial Estate Lassipora, JK, India. It was carefully bottled in a plastic container and was immediately taken to the laboratory for analysis. The effluent was filtered and the heavy metals present in the wastewater sample were determined by Atomic Absorption Spectrometry. The initial concentration of the metal ions Cd(II) and Ni(II) present in the wastewater were found to be 112 and 148 mg/L respectively. Different concentrations of Cd(II) and Ni(II) were prepared from the fertilizer effluent solution by dilution with distilled water for comparison with synthetic metal ion solutions. Synthetic solutions of different concentrations of the Cd(II) and Ni(II) were prepared from their corresponding nitrates.

Column experiments were carried out using a glass column with internal diameter of 1cm. The column was packed with 2g of Willow sawdust. Distilled water was run through the column and equilibrated for an hour. A volume of 100mL of each of the synthetic heavy metal ion solutions with different metal ion concentrations was passed through separate columns at an optimum pH (pH 4 and 7 for Cd(II) and Ni(II) respectively) and at room temperature. The rate of flow of the metal ion solution was kept constant (1mL/min) using a stopcock.. The procedure was repeated for the fertilizer effluent wastewater. The results of column experiments are presented in table 4. The difference between the metal uptake from the synthetic metal ion solution and the effluent may be attributed to the presence of other metal ions and impurities which compete with particular metal ion for the binding sites.

In another experiment, 100mL of the fertilizer industry effluent was passed through the column at an optimum pH and at room temperature and the flow rate was kept constant. The amount of metal ion left in the solution was determined. This solution was again passed through another column and then analyzed for final metal ion concentration. The procedure was repeated till nearly complete removal of metal ions was achieved as shown in table 5.

4. CONCLUSION

- Sawdust of Willow was found to adsorb Cd(II) and Ni(II) substantially from aqueous solution.
- Various thermodynamic parameters like ΔH, ΔS and ΔG were calculated. These thermodynamic parameters together with Langmuir and Freundlich isotherm constants indicated a favorable adsorption of Cd(II) and Ni(II) on the sawdust of Willow
- The adsorption of Cd(II) and Ni(II) on the sawdust of Willow was found to be endothermic and spontaneous in nature.
- The adsorption of Cd(II) and Ni(II) on the sawdust of Willow increased with increase in temperature.
- The maximum adsorption capacity of willow sawdust for Ni(II) and Cd(II) were found to be 7.98 and 7.11 mg/g respectively at optimum conditions.
- The efficacy of sawdust of willow in the treatment of effluent from fertilizer factory has been investigated and the results have been found satisfactory.
- On the basis of the above it can be concluded that sawdust of willow can be effectively used as a low-cost, sustainable and easily available adsorbent for the removal of toxic metals from aqueous solution.

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