

Isotherm studies on removal of lead(II) ions from wastewater by magnetic carbon synthesised from *Euphorbia hirta* leaf extract

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In this article a magnetic carbon (MEHLC) has been synthesised from *Euphorbia hirta* leaf (EHL) extract to investigate the adsorption capacity of lead(II) ions from aqueous solutions and industrial wastewater. The prepared magnetic carbon (MEHLC) is compared with raw material (EHL) under the batch adsorption process such as contact time, pH, adsorbent dose and temperature. The adsorbents are characterized by FT-IR, SEM and EDX studies. The maximum removal is obtained at 300 K and the Langmuir isotherm of MEHLC and EHL is found to be with applicable q_m value of 385.86 and 21.96 mg g⁻¹, respectively. Various thermodynamic parameters, including the standard Gibbs free energy (ΔG°), standard enthalpy (ΔH°) and standard entropy (ΔS°), are evaluated. The MEHLC and EHL are tested with lead(II) plating wastewater through a batch mode process over five cycles; MEHLC showed better results than EHL.

Keywords: Removal of Lead(II), *Euphorbia hirta* leaf, Isotherm, Kinetic parameters

Nowadays, as a result of population and industrial growth, many countries over the world have insufficient water to support both human and ecosystem. Hence, adoption of a water security strategy by treatment of wastewater and its reuse has become a prime issue for those countries. Heavy metals are one of the most common pollutants in wastewater. Various government agencies have imposed strict environmental legislations on these wastewater discharges¹. Among different heavy metals, Lead is one of the toxic heavy metal pollutants, owing to its origin from many industrial processes including the production of batteries, metal products, and devices to shield X-rays, ceramic products, pipe solder, metal plating, and oil refining manufacturing^{2,3}. Lead ions are entering the body via inhalation, ingestion or skin absorption and accumulate mainly in bones, brain, kidney, and muscles and cause many serious problems such as damage of the central nervous system, kidney and liver diseases, anaemia, irritability, weakness of muscles, and sickness even death^{4,5}. Due to the toxic effects of this metal, the removal of this metal from water and wastewater becomes essential for public health and the environment.

In recent years, chemical oxidation, coagulation, membrane processes, ion exchange, distillation, reverse osmosis, biological treatment, solvent extraction,

adsorption and electrochemical techniques were reported as various technologies for removing heavy metals from wastewaters⁶⁻⁸. Due to the limitations of the above methods in terms of health, operational costs, and generation of toxic by-products, the sorption process has been nominated as an efficient and cheaper technology for the removal of heavy metals from wastewater⁹. One such advanced class of adsorbent – magnetic nano-adsorbent with the help of an external magnetic field has been further successful in circumventing the solid-liquid separation problem usually encountered with nanoparticles. Such novel adsorbent, combining both nanotechnology and magnetic separation technique has not only demonstrated high adsorption efficiency due to its large surface to volume ratio, but have also shown additional benefits like ease of synthesis, easy recovery and manipulation via subsequent coating and functionalization, absence of secondary pollutants, cost-effectiveness and environmental friendliness. Till date, several magnetic nanomaterials, including saw dust¹⁰, orange peel¹¹, and cattle horn core¹², *citrus limon* wood¹³, papaya peel waste¹⁴, litchi peels¹⁵, corncob¹⁶ and *Bauhinia purpurea* pods¹⁷ have been explored for the removal of metal ions.

The objectives of this study is to develop an efficient magnetic activated carbon from *Euphorbia hirta* leaves

(MEHLC) by co-precipitation method and its use for remove lead(II) from aqueous solution. The performance of this magnetic carbon is simultaneously evaluated with the raw *Euphorbia hirta* leaves (EHL). The adsorbent were characterized by FT-IR, SEM and EDX techniques. The adsorption capacity of MEHLC and EHL for Pb(II) was investigated by assessing the impact of contact time, pH, and adsorbent dose using batch assays. Equilibrium isotherms, thermodynamics and reusability for the adsorption of Pb(II) ions on MEHLC and EHL are also determined in order to evaluate the adsorption process.

Experimental Section

Reagents and Analysis

All the chemicals used were of analytical reagent (AR) grade or highest purity available from Merck Company in India. The concentration of lead(II) ions before and after the equilibrium were determined by (Elico model - SL 163) atomic adsorption spectrometer (India). The Fourier Transform Infrared spectra were recorded using a model Shimadzu 8400S (Japan) spectrometer with KBr as background. The morphologies of the samples were studied by scanning electron microscope (SEM), model JEOL 6360, Japan). Energy Dispersive X-ray Spectroscopy (EDAX) was used to obtain the composition of elements present in the adsorbents.

Pb(II) solution preparations

1000 mg L⁻¹ of Pb(II) stock solution was prepared by dissolving 1.59 g Pb(NO₃)₂ in 1 L distilled water. The desired concentrations of lead(II) solutions were prepared by diluting the stock solution. The required volume of 0.1 N HCl or 0.1 N NaOH was used to change the pH of the solution. In wastewater studies, the real Lead electroplating wastewater collected from Perunduari in Erode district, Tamil Nadu.

Synthesis of raw *Euphorbia hirta* leaves (EHL)

Euphorbia hirta leaves were collected from local area in Salem district, Tamil Nadu, India. The collected raw material was washed carefully with deionised water to remove dust particles and other impurities. The collected raw materials was dried in a hot air oven at 100°C for 4 h and crushed into powder and stored in a bottle.

Synthesis of magnetic *Euphorbia hirta* leaves based carbon (MEHLC)

About, 10 g of anhydrous ferric chloride (FeCl₃) and 5 g of ferrous chloride (FeCl₂.6H₂O) was mixed

in 200 mL of distilled water and stirring vigorously at 80°C for 30 min. Then 12 g of powered *Euphorbia hirta* leaves was added and the solution was stirred for 1 h. Then 20 mL of 25% NaOH solution was added in dropwise manner and stirring was continued until the black coloured precipitate was obtained. The precipitate was filtered and dried at 100°C for 12 h. The resultant impregnated samples were activated at 450°C for 3 h in a muffle furnace. After cooling, the activated samples were washed with deionised water until the pH of the filtrate was about 6-7, and dried in an hot air oven for 6 h at 110°C. The obtained samples were named as magnetic *Euphorbia hirta* leaves based carbon (MEHLC) and stored in a bottle then used for further experiments.

Batch adsorption studies

Batch experiments were conducted in plastic bottles of 300 mL capacity on a temperature controlled shaker. The effects of the contact time, pH value, and adsorbent dose were investigated using an initial Pb(II) concentration of 20 mgL⁻¹. The effect of a particular parameter was studied by progressive variation of the selected parameter while keeping the other two parameters constant. After the adsorption experiments, the solutions were centrifuged and then filtered the concentration of Pb(II) in the filtrates was determined via atomic absorption spectroscopy at 283.3 nm. The lead(II) removal (%) was calculated using the following equation:

$$\text{Removal (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

The adsorption capacity of Pb(II) ions adsorbed per gram of adsorbent (mg g⁻¹) was calculated by:

$$\text{Adsorption capacity (q}_e\text{)} = \frac{C_0 - C_e}{M} \times V \quad (2)$$

where, C_e and C₀ are the equilibrium and initial concentrations of Pb(II) (mg L⁻¹); V is the volume of Pb(II) solution (L); M is the mass of the adsorbent used (g); q_e is the adsorption capacity at equilibrium (mg g⁻¹), respectively.

Isotherm Studies

Solutions with Pb(II) concentrations of 10-60 mg L⁻¹ were prepared by adequately diluting the stock solutions of Pb(II). The pH was adjusted to 6.0 using 0.1 M HCl and 0.1 M NaOH solutions. A 100 mg sample of the prepared MEHLC and EHL was added

to 100 mL of each metal ion solution, and the solutions were then agitated for 24 h at 300, 310 and 320 K. Subsequently, the suspensions were filtered, and the filtrates were analyzed for Pb(II). Freundlich, Langmuir and Dubinin-Radushkevich isotherms were plotted using standard non linear equations, and the corresponding parameters were calculated from the respective graphs.

Thermodynamic studies

A series of plastic bottles of 300 mL capacity containing 100 mL Pb(II) solutions (20 mg L^{-1}) were kept in a temperature controlled mechanical shaker and the temperature values of the shaker was set at 300, 310 and 320 K for the respective samples. The pH of the solutions was adjusted to 6.0 using 0.1 M HCl and 0.1 M NaOH solutions, and the bottles were agitated mechanically at 220 rpm. At set intervals, the solutions were centrifuged and filtered, and the filtrates were analyzed for Pb(II). The standard free energy (ΔG), enthalpy changes (ΔH), and entropy changes (ΔS) were calculated to assess the feasibility of the adsorption process.

Results and Discussion

FT-IR analysis

FTIR spectroscopy is a useful tool to identify the different functional groups present in an adsorbent. FTIR spectrum of EHL and MEHLC before and after the uptake of Pb(II) ions are shown in Fig. 1. The bands within the range of $3431 - 3448 \text{ cm}^{-1}$ correspond to OH group (alcohols, phenols and carboxylic acids) which is accountable for the metal binding process. The bands observed at $1739 - 1743 \text{ cm}^{-1}$ could be designated the C=O stretching vibration of carboxyl groups. At the same time as comparing the both raw and magnetic carbon, there are various functional group values are shifted on the surface of MEHLC and Fe-O group is observed at a frequency of 582 cm^{-1} . The FTIR spectrum of Pb(II) ions loaded EHL and MEHLC shows that the peaks are shifted slightly from their original arrangement and their values of intensity are also distorted, implicating the participation of these functional groups in the metal binding process.

SEM and EDAX studies

The SEM images shown in Figs. 2 a and b reveal the porous structure of the EHL and MEHLC surface. Comparing the SEM images of the EHL and MEHLC before and after adsorption demonstrates that the

metal ions are adsorbed. The adsorption is also confirmed with an EDX analysis. After adsorption of the metal ions, the pores EHL and MEHLC are covered. The EDX spectra of the Pb(II) ions adsorbed on EHL and MEHLC show that the peaks for the metal ions in addition to the other cations, confirming the adsorption of Pb(II) ions on the surface of the adsorbent (Figs. 2 c and d).

Effect of contact time

Contact time is an important factor for economical adsorption. The effect of contact time on adsorption behaviour of solution (100 mL) containing 20 mg L^{-1} of Pb(II) ions was studied in different time intervals ranging from 0.5 to 5 h, carbon dose of 100 mg and at pH of 5.0 ± 0.3 are shown in Fig. 3. After equilibrating for different time, the solutions were centrifuged, analysed for Pb(II) content and the percent adsorption in each case was determined.

The effect of contact time on the adsorption of Pb(II) ions onto MEHLC and EHL are shown in Fig. 3. The experimental data showed a rapid increase in the initial Pb(II) adsorption up to 1 h. After that, the adsorption rate became slower, and finally, no further significant adsorption was noted beyond 2 h for MEHLC and 3 h for EHL. This could be attributed to a larger number of vacant binding sites available for adsorption during the initial stage, which carried out via physical adsorption or ion exchange on the surface of the adsorbent. After prolonging the contact time, the occupation of the remaining vacant sites was

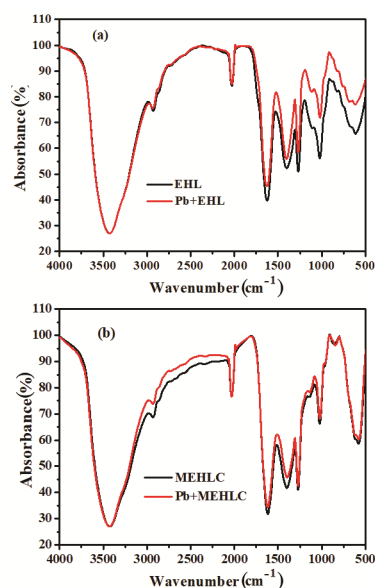


Fig. 1 — FTIR spectra of (a) EHL and (b) MEHLC before and after the adsorption of Lead

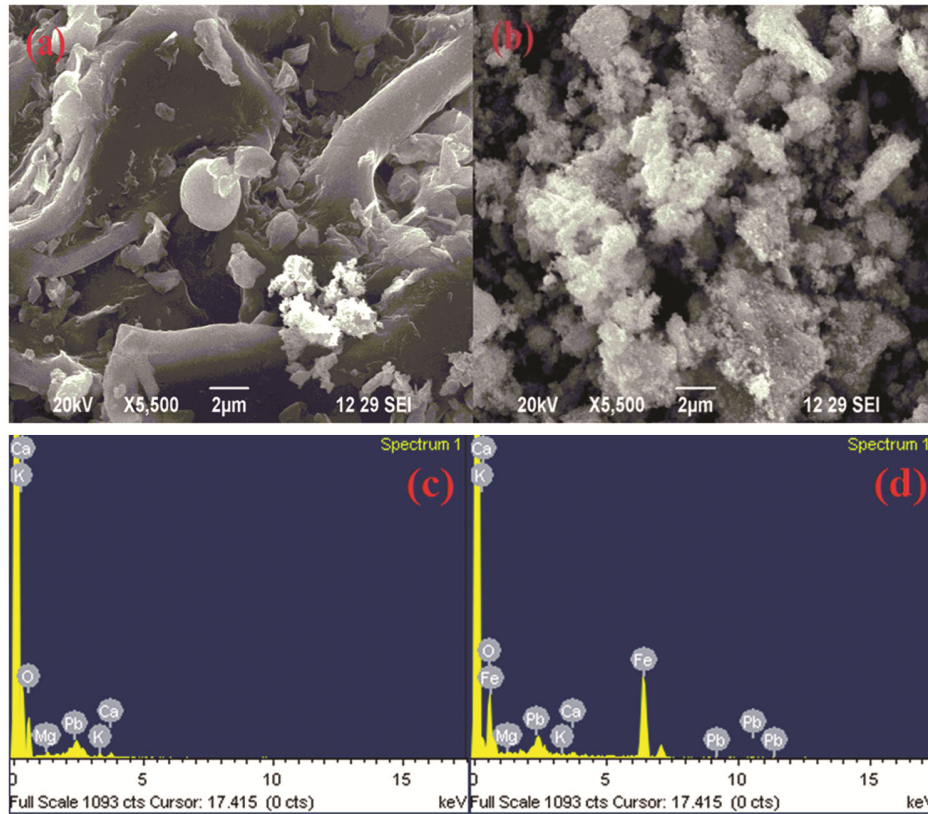


Fig. 2 — (a & b) SEM image of EHL and MEHLC and (c & d) EDX patterns for EHL and MEHLC for after Pb(II) adsorption

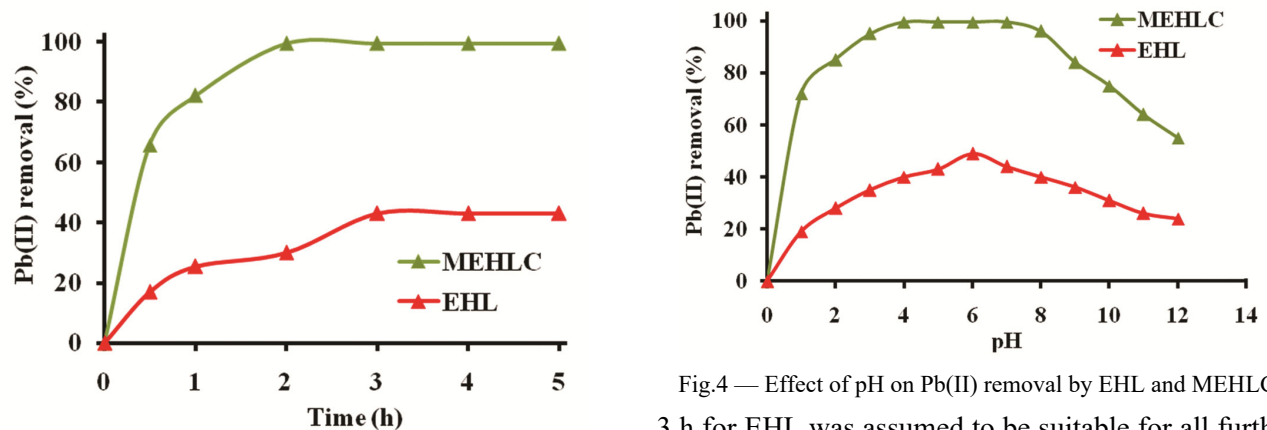


Fig. 3 — Effect of contact time on Pb(II) removal by EHL and MEHLC

difficult as a result of the repulsive forces between Pb^{2+} ions in solid and liquid phase.

The obtained results from the Fig. 3 shows that the maximum removal of 99.5 ± 0.3 % of Pb(II) ions was attaining equilibrium within 2 h for 100 mg of MEHLC. However, in the case of EHL, the equilibrium time of 3 h was used to maximum removal of 43.2 ± 0.4 % of Pb(II) ions. Based on these results, a contact time of 2 h for MEHLC and

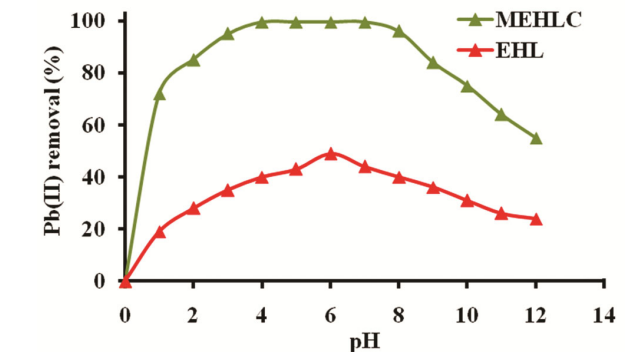


Fig.4 — Effect of pH on Pb(II) removal by EHL and MEHLC
3 h for EHL was assumed to be suitable for all further subsequent studies.

Effect of pH

The pH is a dynamic and very important environmental factor controlling heavy metals' site dissociation, speciation, adsorption, accessibility and solution chemistry. To investigate the effect of pH on Pb(II) adsorption rate was studied about 100 mL of solution containing the concentration of 20 mg L^{-1} , over a pH range of 2.0 to 10.0, adsorbent dose of 100 mg, and at a contact time of 2 h for MEHLC and 3 h for EHL. The results are shown in are exposed in Fig. 4.

It is observed from the figure that the adsorption characteristics are highly pH-dependent and maximum removal of 99.5 ± 0.4 % Pb(II) ions onto MEHLC was achieved over a pH range of 4.0-6.0. However, in the case of EHL the maximum Pb(II) removal was found to be 49 ± 0.4 % at pH of 6.0. It has been observed that under at low pH, the amount of metal ion adsorption was very small, because the active adsorption sites remain protonated. As pH increases, the concentration of H^+ ions decreased, hence they do not compete with metal ions on the adsorption sites, the more adsorption surface with negative charge will easily attract the positively charged metal ions. At higher pH, metal hydroxide starts precipitating from the solution, making actual adsorption studies impossible. Therefore, further experiments were carried out at an optimum pH value of 5.0 for MEHLC and in the case of EHL, the optimum pH value was taken as 6.0 for the removal of Pb(II) ions respectively.

Effect of adsorbent dose

From economic point of view, it is essential to study the influence of adsorbent dose to determine the minimum weight of adsorbent required for the effective removal of metal ions. The effect of carbon dose was studied for the adsorption of 100 mL of solution containing the concentration of 20 mg L^{-1} of Pb(II) ions, MEHLC and EHL dose range from 50-300 mg at an optimum pH and contact time of 2 h for MEHLC and 3 h for EHL. The results are shown in Fig. 5, which indicates that adsorption increased with increasing carbon dose up to a certain value and then became almost constant. It was observed that a minimum MEHLC dose of 100 mg is required for the maximum removal of 99.9 ± 0.1 % Pb(II) ions.

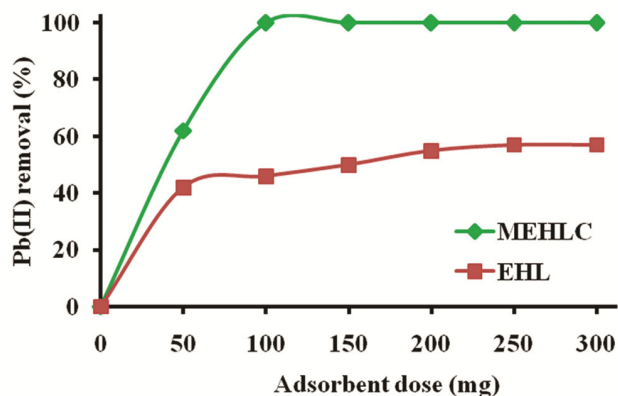


Fig. 5 — Effect of adsorbent dose on Pb(II) removal by EHL and MEHLC

However, in the case of EHL, the maximum Pb(II) removal of 57 ± 0.3 % is obtained by an carbon dose of 250 mg. This may be due to the fact that higher the dosage of adsorbent greater the availability of surface area and the functional groups for metal ions. These chemical groups play an important role in the formation of van der Waals bonding as the functional groups play the main role in binding metals to the adsorbent during adsorption process. This provides more possibilities for adsorption to occur as there was less competition between metals for the binding sites. The above result indicates that MEHLC is 2.5 times more effective than EHL with respect to carbon dose.

Adsorption isotherms

The Freundlich isotherm is regarded as one of the earliest empirical equations, and is shown to be consistent with exponential distribution of the active centers¹⁸. This model assumes that the adsorption of metal ions occurs on a heterogeneous surface. The Freundlich¹⁹ equation can be expressed as follows:

$$q_e = K_F C_e^{1/n} \quad (3)$$

where K_F is the Freundlich constant ($(\text{mg g}^{-1})(\text{L mg}^{-1})^{(1/n)}$) related to the bonding energy and n (g L^{-1}) is a measure of the deviation from linearity of adsorption. This value indicates the degree of non-linearity between solution concentration and adsorption as follows: if $n=1$, adsorption is linear; if $n<1$, adsorption is a chemical process; if $n>1$, adsorption is a physical process.

The Langmuir isotherm model is commonly applied to adsorption on a completely homogenous surface²⁰. This model assumes a uniform energy for adsorption on the substrate surface, and that maximum adsorption depends on the saturation level of the monolayer. The Langmuir model can be expressed as follows:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (4)$$

where q_m (mg g^{-1}) is the maximum monolayer adsorption capacity, and K_L (L mg^{-1}) Langmuir constant relating to adsorption energy.

The Dubinin-Radushkevich²¹ isotherm is explored to discover the adsorption mechanism based on the potential theory assuming a heterogeneous surface. Dubinin-Radushkevich isotherm is expressed as follows:

$$q_e = q_{mD} e^{-\beta e^2} \quad (5)$$

where q_{mD} (mg g^{-1}) is the Dubinin-Radushkevich monolayer capacity, β is a constant associated to sorption energy, and ε is the Polanyi potential which is interrelated to the equilibrium concentration as follows

$$\varepsilon = RT \ln\left[1 + \frac{1}{C_e}\right] \quad (6)$$

where R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}$) and T is the absolute temperature. The constant β gives the mean free energy, E , of sorption per molecule of the sorbate when it is transferred to the surface of the solid from infinity in the solution and can be computed using the relationship:

$$E = \left[\frac{1}{\sqrt{2\beta}}\right] \quad (7)$$

The magnitude of E is used to decide the type of adsorption mechanism. When one mole of ions is transferred to the adsorbent surface, if the value of E is less than 8 kJ mol^{-1} , it is physical adsorption²², if the value is between 8 and 16 kJ mol^{-1} , it indicates the adsorption process follows ion-exchange²³, and if its value is in the range of 20 - 40 kJ mol^{-1} , it indicates chemisorptions²⁴.

The isotherm constants, correlation coefficients (R^2), sum of squares error (SSE) and root mean squared error (RMSE) values were calculated at different temperatures from the plot of q_e versus C_e

(Fig. 6a and b) and are summarised in Table 1. The R^2 values nearer to 1 and small SSE, RMSE values indicate better curve fitting. Based on the R^2 , SSE and RMSE values from Table 1, the Langmuir isotherm model exhibited a better fit for EHL and MEHLC to the adsorption Pb(II) ions. The best fit of equilibrium data in Langmuir adsorption isotherm model for the maximum monolayer adsorption capacity of lead(II) ions onto MEHLC was found to be 385.86 mg g^{-1} , which was about 17.6 times greater than that of EHL (21.96 mg g^{-1}) at 300 K , respectively. The maximum monolayer adsorption capacity (q_m) decreases with the increasing temperature, representing an exothermic process. The calculated E values of the present study is below 8 kJ mol^{-1} , which indicates that the removal of Pb(II) ions onto the EHL and MEHLC follows physical adsorption type. Therefore, the adsorption of lead(II) ions onto MEHLC surface is a complex, involving more than one mechanism.

The Pb(II) adsorption capacity was compared to various adsorbent and are listed in Table 2. The value of Pb(II) ions sorption observed in the present study is in good agreement with values found by other researchers. Differences of metal uptake are due to the properties of each adsorbent such as structure, functional groups and surface area. Therefore, it could be concluded that the MEHLC has a promising adsorbent for the removal of Pb(II) ions from aqueous solutions.

Table 1 — Adsorption isotherm constants for the removal of Pb(II) ions by MEHLC and EHL at different temperatures

Isotherm model	Parameters	MEHLC			EHL		
		300 K	310 K	320 K	300 K	310 K	320 K
Freundlich	K_F	12.14	8.815	6.728	4.527	2.747	2.035
	n (g L^{-1})	1.965	1.950	1.833	2.246	1.650	1.531
	SSE	19.58	11.95	15.96	11.35	10.56	9.670
	RMSE	2.212	1.778	1.997	1.685	1.359	1.215
	R^2	0.969	0.978	0.965	0.936	0.956	0.963
Langmuir	q_m (mg g^{-1})	385.86	306.75	281.50	21.69	18.57	17.20
	K_L (L mg^{-1})	0.189	0.121	0.060	0.082	0.071	0.065
	SSE	1.567	1.722	1.621	0.608	0.878	0.980
	RMSE	0.990	0.656	0.809	0.450	0.478	0.560
	R^2	0.996	0.998	0.995	0.997	0.996	0.995
Dubinin- Radushkevich	q_{mD} (mg g^{-1})	40.86	30.75	25.35	20.37	15.45	12.55
	β ($\text{mg}^2 \text{ J}^{-1}$) $\times 10^{-7}$	1.529	1.356	1.124	9.236	7.826	5.526
	E (kJ mol^{-1})	1.667	1.446	1.244	0.714	0.514	0.345
	R^2	0.889	0.838	0.825	0.908	0.890	0.850
	SSE	105.6	98.56	78.54	16.24	14.25	12.65
Thermodynamic	RMSE	5.137	4.567	4.878	2.015	3.058	4.578
	ΔG^0 (kJ mol^{-1})	-127.20	-87.629	-48.288	-0.998	-0.773	-0.532
	ΔH^0 (kJ mol^{-1})		-133.69			-10.716	
	ΔS^0 ($\text{kJ mol}^{-1}\text{K}^{-1}$)		-0.403			-0.033	

Effect of temperature and thermodynamic parameters

The batch adsorption studies were performed at different temperatures of 300, 310 and 320 K for the initial Pb(II) ions concentration of 20 mg L⁻¹ at constant EHL and MEHLC dose of 1 and 2.5 g L⁻¹ at an optimum pH value of 5. The adsorption percentage of Pb(II) ions decreases with the increase in temperature (Fig. 7a). This is mainly due to the decrease in surface activity suggesting that the adsorption between lead(II) and EHL and MEHLC is an exothermic process.

Thermodynamic parameters such as free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) change of adsorption can be evaluated from the following equations

$$K_c = \frac{C_a}{C_e} \quad (8)$$

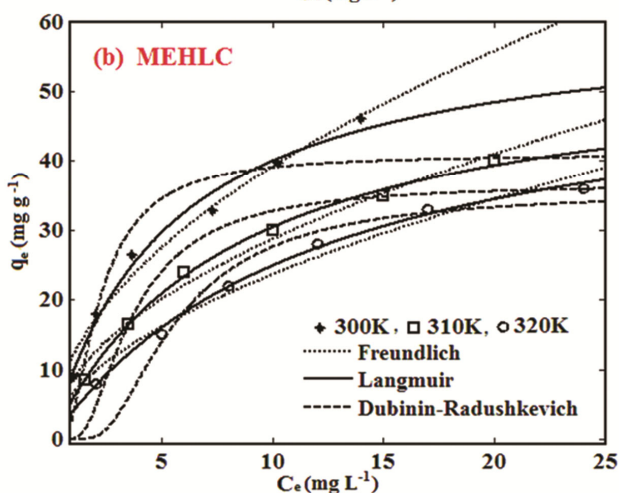
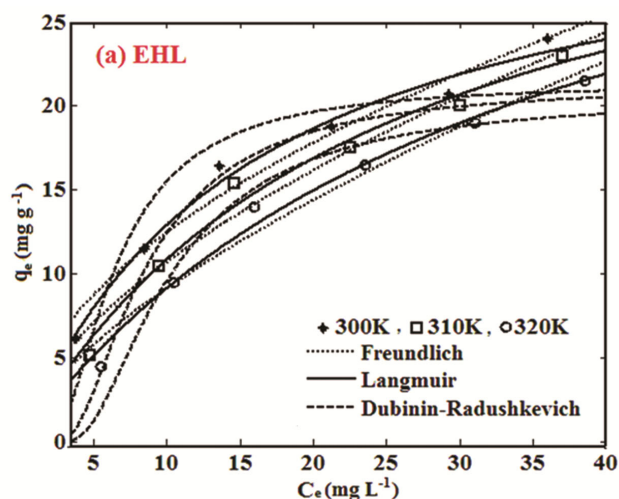


Fig. 6 — The nonlinear isotherm for the removal of lead(II) ions onto EHL and MEHLC

$$\Delta G^0 = -RT \ln K_c \quad (9)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (10)$$

$$\ln K_c = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (11)$$

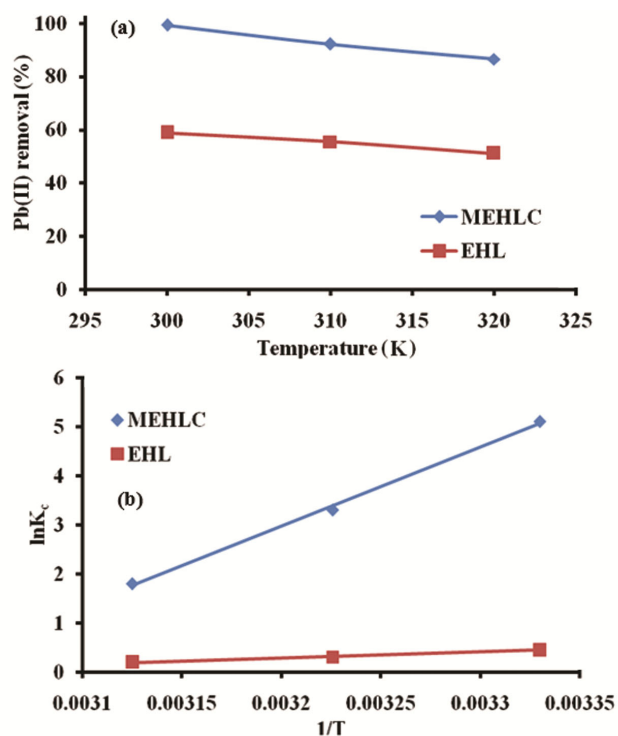


Fig. 7a — (a) Effect of temperature on Pb(II) removal by EHL and MEHLC and (b) Thermodynamic plots for the removal of Pb(II) ions by EHL and MEHLC

Table 2 — Langmuir Monolayer adsorption capacities in the literature for the removal of Pb(II)

Adsorbent	q_m (mg g ⁻¹)
Peanut shell ²⁵	188.68
Mangosteen shel ²⁶	58.48
Corn husk ²⁷	2.814
Rice husk ²⁸	252.52
Cocoa pod husk ²⁹	2.426
<i>Terminalia mantaly</i> seed husk ³⁰	99.95
Durian husk ³¹	36.10
Sunflower seed husks ³²	74.07
<i>Jatrophas curcas</i> husk ³³	44.05
Hazelnut husk ³⁴	109.9
<i>Citrus limetta</i> leaves ³⁵	69.82
Neem (<i>Azadirachta indica</i>) leaf ³⁶	205.6
Banana peel ³⁷	34.5
Pineapple fruit peel ³⁸	28.55
Prickly pear seed cake ³⁹	158.4
<i>Moringa oleifera</i> leaves ⁴⁰	45.83
EHL (Present study)	21.96
MEHLC (Present study)	385.86

Table 3 — Characteristics of lead plating industry wastewater

Parameter	Concentration
pH	2.90
Total solid, mg L ⁻¹	4569.00
Turbidity, NTU	15.00
Chloride, mg L ⁻¹	569.00
Sulphate, mg L ⁻¹	1036.00
COD, mg L ⁻¹	36.00
Iron, mg L ⁻¹	17.50
Lead, mg L ⁻¹	150.00
Sodium, mg L ⁻¹	258.00
Calcium, mg L ⁻¹	59.00
Magnesium, mg L ⁻¹	146.00

Table 4 — Five cycles of Pb(II) adsorption-desorption with 0.4 N HCl as the desorbing agent

Cycles	Pb(II) concentration (mg L ⁻¹)	EHL		MEHLC	
		Adsorption (%)	Recovery (%)	Adsorption (%)	Recovery (%)
1	150	67.42	61.41	99.40	99.00
2	150	63.39	36.57	99.17	99.05
3	150	56.18	34.14	99.22	98.74
4	150	49.15	33.54	99.10	97.80
5	150	45.35	30.25	99.90	95.13

where, K_c is the equilibrium constant (L g⁻¹), C_e is the equilibrium concentration (mg L⁻¹), C_a is the amount of lead(II) adsorbed on the adsorbent per liter of solution at equilibrium (mg L⁻¹), R is the gas constant (8.314 kJ mol⁻¹ K) and T is the absolute temperature (Kelvin). The values of enthalpy change (ΔH°) and the entropy change (ΔS°) were determined from the slope and the intercept from the plot of $\ln K_c$ versus $1/T$ (Fig. 7b) and are listed in Table 1. The negative value of ΔG° implies that the adsorption of Pb(II) ions onto EHL and MEHLC was spontaneous and feasible. The ΔG° value is more negative when decreasing the temperature, suggesting that lower temperatures favour the adsorption. The negative ΔH° value indicates the exothermic nature of adsorption and the ΔS° can be used to describe the randomness at the adsorbent- solution interface during the sorption.

Removal of lead(II) from electroplating wastewater and Regeneration studies

The batch experiments with real Pb electroplating wastewater collected from Perunduari in Erode district, Tamilnadu. The Pb electroplating wastewater characteristics are shown in Table 3. As the wastewater containing 150 mg L⁻¹ Pb(II) ions, the optimum EHL and MEHLC doses of 3 and 1 g L⁻¹ were required for the maximum removal of 67 (± 0.4) and 99 (± 0.5)%, respectively. Therefore, MEHLC is

3 times more effective than EHL when treating Pb plating wastewater due to ion-exchange capacity is observed in MEHLC.

The applicability of the adsorbent for repeated uses was determined by 0.4 N HCl was used to regenerate the adsorbent over five cycles of operation. From the Table 4, it is clearly indicated that the MEHLC can be used repeatedly for five cycles of operations without affecting its adsorption capacity for Pb(II) ions. However, the recovery of Pb(II) ions decreased in MEHLC from 99 to 95% during the five cycles because the Pb(II) ions were strongly bound to the new opening sites. In the case of EHL (Table 4), both adsorption and desorption values decreased rapidly. These results showed that MEHLC has a greater potential for repeated use and recovery. The attrition losses were also calculated at the end of the fifth cycle. The MEHLC showed 2.0 % losses on average, while EHL showed that 6 – 7% losses at the end of the cycle during batch mode operations.

Conclusion

The *Euphorbia hirta* leaf and its modified magnetic carbon can be used to remove 67 to 99% of the Pb(II) from aqueous solutions. The presence of hydroxyl, carboxylic and Fe-O groups in MEHLC is confirmed by FTIR spectroscopy, imparting ion exchange properties to the MEHLC. The equilibrium data agreed with the Langmuir isotherm, and the adsorption capacity (Q_m) of MEHLC is 17.6 times greater than that of EHL. The thermodynamic parameters indicate that the adsorption process is spontaneous, feasible and exothermic. The experiments with Pb(II) electroplating wastewater revealed that MEHLC is more effective than EHL. The MEHLC was tested for five adsorption and regeneration cycles for the removal of Pb(II) ions from wastewater, revealing lesser tendency toward attrition when compared to EHL. Therefore, the present studies reveal that the magnetic carbon derived from *Euphorbia hirta* leaf is a very effective and inexpensive adsorbent for removing lead(II) from aqueous systems.

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