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Adsorption of Toxic Metal Ions from Aqueous Solutions by Modified Cellulosic Waste Material

ARVIND DIXIT[1,*], ANURADHA TIWARI[1], SUNIL KUMAR YADAV[2] and BHAKTI VIJAY SHUKLA[3]

[1]Department of Chemistry, V.S.S.D. College, Kanpur-208 002, India
[2]Department of Chemistry, Harcourt Butler Technological Institute, Kanpur-208 002, India
[3]Extension Unit, Fragrance & Flavour Development Centre, Kanpur-208 012, India

*Corresponding author: E-mail: dixit_arvind2@yahoo.co.in

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The adsorption of Pb(II), Hg(II) and Ni(II) from aqueous solutions by cellulosic material was studied in a batch adsorption system. Factors influencing Pb(II), Hg(II) and Ni(II) adsorption such as metal ion concentration, pH, contact time and adsorbent dosage were investigated. The adsorption process was relatively fast and equilibrium was established with in 4 h. Maximum adsorption of metal ions and a comparison of the kinetic models on the overall adsorption rate showed that the adsorption system was best described by the pseudo second-order kinetics. The fast kinetics results and high adsorption capacity indicated that date pits fibre can be applied as the selective adsorbent for the treatment of heavy metal ions from aqueous solutions. The adsorption mechanism was suggested to be complexation.

Key Words: Adsorption, Toxic metal ions, Date stem, Batch studies, Kinetics isotherms.

INTRODUCTION

Industrial, agricultural and domestic activities of human have affected the environmental system, resulting in drastic problems such as the generation of wastewater containing high levels of pollutants. Although many heavy metals are necessary in small amounts for normal development of the biological cycles, most of them become toxic at high concentrations. Lead, mercury, nickel, zinc, copper and chromium are often detected in appreciable amounts in industrial wastewaters, which originate from mining activities, metal plating, smelting, paint manufacture, pigment manufacture, pesticides, tanneries, printing and photographic industries, *etc.*[1]. Since heavy metals are non-biodegradable and can be accumulated in living tissues causing various diseases and disorders, they must be removed from solution prior to their discharge. To date, various methods including chemical treatment with lime, precipitation, ion-exchange, reverse osmosis, electro-dialysis, membrane filtration, solvent extraction and adsorption are often used for the removal and recovery of heavy metals from wastewaters. Among them, adsorption is the most effective and widely used method for the removal of different pollutants[2]. Recently, much attention is given to prepare adsorbents from various wastes generated from forestry[3], fishery[4,5] and by-products of agriculture[6-12].

According to hard and soft acids and bases (HSAB) classification system, sulfur can be considered as a soft ligand group having strong affinity for a number of solt metals such as lead, cadmium, copper, *etc.* Date pits fiber consists of three main components, namely cellulose, hemi cellulose and lignin, besides other minor constituents such as oil, protein, *etc.*[13]. Many of these contain several hydroxyl functional groups, which make the date pits fiber a potential substrate for a novel date pits fibre xanthates are formed by reacting an organic hydroxyl-containing substrate with carbon disulfide under caustic condition[14]. Adsorbent by xanthation process, along with the detailed investigations of the effect of various parameters including equilibrium pH, contact time, initial concentration, kinetic models as well as isotherm models on adsorption of Pb(II), Hg(II) and Ni(II).

EXPERIMENTAL

All reagents and chemicals used in this study were of AR grade. The stock solutions (1000 mg/L) of lead, nickel and mercury were prepared appropriately in double-distilled water from their nitrate and chloride salts respectively. The pH of experimental solutions was adjusted by contacting with hydrochloric acid and sodium hydroxide. In all the experimental work, double-distilled water was used.

Preparation of adsorbent materials: Date pits were collected from rural areas near Kanpur city (India). It was dried at 80 ± 5 ºC for 24 h and date pits fibers were separated manually and grounded into fine particles with the help of an electric grinder. It was sieved for uniform particle size of

130 µm. Then 50 g of date fibers (DF) powder was treated with 100 mL concentrated H_2SO_4 and stirred for 1h and left overnight. It was washed with demineralized water to remove excess acid and any other soluble substances till neutrality and sun dried. 25 g of the date fibers was added into 200 mL of 4 M NaOH solution and shaken for 1 h. Further 25 mL of CS_2 was added and stirred for 3 h then left for overnight. It was filtered and repeatedly washed with demineralized water until the pH of the suspension became neutral. This xanthated date fibre (XDF) was used as an adsorbent. The properties of xanthated date fibre are summarized in Table-1.

TABLE-1
PROPERTIES OF XANTHATED DATE FIBER (XDF)

Bulk density (g/ c.c.)	1.12
Moisture (%)	13.6
Ash content (%)	2.76
Matter soluble in water (%)	0.0
Matter soluble in acid (%)	0.0
pH	7.8

Metal binding experiments: Adsorption of metal ions by the active sites on the surface of an adsorbent is affected by several factors such as pH of solution, initial metal ion concentration, contact time, agitation speed and the amount and particle size of the adsorbent. Tests were carried out in Erlenmeyer flasks placed in a orbital shaker at 30 ºC. Typically, 0.05 g of the xanthated date fibre was contacted with 20 mL of Pb(II), Hg(II) and Ni(II) solutions (100 mg/L). After 2 h of contact time, the suspension was filtered and the filtrate was analyzed for Pb(II), Hg(II) and Ni(II) by spectrophotometric method[15] or EDTA titration method. The uptake of metal ions was determined according to the following equation:

$$q_e = \left(\frac{C_i - C_f}{m}\right)V \quad (1)$$

where C_i and C_f (mg/L) are the initial and final metal ions concentrations in solution, respectively, V (L) is the solution volume and m (g) is the weight of the adsorbent used.

RESULTS AND DISCUSSION

Effect of contact time: Preliminary kinetic experiments carried out to asses the adsorption equilibrium time of metal ions on xanthated date fibre work performed. The results are presented in Fig. 1 for Pb(II), Hg(II) and Ni(II). It is apparent from the figure that significant removal of metal ions occurred in 0.5 h and no appreciable changes in terms of removal were noticed after 2 h. The adsorption plot reveals that the rate of per cent adsorption of Pb(II), Hg(II) and Ni(II) is initially high which is probably due to the availability of larger surface area of the xanthated date fibre for the adsorption of metal ions. As the surface adsorption sites become exhausted, the rate of uptake is controlled by the rate of transport from the exterior to the interior site of the adsorbent particles[16]. In all the subsequent experiments the equilibrium time was maintained at 2 h.

Effect of pH: pH of the solution is an important parameter affecting metal ion adsorption. This is because hydrogen ions competing with positively charged metal ions on the active sites of the adsorbents. The effect of pH on the adsorption of

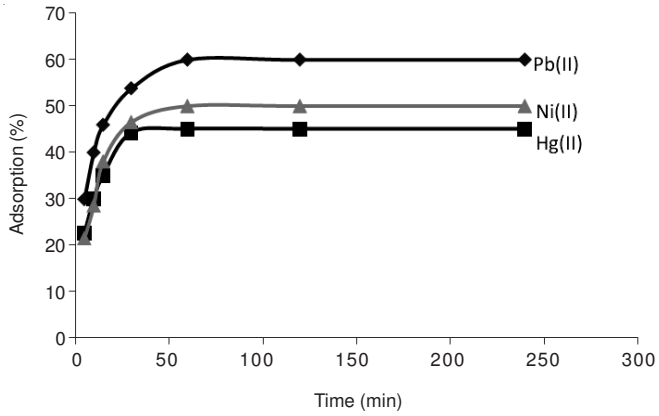


Fig. 1.

Pb(II), Hg(II) and Ni(II) on xanthated date fibre have been studied by varying it in the range 1-10 as shown in Fig. 2 It is evident that the uptake of metal ions depends on pH, it increases with increase in pH reaching maximum adsorption at pH 5,6 and 4.5 for Pb(II), Hg(II) and Ni(II) respectively.

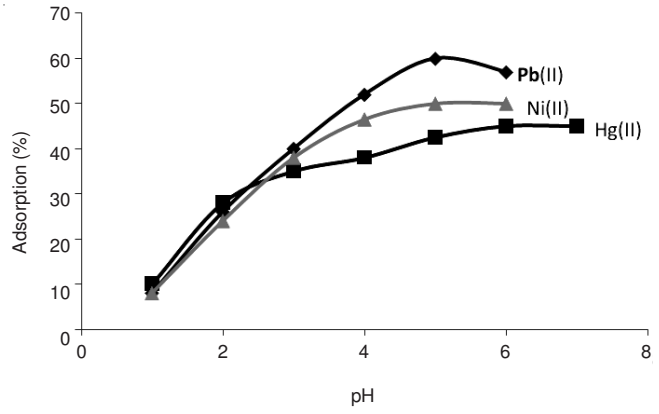


Fig. 2.

Effect of concentration: In batch adsorption processes, the initial metal ion concentration in the solution plays a key role as a driving force to overcome the mass transfer resistance between the solution and solid phases. Therefore, the amount of metal ions adsorbed was expected to be higher with a higher initial concentration of Pb(II), Hg(II) and Ni(II) ions. The effect of initial concentration of Pb(II), Hg(II) and Ni(II) ions at optimum pH, while keeping the dosage (2.5 g/L) constant, the per cent adsorption increased with the increase of initial Pb(II), Hg(II) and Ni(II) ions concentration as shown in Fig. 3. As a result of the above observations it was indicated that the adsorption process of Pb(II), Hg(II) and Ni(II) ions on xanthated date fibre were to be dependent on concentration of adsorbate upto some extent.

Effect of adsorbent dose: The results for adsorptive removal of Pb(II), Hg(II) and Ni(II) with respect to adsorbent dose are shown in Fig. 4 over the range 2.5-5.0 g/L, at optimum pH of maximum adsorption. It was observed that there were an increase in percentage removal of Pb(II), Hg(II) and Ni(II) with adsorbent dose due to the greater availability of the adsorption sites or surface area and pore volume at higher adsorbent dosage providing more functional groups that result in a higher metal ions adsorption on adsorbent[17].

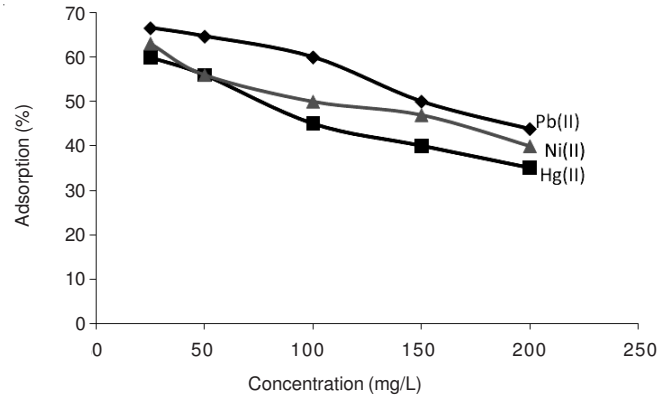


Fig. 3.

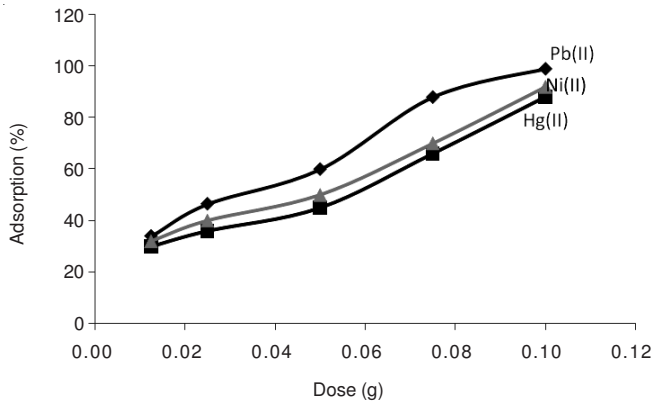


Fig. 4.

Adsorption isotherm studies: To quantify the adsorption capacity of xanthated date fibre for the removal of Pb(II), Hg(II) and Ni(II) from aqueous solutions, the Langmuir isotherm model was used.

Langmuir model: This model assumes that the adsorption occurs at specific homogeneous sites on the adsorbent and is used successfully in many monolayer adsorption processes[18]. The data of the equilibrium studies for adsorption of Pb(II), Hg(II) and Ni(II) onto xanthated date fibre follow the following form of Langmuir model:

$$\frac{C_e}{q_e} = \frac{1}{bK_L} + \frac{C_e}{b} \quad (2)$$

where C_e is the equilibrium concentration (mg/L) and q_e is the amount of metal ions adsorbed per specified amount of adsorbent (mg/g), K_L is the Langmuir equilibrium constant and b is the amount of adsorbate required to form a monolayer. Hence, a plot of C_e/q_e *versus* C_e should be a straight line with a slope (1/b) and an intercept as ($1/bK_L$). The Langmuir type adsorption isotherm indicates surface homogeneity of the adsorbent and hints towards the conclusion that the surface of adsorbent is made up of small adsorption patches which are energetically equivalent to each other in respect to adsorption phenomenon. The correlation coefficient (R^2) value indicated that the adsorption data of Pb(II), Hg(II) and Ni(II) ions onto XDF was well fitted to the Langmuir isotherm. The values of constants K_L and b were calculated and reported in Table-2.

Kinetic studies: The modeling of the kinetics of adsorption of Pb(II), Hg(II) and Ni(II) ions on XDF was investigated by pseudo-second-order model. The conformity between experimental data and the model predicted values was expressed by correlation coefficient (R^2).

TABLE-2
LANGMUIR ADSORPTION ISOTHERM CONSTANTS FOR Pb(II), Hg(II) AND Ni(II) IONS ON XANTHATED DATE FIBER

Isotherm Langmuir	Constants		
	b (mg/g)	K_L (L/mg)	R^2
Pb(II)	54.4	0.175	0.992
Hg(II)	31.8	0.136	0.991
Ni(II)	40.4	0.154	0.990

Pseudo-second-order model: The kinetic data were analyzed using the pseudo-second-order model which, can be expressed as:

$$\frac{t}{q} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right)t \quad (3)$$

$$h = k_2 q_e^2 \quad (4)$$

where h is the initial adsorption rate (mg/g min).The plot of t/q *versus* t should give a linear relationship, from which, q_e and k_2 can be determined from the slope and intercept of the plot. The k_2 and q_e determined from the model are presented in Table-3 along with the corresponding correlation coefficient (R^2) values. It can be seen from the table that the adsorption of Pb(II), Hg(II) and Ni(II) ions perfectly follows the pseudo-second-order kinetic model.

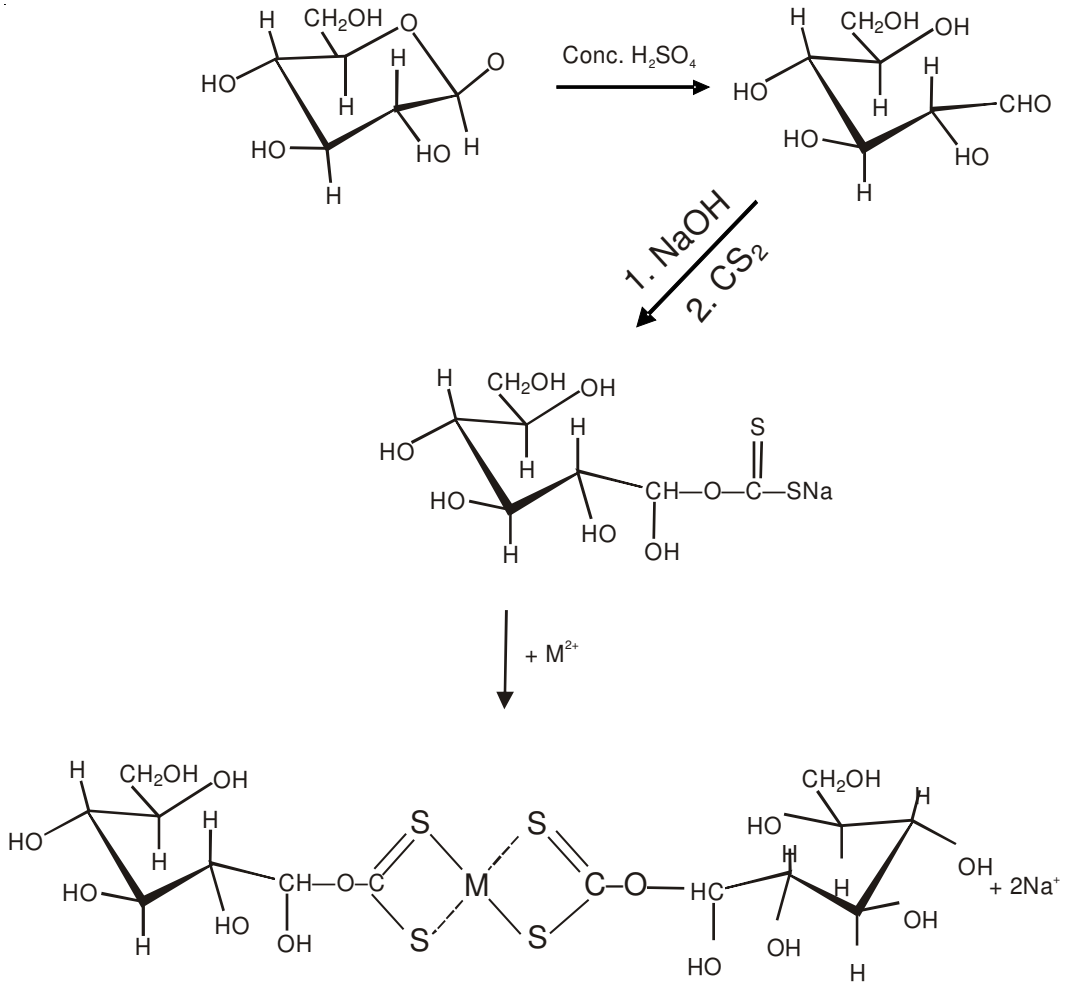
TABLE-3
PSEUDO-SECOND-ORDER MODELS FOR ADSORPTION OF Pb(II), Hg(II) AND Ni(II) IONS ON XANTHATED DATE FIBER

Concentration (100 mg/L)	Pseudo second order		
	K_2 (g/ mg min)	q_e (mg/g)	R^2
Pb(II)	0.0054	27.54	0.999
Hg(II)	0.0042	22.10	0.998
Ni(II)	0.0038	18.92	0.999

Mechanism of the adsorption: The xanthated date fiber can adsorbs metal ions through complexation processes. The complex formation occurs between four sulfur atoms and one divalent Pb(II), Hg(II) and Ni(II) ion (**Scheme-I**). This phenomenon can be explained by proposing that Na^+ ions were released into the solution according complexation mechanisms.

Conclusion

A new adsorbent xanthated date fibre was prepared by treating the charred date pits fiber with CS_2 under alkaline condition. The adsorption of Pb(II), Hg(II) and Ni(II) ions on the activated carbon is found to be dependent on metal ions concentration, pH, time and adsorbent dosage. The optimum parameters for this study were pH 5, 6 and 4.5 respectively. Experimental results indicated that the pseudo second order reaction kinetics provided the best description of the data. The isotherm study indicated that adsorption data correlated well with Langmuir isotherm model. The adsorption process of Pb(II), Hg(II) and Ni(II) ions on xanthated date fibre proceeds according to complexation mechanism. This study demonstrated that the xanthated date fibre could be used as potential adsorbent for the treatment of wastewater containing heavy metal ions.



Scheme-I: Proposed adsorption mechanism:complexation

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