

Preparation and Characterization of Modified Date Palm Trunk for Adsorption of Hg(II) from Aqueous Solutions

Meenakshi Pandey^a, Abhilekha Sharma^a,
^aDepartment of Chemistry,
Noida International University Greater
Noida (U.P.) India

Sunil Kumar Yadav^b
^bDepartment of Chemistry,
Harcourt Butler Technical University,
Kanpur (U.P.) India

Brahm Kumar Tiwari^{c*}
^cCollege of Biotechnology,
I.T.S Paramedical College Murad Nagar,
Ghaziabad (U.P.) India

Abstract-The potential of ethylenediamine modified date palm trunk (MDPT) for the adsorption of Hg(II) from aqueous solutions. Factors influencing mercury(II) adsorption onto MDPT such as initial Hg(II) concentration (12.5–100 mg/L), pH (1–6), contact time (5–120 min), and adsorbent dosage (2.0–20.0 g/L) were investigated. The adsorption equilibrium was established within 120 min. Maximum adsorption of Hg(II) occurred at pH~5. Before and after adsorption, MDPT was characterized by Fourier transform infrared spectroscopy (FTIR) and in order to prove its Hg(II) adsorption capacity. The results show that the adsorption rate could be well fitted by pseudo-second-order rate model, and the adsorption isotherm data obeyed Langmuir model. The adsorption capacity for Hg(II) was found to be 29.25 mg/g. Evidently, the high efficiency and fast removal of mercury using MDPT suggest the synthesis of modified adsorbents with similar physical and chemical properties of MDPT as a valuable and promising wastewater treatment.

Keywords: Adsorption, Hg(II), ethylenediamine modified date palm trunk, adsorption isotherms

1. INTRODUCTION

Mercury is considered severe toxic and more hazardous to the environment and organisms because of its serious effect on vital organs [1]. Even low doses of mercury accumulation in various organs (e.g. liver, kidneys, brain, spleen and bones) may cause adverse effects like carcinogenic and mutagenic troubles, serious intestinal and urinary complications and even death in more severe cases [2]. Mercury usually enters food chain as methyl mercury through bacterial transformation of a wide variety of food, especially fish. According to the standards, the tolerance limit of Hg(II) for discharge into inland surface waters is 10 µg/L and for drinking water it is 1 µ/L [3]. The principal sources of mercury pollution in aquatic environment are the chloralkali plants, paper and pulp industries, oil refining, electrical, rubber processing and fertilizer industries [4]. Therefore, the removal of Hg(II) from wastewater is an important issue. The techniques available for the removal of mercury from solutions include chemical precipitation [5], reverse osmosis and ion exchange [6]. The main shortcomings of these methods are

their costs, incomplete metal removal, high energy requirements and generation of toxic sludge. Adsorption is the most preferred method for removal of heavy metals from aqueous solutions due to its simplicity and its high effectiveness [7-9].

In recent years, many agro wastes, including sawdust [10], carrot residue [11], sugar beet pulp [12], tree fern [13], rice husk [14], papaya seed carbon [15], eucalyptus bark [16] and date palm trunk [17], had been used to adsorb heavy metals from aqueous solution. The agricultural wastes being abundantly available with low cost mainly comprise of cellulose which is a natural biopolymer with sorption property. For improving the adsorption capacities of agro wastes, various chemical modifications have been reported [18, 19].

The purpose of this study is to utilize date palm trunk (cellulosic agro wastes) after its chemical modification as a potential adsorbent for treatment of wastewater containing mercury(II). The values of well-known kinetics and isotherms studies have been performed to elucidate the equilibrium adsorption behavior of Hg(II) onto the adsorbent. The effect of contact time, pH, concentration and dosage on the adsorption capacity has been investigated.

2. EXPERIMENTAL

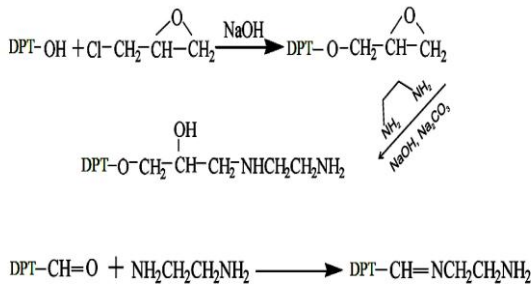
2.1 Materials

A stock solution of Hg(II) was prepared by dissolving mercury(II) chloride (E-Merck, Germany) in double distilled water and diluting up to 1 L (1000 mg/L Hg(II)). Working solutions were prepared by further diluting the stock solution.

2.2 Preparation of MDPT

Date palm trunk (DPT) was obtained from rural areas around Kanpur (India), cut into a length of approximately 1 cm, washed thoroughly with demineralized water (DMW) to remove water soluble materials, dried overnight at 100 ± 2°C in a hot air oven, and allowed to cool down to room temperature. It was ground and sieved to obtain an average particle size of 75 µm. DPT powder (10 g) was treated with 80 mL of NaOH solution (1.25 mol/L) and epichlorohydrin

(30 mL) at 40 °C for 1 h. Then mixture was filtered, rinsed with water, oven-dried and stored in a desiccator. During the treatment, the hydroxyl groups of DPT reacted with epichlorohydrin. Modified date palm trunk was prepared by adding ethylenediamine (10 mL), water (100 mL) and Na₂CO₃ (1 g) to the epichlorohydrin treated DPT. The mixture was stirred using magnetic stirrer at 60 °C for 2 h, MDPT was filtered, washed with water, dried and stored in desiccator. The following chemical reactions occurred during the modification.



2.3 Batch adsorption experiments:

Batch adsorption experiments were performed in closed Erlenmeyer flasks using orbital shaker at room temperature (30 °C). In this study, MDPT (0.1 g) was put into a Erlenmeyer flask (100 mL) containing 50 mL Hg(II) solution of predetermined initial Hg(II) concentrations (12.5-100 mg/L) and at pH (2.0–6.0). The initial pH of the solution was adjusted to the desired value by addition of small amount of 0.1N HCl or NaOH. The mixture was shaken at 150 rpm. The sample solution was filtered using Whatman No.4 filter paper and the filtrate was analyzed for Hg(II) concentration by standard EDTA titration; using 1-(2-pyridylazo)-2-naphthol (PAN) indicator or spectrophotometric method using diphenylthiocarbazone [20]. The amount of Hg (II) adsorbed (q_e) was calculated using Eq. (1):

$$q_e = \left(\frac{C_i - C_e}{M} \right) V \tag{1}$$

where C_i and C_e (mg/L) are the initial and final Hg(II) concentrations, respectively, V is the solution volume (L), and M is the weight of the adsorbent (g).

3. RESULTS AND DISCUSSION

3.1 FT-IR analysis:

FTIR spectra (fig. 1) shows MDPT and Hg(II) loaded MDPT. The broad peak around 3410 cm⁻¹ in MDPT is attributed to -NH stretching vibration. This absorption band is shifted towards lower wave number (3381 cm⁻¹) in case of with Hg(II) adsorbed MDPT. This suggests the formation of complex between Hg(II) ions and N-atoms (The characteristics band at 1056 cm⁻¹ corresponding to C-O-C stretching is observed in both spectra).

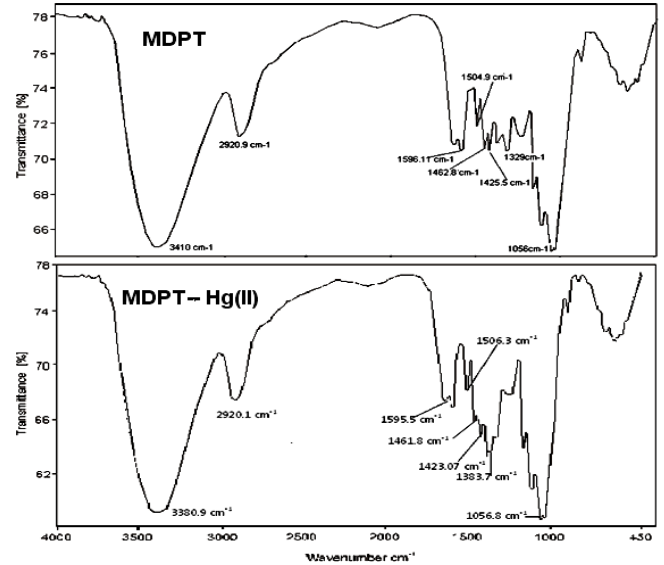


Figure 1. FT-IR spectra of (a) MDPT and (b) Hg(II)-loaded MDPT.

3.2 Effect of contact time:

After fixing the pH and adsorbent dosage, the effect of contact time on removal of Hg(II) ions was investigated using various initial concentrations of Hg(II). Figure 2 shows that with increase in contact time removal increases rapidly during the first 30 min, and then no appreciable change in terms of the removal of Hg(II) ions was observed after 60 min. This behavior may be due to saturation of the available adsorption sites present on MDPT. At the initial stage, the removal efficiency was rapid due to abundant availability of active binding sites on the biomass and with gradual occupancy of these sites; sorption became less efficient in the later stages. The equilibrium is established with in 120 min.

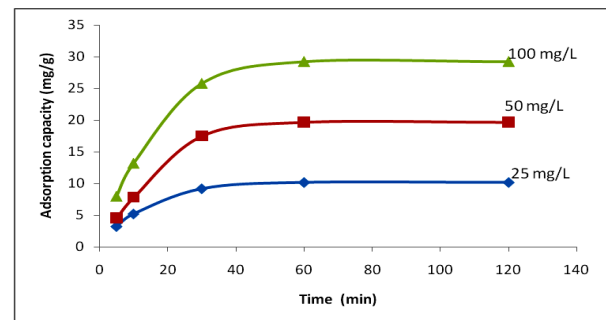


Figure 2. Effect of contact time on the adsorption of Hg(II) onto MDPT.

3.3 Effect of initial pH of solution:

The effect of pH on the adsorption of Hg(II) ions onto MDPT was studied at pH 1–6 for initial Hg(II) ion concentration (25-100 mg/L). Because of the precipitation of insoluble mercury compound occurred at pH value greater than 7 [21], the effect of initial pH was studied over the pH range from 1.0 to 6.0 with other experimental parameters fixed as follows: Hg (II) concentration (25-100 mg/L), MDPT dose (2.0 g/L), contact time (120 min) and agitation speed/rpm; 150. The effect of initial pH on removal percentage of Hg (II) is elucidated in Figure 3.

The amount of Hg (II) removal increases as the initial pH value of Hg (II) solution increases. The maximum value of Hg (II) removal appeared in the range of pH 4 to 6. For further, adsorption studies, optimum pH was 5.

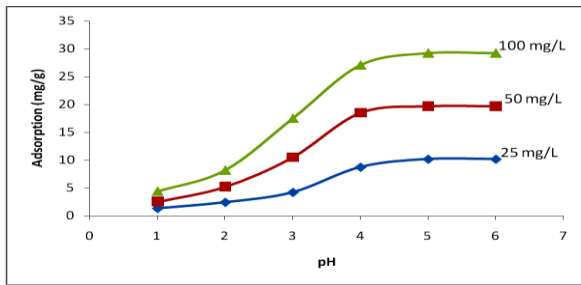


Figure 3. Effect of pH of solution on the adsorption of Hg(II) onto MDPT.

3.4 Effect of initial concentration of Hg (II):

A plot of adsorption capacity/ % removal vs. concentration (Figure 4) shows that adsorption capacity increases (5.3-29.25 mg/g) and % removal decreases (85.7-67.2 g) with the increasing initial Hg(II) concentration (12.5–100.0 mg/L). This seems to be due to the increase in the driving force of the concentration gradient with an increase in the Hg(II) initial concentration.

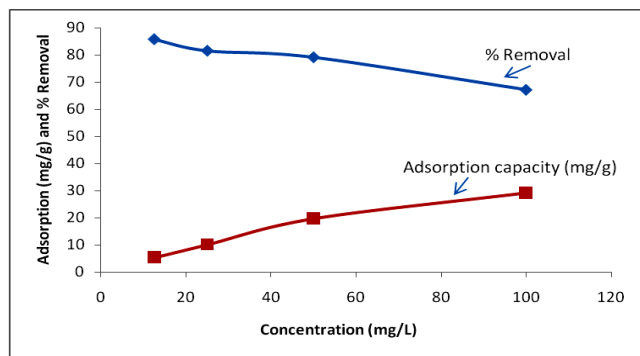


Figure 4. Effect of concentration on the adsorption of Hg(II) onto MDPT.

3.5 Effect of adsorbent dose:

An effect of dosage on the removal of Hg (II) ions is shown in Figure 5. It has been observed that the removal of Hg(II) increases rapidly with increasing dosage from 2.0 to 20.0 g/L while the other experimental variables were fixed (pH 5.0, initial concentration of Hg(II); 100 mg/L, contact time; 120 min; agitation speed/rpm; 150). A plot of adsorbent dose vs. % removal of Hg(II) adsorption is presented in Figure 5. The Hg(II) removal increases from 67.2–99.4% with increasing adsorbent dose. This may be due to an increased adsorbent surface area and availability of more adsorption sites or more functional groups resulting from the increased dose of the adsorbent.

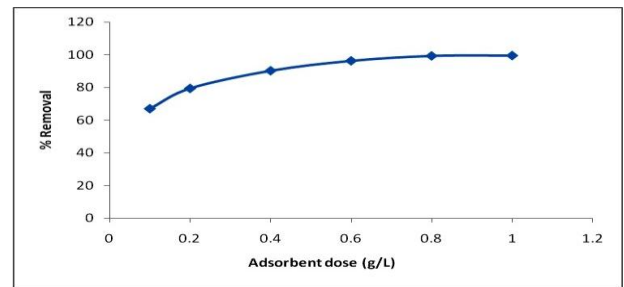


Figure 5. Effect of adsorbent dose on the adsorption of Hg(II) onto MDPT.

3.6 Adsorption isotherms:

The adsorption isotherms for the Hg (II) removal were studied using an initial concentration of Hg (II) between 12.5 and 100 mg/ L. The sorption equilibrium data of Hg (II) ion on to MDPT were analysed in terms of Langmuir and Freundlich for the purpose of interpolation and limited extrapolation of the data. The following Langmuir adsorption isotherm [22] equation is used:

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

where q_e is the amount of Hg(II) adsorbed per unit mass of adsorbent (mg/g), C_e is the equilibrium concentration of the Hg(II) in solution (mg/L), b is the maximum Hg(II) uptake (mg/g), K_L is the Langmuir binding constant (L/ mg) relating the free energy of adsorption. K_L values between 0 - 1 indicate that the adsorption process is favorable. Hence, a plot of C_e/q_e versus C_e should be a straight line with a slope (1/b) and an intercept (1/bK_L) as shown in Fig. 6. The Langmuir constant and its correlation coefficient evaluated from the adsorption for Hg(II) are given in Table 1. The high value of Langmuir coefficient ($R^2 = 0.99$) confirms that the Langmuir isotherm is the best fit for the adsorption of Hg(II) onto MDPT.

The essential characteristics of the Langmuir isotherm can be conveniently expressed in terms of a dimensionless term R_L (a constant separation factor or equilibrium parameter for a given isotherm) and is defined as:

$$R_L = \frac{1}{1 + K_L C_i} \quad (3)$$

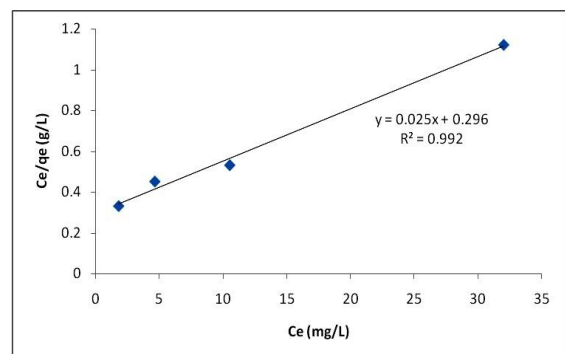


Figure 6. Langmuir isotherms for adsorption of Hg(II) onto MDPT.

where C_i is the initial concentration of Hg(II) and R_L value indicates the type of the isotherm. According to Mckay et al. [23] R_L values between 0 and 1 indicate the isotherm favourable, and it is unfavourable if $R_L > 1$. Thus the obtained R_L values (0.1 - 0.479) indicate that the adsorption of Hg (II) onto MDPT is favourable. Freundlich adsorption isotherm [24] is an empirical relationship established upon adsorption onto a heterogeneous surface on the assumption that different sites with several adsorption energies are involved, and is given below:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

where q_e and C_e are the equilibrium concentrations of Hg (II) in the adsorbed and liquid phases in mg/g and mg/L, respectively. K_F and n are the Freundlich constants. Thus a plot of $\ln q_e$ versus $\ln C_e$ should be a straight line with a slope of $1/n$ and an intercept of $\ln K_F$ as shown in Figure 7. The value of the Freundlich constant (n) was 1.76 for MDPT (Table 1) showing that the adsorption process may be favorable. R^2 value (< 0.99) obtained from Freundlich isotherm indicated that Freundlich model is not suitable.

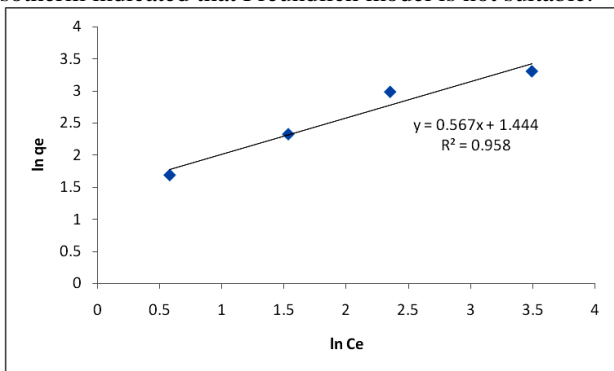


Figure 7. Freundlich isotherms for adsorption of Hg(II) onto MDPT.

On the whole, the Langmuir isotherm displays a higher regression coefficient (R^2) compared to the Freundlich isotherm and the adsorption data fit better with the Langmuir adsorption isotherm model.

Table 1: Langmuir and Freundlich parameters for the adsorption of Hg (II) onto the MDPT.

Isotherm	Parameters	Values
Langmuir	b (mg/g)	39.21
	K_L (L/mg)	0.087
	R^2	0.992
Freundlich	K_F (mg/g)	4.22
	n	1.76
	R^2	0.958

7 Adsorption kinetics study:

3.7.1 Pseudo-first-order model:

The pseudo-first-order rate model of Lagergren [25] is based on the solid adsorbent capacity and is generally expressed as follows:

$$\log(q_e - q_t) = (\log q_e) - \left(\frac{k_1}{2.303}\right) t \quad (5)$$

where q_e is the amount of solute adsorbed at equilibrium per unit weight of the adsorbent (mg/g), q_t is the amount of solute adsorbed at any time (mg/g) and k_1 (min^{-1}) is the adsorption rate constant. Values of k_1 calculated from the plots of $\log(q_e - q_t)$ versus t at different initial concentrations are summarized in Table 2. The values of pseudo-first order rate constants, k_1 and q_e were calculated from the slopes and the intercepts of the plots of $\log(q_e - q_t)$ versus time (Figure not shown). The k_1 values, the correlation coefficient R^2 , and theoretical and experimental equilibrium adsorption capacity q_e are given in Table 2. The R^2 values presented in Table 2 suggest that adsorption of Hg(II) onto MDPT does not follow pseudo-first-order kinetics. In addition the theoretical and experimental equilibrium adsorption capacities, q_e obtained from these plots varied widely. This confirms that the pseudo-first-order model was not appropriate for describing the adsorption kinetics of Hg(II) onto MDPT.

3.7.2 Pseudo-second-order model:

The pseudo-second order model [26] can be expressed as:

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2}\right) + \left(\frac{1}{q_e}\right) t \quad (6)$$

where k_2 (g/mg min) is the rate constant of the pseudo-second-order equation, q_e (mg/g) is the maximum adsorption capacity, and q_t (mg/g) is the amount of adsorption at time t (min). The plot of t/q_t versus t (Figure 8) shows a linear relationship. The value of q_e (mg/g) and k_2 (g/mg min) are determined from the slope and intercept of the plot. The results are summarized in Table 2 for each initial concentration. It can be seen that the calculated coefficient of determination (R^2) is very close to unity and that $q_{e(\text{cal})}$ values agree with the experimental values. From Table 2, it is evident that the calculated q_e values agree with experimental q_e values, and also the correlation coefficients for the pseudo-second order kinetics plots at all the studied concentrations are higher ($R > 0.99$). It can be concluded that the adsorption proceeds via pseudo-second-order mechanism rather than a pseudo first-order mechanism.

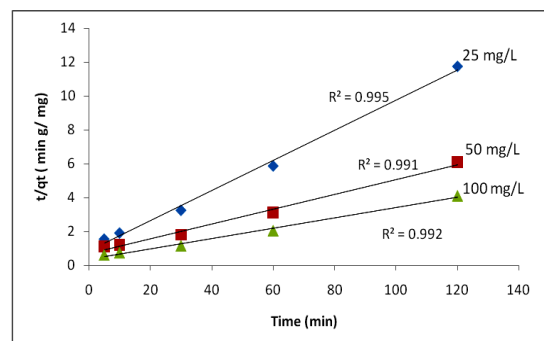


Figure 8. Pseudo-second-order kinetic plot for adsorption of Hg(II) onto MDPT.

Table. 2: Pseudo-first-order and pseudo-second-order models for adsorption of Hg(II) onto MDPT.

Initial Conc. (mg/L)	q _{e-exp.} (mg/g)	Pseudo first order		
		k ₁ (min ⁻¹)	q _{e (cal)} (mg/g)	R ²
25	10.2	0.015	4.48	0.842
50	19.7	0.022	8.65	0.930
100	29.25	0.024	15.14	0.976
Initial Conc. (mg/L)	q _{e-exp.} (mg/g)	Pseudo second order		
		k ₂ (g mg ⁻¹ min ⁻¹)	q _{e (cal)} (mg/g)	R ²
25	10.2	0.0091	11.23	0.995
50	19.7	0.0027	23.25	0.991
100	29.25	0.0024	33.33	0.992

3.8 Desorption studies:

Desorption study is an important for the recycling of the adsorbent, and the recovery of the adsorbent surface, to enhance the economical value of adsorption process. Desorption studies were carried out by batch method. Elution using HCl (0.1 M) in the Hg(II) desorption, and the successive adsorption-desorption was carried out four times.

3.9 Removal of Hg(II) from chloro alkali waste water

Chloro-alkali wastewater contains a high concentration of different ions, e.g. Cl⁻, Na⁺, Ca⁺⁺ and Mg⁺⁺, which can interfere during the adsorption of Hg(II) on the MDPT. Therefore, the selectivity of adsorbent is an important factor. MDPT is a good adsorbent with high capability of Hg(II) ion removal (99.7%) from chloro-alkali wastewater.

4. CONCLUSIONS

Adsorption process revealed that the initial uptake of Hg(II) was rapid and equilibrium was achieved within 120 min. The optimum pH for maximum adsorption was found to be 5. An adsorbent dosage of 20.0 g/L was required to remove 99.4% Hg(II) from a solution of initial concentration, 100 mg/L. Experimental results indicate that the adsorption process follows a pseudo-second-order reaction kinetics. The isotherm studies show that the adsorption data correlate well with the Langmuir isotherm model. The adsorption process of Hg(II) ions on MDPT is mainly due to the complexation of Hg(II) ions with MDPT. This study demonstrates that the MDPT can be used as a potential adsorbent for the treatment of wastewater containing Hg(II) ions.

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