



## Synthesis of magnetic activated carbon from *Citrus hystrix* (Kaffir lime or Kolumichai) leaves with excellent Pb(II) adsorption performance towards electroplating wastewater

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The adsorption behaviour of Pb(II) ions from aqueous solution has been successfully tested by magnetic activated carbon prepared from novel adsorbent such as *Citrus hystrix* leaves (MCHLAC) by co-precipitation method and followed by thermal activation. The optimum contact time for the removal Pb(II) ions onto MCHLAC is found to be 90 min, and the optimum pH ranged from 5.0–7.0 respectively. The functionality, surface morphology and elemental composition of MCHLAC have been explored by FTIR, SEM and EDX analysis. The equilibrium data agree well with Langmuir model, which confirm the monolayer coverage of Pb(II) ions onto MCHLAC and the maximum monolayer adsorption capacity is 345.65 mg g<sup>-1</sup>. The kinetic data follow by pseudo-second order model with film diffusion process. Thermodynamic studies indicate that the process of uptake of lead(II) ions is spontaneous and exothermic. A single-stage batch adsorber is designed using the Langmuir adsorption isotherm equation. The regeneration study show that MCHLAC could be effectively utilized for the removal of Pb(II) ions for seven cycles of operation.

**Keywords:** *Citrus hystrix* leaves, Isotherm, Lead(II), Thermodynamics

Water contamination caused by heavy metals has been considered a serious global environmental issue owing to toxicity and non-biodegradable in human body. Recently, increased in industrial growth and technological activities are released the large amount of heavy metals into water bodies has become a number of environmental problems. Lead has been recognized as one of the most hazardous heavy metals, which can be often found in various industries such as electroplating, smelting, pigment, alloying, printing and battery manufacturing etc<sup>1</sup>. At very low concentration of lead may cause various severe health problems in vital organs of humans, such as damage to liver, kidney, brain cells, nervous system, blood composition, reproductive system and mental retardation etc<sup>2</sup>. As per World Health Organization<sup>3</sup> (WHO), the maximum permissible limit of lead in drinking water is 0.01 mg L<sup>-1</sup>. Therefore, the removal of lead(II) from polluted water bodies is a vital task to protect the environment.

A numerous technology have been developed to removal of lead(II) from aqueous solution such as ion exchange, chemical precipitation, coagulation and

floatation, electrochemical treatment and reverse osmosis<sup>4,5</sup>. However, these technologies require expensive treatment and disposal of secondary toxic metal sludge is very difficult when lead is present at very low concentrations. At present, scientists have been considered adsorption by magnetic activated carbon is an efficient, effective and economical method for wastewater purification. The synthesis of magnetic nanoparticle loaded activated carbon prepared from various agricultural waste such as peanut shell<sup>6</sup>, orange peel<sup>7</sup>, tea waste<sup>8</sup>, oak powder<sup>9</sup>, Saccharum officinarum leaves<sup>10</sup>, oil palm fruit bunch fibers<sup>11</sup>, cellulose and *ceiba pentandra*<sup>12</sup>, aloe vera leaves ash<sup>13</sup>, cashew nut shell resin<sup>14</sup>, pinecone<sup>15</sup>, sugarcane bagasse<sup>16</sup>, eucalyptus (blue gum) leaf residue<sup>17</sup>, pinewood<sup>18</sup>, rice husk biochars<sup>19</sup>, have been successfully used for the removal of heavy metal ions from aqueous solution.

The aim of the present research is focused to investigate a new magnetically loaded activated carbon prepared from agricultural waste, such as *Citrus hystrix* leaves is used as a adsorbent for the removal of lead(II) ions from aqueous solution. The

adsorption capacity of the adsorbent was evaluated using batch experiments such as contact time, pH, MCHLAC dose and temperature. Adsorption isotherms and kinetics were investigated and different adsorbent models were used to evaluate the experimental data and to elucidate the possible adsorption mechanism. Thermodynamic studies were also carried out to estimate the standard free energy ( $\Delta G^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ). A single-stage batch adsorber was designed for different carbon dose/ effluent volume ratios using the Langmuir equation.

## Experimental Section

### Reagents and analysis

All the chemicals were used 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 performed using a model Shimadzu 8400S (Japan) Spectrometer with KBr as background. The morphologies of the samples were characterized by Scanning electron microscope (SEM, model JEOL 6360, Japan). Energy-Dispersive X-ray Spectroscopy was noted to obtain the composition of elements present in the adsorbents.

### Pb(II) solution preparations

1000 mg L<sup>-1</sup> of Pb(II) stock solution was prepared by dissolving 1.59 g Pb(NO<sub>3</sub>)<sub>2</sub> in 1 liter 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, Tamilnadu.

### Synthesis of magnetic *Citrus hystrix* leaves based activated carbon (MCHLAC)

The raw *Citrus hystrix* leaves were collected from Sengunthar arts and science college campus, Namakkal, Tamil Nadu, India, and washed with deionised water to remove impurities. Then the materials was dried in a hot air oven at 100°C for 8 h and crushed into powder. About, 12 g of anhydrous ferric chloride (FeCl<sub>3</sub>) and 6 g of ferrous chloride (FeCl<sub>2</sub>.6H<sub>2</sub>O) were dissolved in 200 mL distilled water with vigorous stirring at 80°C for 30 min. Then 10 g of powered *Citrus hystrix* leaves was added and

stirred the mixture for 1 h and 20 mL of 25 % NaOH solution was added in drop wise 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 sample was washed with deionised water until the pH of the filtrate was about 6.0 -7.0 and dried in an oven at 110°C for 6 h. The obtained samples were named as magnetic *Citrus hystrix* leaves based activated carbon (MCHLAC) and stored in a bottle then used for further experiments.

### Batch adsorption studies

Batch adsorption experiments were conducted in plastic bottles of 300 mL capacity on a temperature controlled shaker. 0.1 g of adsorbent was added to 100 mL of Pb(II) solutions of 20 mg L<sup>-1</sup> concentration at a predetermined pH at room temperature and agitated for a definite period of time. For optimization, contact time was varied between 30 to 150 min for 20-100 mg L<sup>-1</sup> Pb(II) concentrations, solution pH between 2 to 10 and MCHLAC dose between 0.02 to 0.14 g. Adsorption isotherms were conducted with 10-60 mg L<sup>-1</sup> of Pb(II) solutions by adding 0.1 g of adsorbent and equilibrated for 24 h at different temperatures (27-47°C). In kinetic studies, contact time was varied from 30-120 min by adding 0.1 g of adsorbent, for various Pb(II) concentrations over the range of 20- 40 mg L<sup>-1</sup> at optimum pH and at different temperatures (27, 37, and 47 °C) respectively. The batch experiments were repeated for three times and the average results are presented in this work.

At the end of agitation, the solutions were centrifuged and the concentration of Pb(II) ions were determined by an atomic absorption spectrophotometer (Elico Model-SL 163). The lead(II) removal (%) was calculated using the following equation:

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

The adsorption capacity of Pb(II) ions adsorbed per gram of adsorbent (mg g<sup>-1</sup>) was calculated by

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

where C<sub>e</sub> and C<sub>0</sub> are the equilibrium and initial concentrations of lead(II) (mg L<sup>-1</sup>); V is the volume of lead(II) solution (L); M is the mass of the adsorbent

used ( $g$ );  $q_e$  is the adsorption capacity at equilibrium ( $mg\ g^{-1}$ ), respectively.

## Results and Discussion

### Fourier transforms infrared spectroscopy analysis

The chemical functional groups such as carboxyl, hydroxyl and Fe-O were identified as potential adsorption sites which are responsible for binding the metallic ions to the adsorbent. The adsorption capacity of MCHLAC depends upon the porosity as well as the chemical reactivity of functional groups at the surface. This reactivity creates an imbalance between the forces at the surface when compared to those within the body, thus leading to a molecular adsorption by the vander waals force. Knowledge on surface functional groups would give an insight to the adsorption capability of the MCHLAC. The FTIR spectrum of before and after the adsorption of lead(II) ions onto MCHLAC are shown in Figs 1(a) and (b). The broad bands around at  $3474\ cm^{-1}$  corresponds to OH (hydroxyl) group. The band at 2922, 1701, 1551, 1464 and  $551.64\ 3474\ cm^{-1}$  were stands for aliphatic C-H, C=O (carbonyl), C-C (aromatic), C-H (alkane) and Fe-O group<sup>20,21</sup>. When comparing the two spectra from Figs 1(a) and (b), the above mentioned peak values were shifted, and it indicates that the presence of ionisable functional groups such as carboxyl, hydroxyl and Fe-O groups that were able to bind with heavy metal ions, in particularly lead(II) ions, were present in the MCHLAC.

### Scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDX) studies

The surface morphology of adsorbent was observed by Scanning electron microscopy (SEM). The SEM images of MCHLAC before and after the adsorption of lead(II) ions are given in Figs 2 (a) and (c). The SEM images revealed that the MCHLAC surface texture is uneven and irregular. After adsorption, the lead(II) ions cover the most of the available pores

present in spent MCHLAC adsorbent causing the surface to become saturated.

The elemental composition of the samples were analysed using Energy dispersive analysis system of X-ray (EDX). The EDX analysis for before and after the adsorption of lead(II) ions onto MCHLAC are shown in Figs 2 (b) and (d). The spectrum of MCHLAC shows that the presence of C, O, Cl, Ca and Fe in the structure. In addition to that, the existence of  $Pb^{2+}$  in the EDX spectrum may also be considered in the support successful adsorption of the metal.

### Effect of equilibrium time and initial metal ion concentration

The equilibrium time is plays an important role in the removal of pollutants from wastewater. The effect of contact time with various concentrations of lead(II) ions onto MCHLAC is shown in Fig. 3. The performance of lead(II) adsorption capacity was studied by varying contact time from 30-150 min using different lead(II) ion concentrations of 20-100  $mg\ L^{-1}$  and a constant adsorbent dose of  $0.1\ g\ L^{-1}$  at pH 7.0. It could be examined from the Fig. 3(a), the rate of removal is faster at the early stage and achieving equilibrium in 90 min. The faster lead(II) removal rate at the beginning stage is due to the larger availability of uncovered adsorption sites of MCHLAC. After that the equilibrium time, the available stimulatory forces were weakened to reach the empty surface area so that the adsorption was reduced<sup>22,23</sup>. Therefore, the contact time was considered as 90 min for MCHLAC in all subsequent experiments.

### Effect of pH

The pH of the initial solution, which determines both the nature of the metallic species and the charge on the adsorbent surface, is one of the most important parameters affecting the sorption process. In order to illuminate the sorption mechanism, the sorption tests should be performed at the optimum pH zone. The

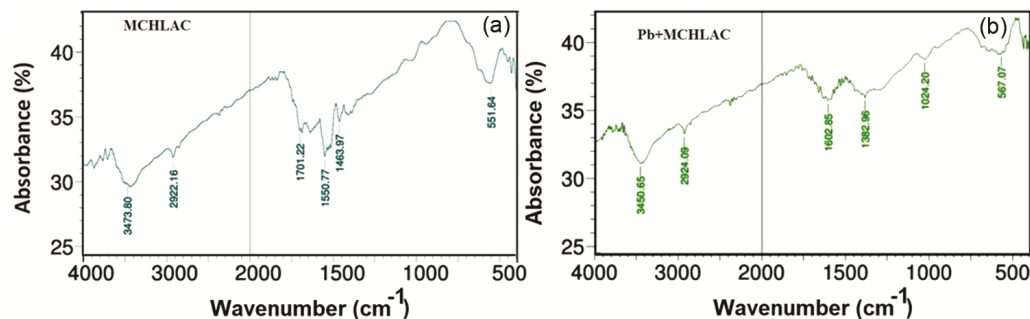


Fig. 1— (a, b) FT-IR image of MCHLAC before and after the adsorption of Pb(II) ions

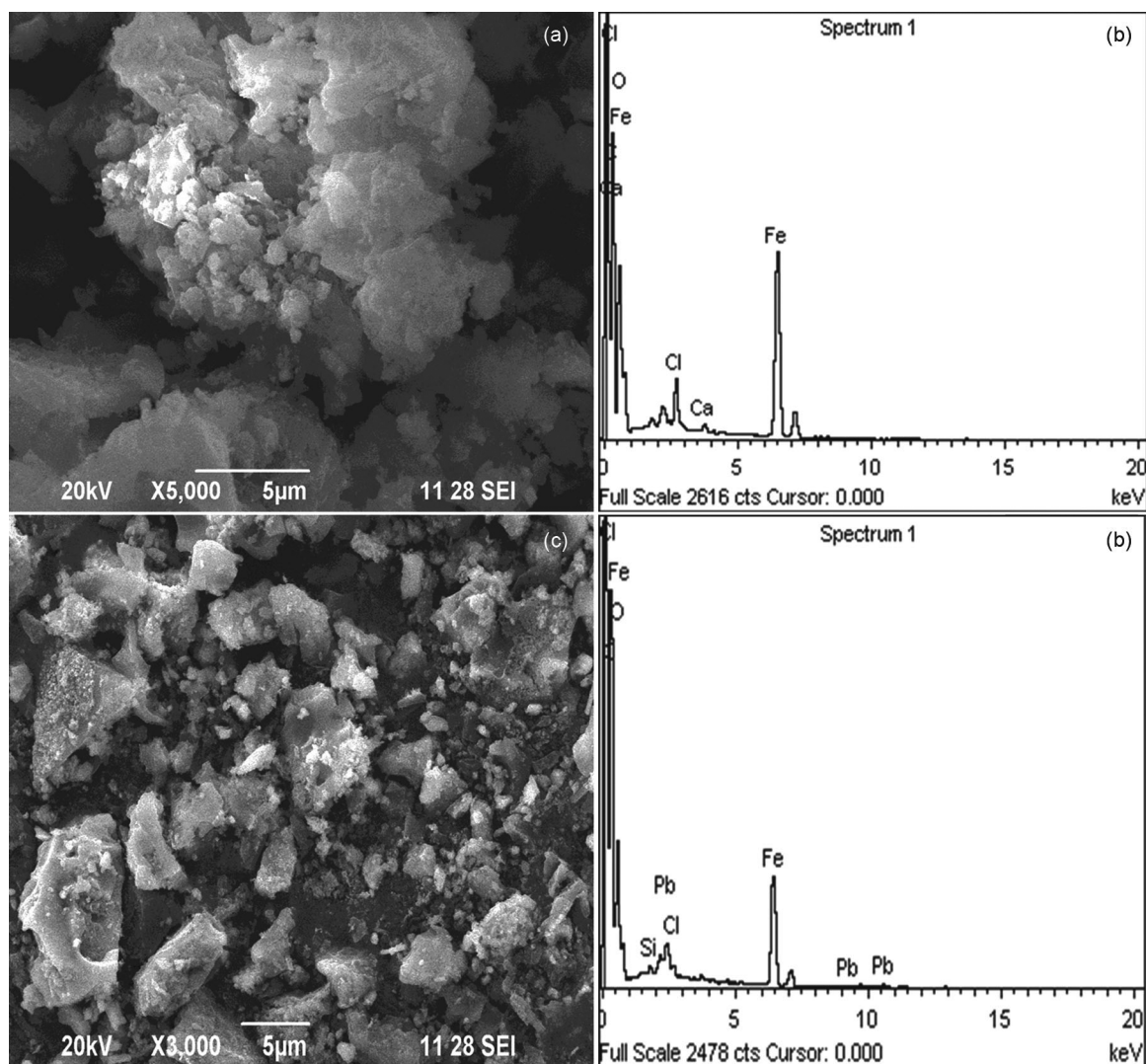


Fig. 2— (a, b, c, d) SEM micrographs and EDAX images for before and after the adsorption of lead(II) ions onto MCHLAC

effect of  $pH$  on the removal of lead(II) ions from aqueous solution onto MCHLAC was studied over a  $pH$  range of 2-10, keeping all other parameters constant as shown in Fig. 3(b). The result from the Fig. 4 represent that the uptake of lead(II) ions was found to increase with increase in  $pH$  and the maximum removal of 99.7 % at over a  $pH$  range of 5.0 – 7.0. The  $pH$  dependence of adsorption efficiency could be explained by the functional groups involved in metal uptake and metal chemistry<sup>24, 25</sup>. The FTIR spectroscopic analysis showed that the MCHLAC has a variety of functional groups such as carboxyl, hydroxyl and Fe-O groups which were involved in almost all the potential binding mechanisms. Moreover, depending on the solution  $pH$ , the functional groups participate in metal ion bindings. At low  $pH$  values,  $H_3O^+$  ions were covered at the surface

of MCHLAC and thereby, preventing the uptake of lead(II) ions. At higher  $pH$ , the negative charge was present at the surface of MCHLAC, due to the dissociation of functional group on the adsorbent surface and thereby creating repulsions to the negatively charged adsorbate species namely  $Pb(OH)_3$  and  $Pb(OH)_4^{2-}$  and thus the removal of lead(II) is less favoured<sup>26</sup>. The high lead(II) adsorption efficiency was observed at  $pH$  value of 6.0 indicate that there was no precipitation occurred in the lead(II) sorption system. Therefore, the optimum  $pH$  value of 6.0 was selected for the rest of the adsorption experiments.

#### Effect of adsorbent dose

The amount of adsorbent is the most valuable parameter. This is because the active surface of the adsorbents solely depends on its amount. Adsorbent

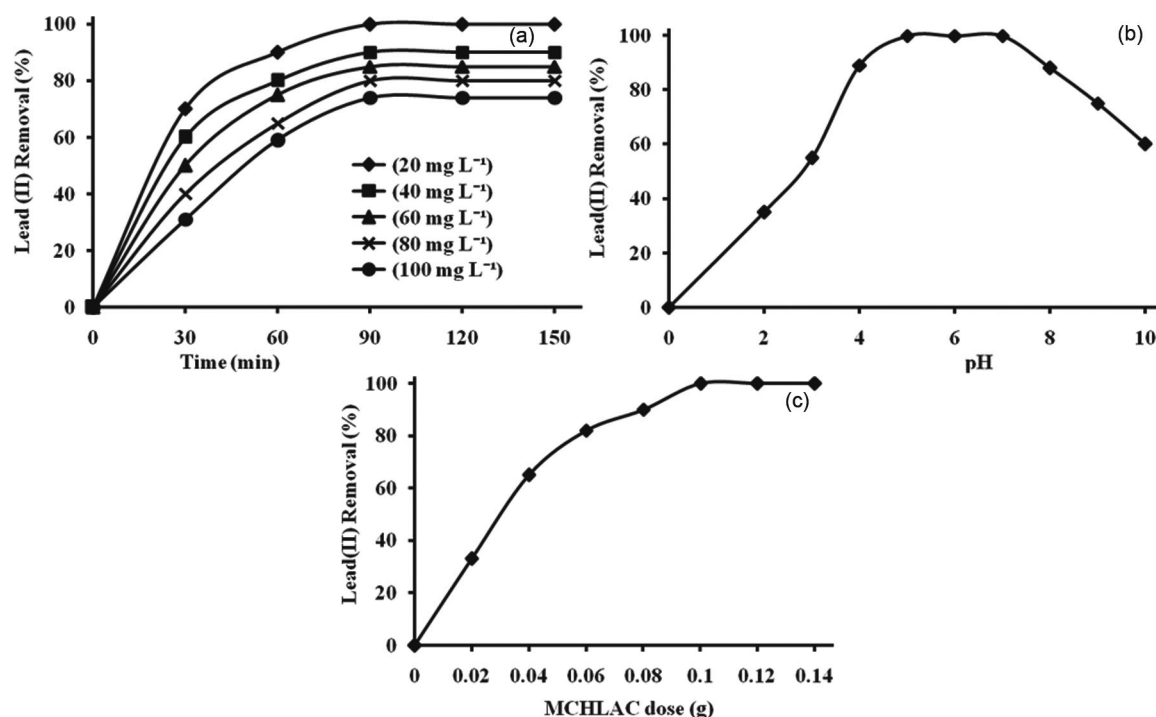


Fig. 3 — (a) Effect of contact time for the removal of Pb(II) ions onto MCHLAC at different lead(II) concentrations; (b) Effect of pH for the removal of Pb(II) ions onto MCHLAC and (c) Effect of MCHLAC dose for the removal of Pb(II) ions

dose is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of the adsorbate. The effect of adsorbent dose was tested by varying the MCHLAC dose from 0.02 to 0.14 g in 100 mL of 20 mg L<sup>-1</sup> lead(II) solutions containing an optimum pH and contact time of 6.0 and 90 min. Figure 3(c) indicates that the uptake of lead(II) ions was increased with increase in the amount of MCHLAC dose from 0.02 to 0.1 g and after that the removal percentage was not changed and attained the maximum removal of  $99.5 \pm (0.4) \%$  at 0.1g respectively. At very lower MCHLAC dose, it is known that the adsorbent surface becomes saturated with the metal ions, while the residual metal ion concentration in the solution is high<sup>27</sup>. Therefore, the increase in MCHLAC dose means an adequate amount of active sites on the adsorbent surface for repositioning metal ions and their penetration into the structure of adsorbent. According to the experimental result, the optimum MCHLAC dose for the maximum removal of Pb<sup>2+</sup> from aqueous solution was recorded as 0.1 g L<sup>-1</sup>.

#### Adsorption isotherms studies

The isotherm studies were providing extremely valuable information about the equilibrium relationship between quantity of adsorbed lead(II)

ions on the MCHLAC surface and the concentration of lead(II) ions presented in the solution. To estimate the performance of lead(II) adsorption onto MCHLAC were utilized by various nonlinear adsorption models such as Freundlich<sup>28</sup>, Langmuir<sup>29</sup>, Dubinin-Radushkevich<sup>30</sup>, Temkin<sup>31</sup>, and Sips<sup>32</sup> isotherms using MATLAB R2010b at different temperatures (27 -47°C).

#### Freundlich model

The heterogeneous adsorbent surface of the empirical nonlinear Freundlich isotherm equation is given by:

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

where  $K_F$  is the Freundlich adsorption constant ((mg g<sup>-1</sup>)(L mg<sup>-1</sup>)<sup>(1/n)</sup>) and  $1/n$  (g L<sup>-1</sup>) is the measure of the intensity of adsorption which is used to determine the types of adsorption process as follows: if  $n=1$  (linear);  $n<1$  (chemical process);  $n>1$  (physical process).

#### Langmuir model

The assumption of Langmuir isotherm model describes that the monolayer adsorption on a structurally homogeneous adsorbent, where all the

adsorption sites are indistinguishable and energetically equivalent. The expression for the nonlinear Langmuir adsorption equation is defined as follows:

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

where  $q_m$  ( $\text{mg g}^{-1}$ ) is the maximum monolayer adsorption capacity of adsorption, and  $K_L$  ( $\text{L mg}^{-1}$ ) is the Langmuir constant. The dimensionless factor " $R_L$ " value is used to determine whether the adsorption process is favourable or unfavourable can be expressed as follows<sup>33</sup> :

$$R_L = \frac{1}{1 + K_L C_0} \quad \dots (5)$$

where  $K_L$  is the Langmuir sorption constant and  $C_0$  is the initial Cd(II) ion concentration. The  $R_L > 1$  for unfavourable adsorption,  $R_L = 1$  for linear adsorption,  $0 < R_L < 1$  for favourable adsorption, and  $R_L = 0$  for irreversible process.

#### Dubinin-Radushkevich model

Dubinin –Radushkevich isotherm is used to determine whether the process of adsorption is chemical or physical character. The nonlinear form of isotherm equation is expressed as:

$$q_e = q_{mD} e^{-\beta \varepsilon^2} \quad \dots (6)$$

where  $q_{mD}$  ( $\text{mg g}^{-1}$ ) is the Dubinin-Radushkevich adsorption capacity,  $\beta$  is a constant related to sorption energy, and  $\varepsilon$  is the Polanyi potential which is related to the equilibrium concentration as follows

$$\varepsilon = RT \ln \left[ 1 + \frac{1}{C_e} \right] \quad \dots (7)$$

where  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{ K}$ ) and  $T$  is the absolute temperature. The activity coefficient ( $\beta$ ) is the useful to calculate the mean adsorption free energy  $E$ , and defined as follows:

$$E = \left[ \frac{1}{\sqrt{2\beta}} \right] \quad \dots (8)$$

The  $E$  value provides helpful knowledge about that the type of adsorption mechanism. If the value of  $E < 8 \text{ kJ mol}^{-1}$  is represents the physisorption, if the value of  $E$  lies between  $8$  and  $16 \text{ kJ mol}^{-1}$ , indicates that the process of adsorption is either ion-exchange or chemical in nature<sup>34,35</sup>.

#### Temkin model

The Temkin isotherm model represent that the heat of adsorption decreases linearly with the surface

coverage due to adsorbent – adsorbate interaction. The nonlinear form of Temkin isotherm equation is given as follows:

$$q_e = B \ln(AC_e) \quad \dots (9)$$

where  $A$  ( $\text{L mg}^{-1}$ ) is the Temkin isotherm constant and  $B$  is a constant correlated to the heat of adsorption ( $\text{kJ mol}^{-1}$ ).

#### Sips model

The Sips proposed a three – parameter equation, which is an extension of Freundlich-Langmuir model with a finite saturation capacity at high concentration. The nonlinear form of Sips equation is explored as follows:

$$q_e = q_{\max} \frac{K_s C_e^\gamma}{1 + K_s C_e^\gamma} \quad \dots (10)$$

where  $q_{\max}$  and  $K_s$  are representing the Sips maximum adsorption capability and equilibrium constant. The value of  $\gamma$  indicates the heterogeneity surface lies in between  $0$  and  $1$ . If  $\gamma = 1$ , the Sips isotherm resembles to the Langmuir isotherm predicting homogeneous adsorption, If  $\gamma < 1$ , it describe the heterogeneous system.

The better fitting of five nonlinear isotherm model was evaluated by determining the correlation coefficients ( $R^2$ ), sum of squares error (SSE) and root mean squared error (RMSE) using MATLAB R2010b from the plot of  $q_e$  versus  $C_e$  (Fig. 4). The calculated nonlinear isotherm parameters were listed in Table 1. As seen from Table 1, the higher  $R^2$  and lower RMSE, SSE values suggest that Langmuir isotherm was the most excellent fit for the adsorption of lead(II) ions onto MCHLAC at varies temperatures ( $27 - 47^\circ \text{C}$ ).

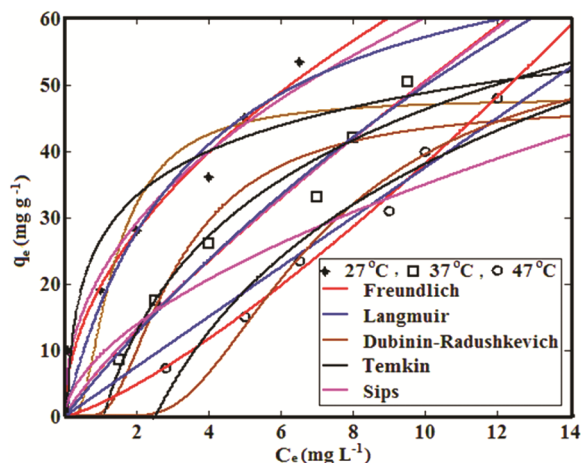


Fig. 4 — The nonlinear adsorption isotherm for the removal of lead(II) ions by MCHLAC

The calculated Langmuir monolayer adsorption capacity of lead(II) ions onto MCHLAC was found to be 345.65 mg g<sup>-1</sup>. Hence, the good fit of equilibrium data in Langmuir isotherm expression for MCHLAC confirmed the monolayer adsorption of Pb(II) ions. Furthermore, the R<sub>L</sub> values for the Langmuir isotherm fall between 0 and 1, indicating a favourable adsorption of Pb(II) ions onto MCHLAC. The estimated values of E of the present study was below 8 kJ mol<sup>-1</sup>, which indicate that the adsorption of lead(II) ions onto MCHLAC follows the physical adsorption type. From the above result indicated that the adsorption of lead(II) ions onto MCHLAC surface was a complex and involving more than one mechanism present in the adsorbent.

The performance of synthesised MCHLAC was compared with various numerous adsorbent for the

Table 1 — Nonlinear fitting isotherm constants and thermodynamic parameters for the removal of lead(II) ions

Isotherm model	Parameters	MCHLAC		
		27 °C	37 °C	47 °C
Freundlich	K <sub>F</sub> (mg g <sup>-1</sup> )	9.670	7.359	5.432
	n (g L <sup>-1</sup> )	2.479	1.195	0.779
	SSE	48.68	37.05	25.79
	RMSE	3.830	3.043	1.176
	R <sup>2</sup>	0.964	0.969	0.959
Langmuir	q <sub>m</sub> (mg g <sup>-1</sup> )	345.65	273.67	235.85
	K <sub>L</sub> (L mg <sup>-1</sup> )	0.197	0.185	0.174
	SSE	1.121	1.080	1.011
	RMSE	0.453	0.575	0.467
	R <sup>2</sup>	0.994	0.993	0.994
Dubinin-Radushkevich	q <sub>mD</sub> (mg g <sup>-1</sup> )	37.45	26.27	17.80
	β x 10 <sup>-7</sup> ((mol.K kJ <sup>-1</sup> ) <sup>2</sup> )	1.051	1.665	1.748
	E (kJ mol <sup>-1</sup> )	1.752	1.650	1.345
	SSE	45.68	50.18	39.29
	RMSE	3.456	2.898	2.664
Temkin	R <sup>2</sup>	0.940	0.955	0.975
	A (L mg <sup>-1</sup> )	12.15	11.10	10.49
	B	4.982	5.435	6.772
	b(kJ mol <sup>-1</sup> )	1.075	0.909	0.769
	SSE	18.65	15.45	12.54
Sips	RMSE	22.23	12.70	11.45
	R <sup>2</sup>	0.854	0.598	0.878
	q <sub>max</sub> (mg g <sup>-1</sup> )	48.42	39.85	31.43
	K <sub>s</sub> (L/mg)	0.176	0.152	0.137
	γ	0.993	0.822	0.654
Thermodynamic	R <sup>2</sup>	0.967	0.969	0.751
	SSE	44.23	37.26	89.92
	RMSE	3.840	3.524	9.870
	ΔG <sup>0</sup> (kJ mol <sup>-1</sup> )	-10.528	-10.114	-9.882
	ΔH <sup>0</sup> (kJ mol <sup>-1</sup> )		-11.37	
	ΔS <sup>0</sup> (kJ mol <sup>-1</sup> K <sup>-1</sup> )		-0.032	

uptake of lead(II) ions form water was illustrated in Table 2. The adsorbent used in this study is both economical and has a high sorption capacity, thereby making it a suitable for the removal of lead(II) ions from aqueous solution.

#### Effect of temperature and thermodynamic studies

Temperature is one of another important parameter affecting the adsorption process that may decrease or increase the removal of metal ions by adsorbent. The lead(II) adsorption experiment were performed in 100 mL of lead(II) solutions containing 20 mg L<sup>-1</sup> at four different temperatures varied in the range of 25-55°C under optimum pH, time and dose at 6.0, 90 min and 0.1 g respectively. The effect of temperature for the removal of lead(II) ions are represented in Fig. 5(a). From the Fig. 5(a) established that the temperature increases, the removal of lead(II) ion was decreased. This suggested that the removal of lead(II) ions onto MCHLAC was suitable at lower temperature and the nature of reaction was exothermic. At higher temperature, the removal of lead(II) ions was dropped due to shrinkage and changes in the active adsorption sites on the surface of MCHLAC.

The thermodynamic parameters were used to explain the feasibility, spontaneity and the interactions of adsorbate-adsorbent character. The change in free energy (ΔG<sup>0</sup>) for the adsorption of lead(II) ions onto MCHLAC was calculated by the following equation:

$$\Delta G^0 = -RT \ln K \quad \dots (1)$$

where R is a equilibrium constant and calculated by the Langmuir constant q<sub>m</sub> and K<sub>L</sub>. The enthalpy

Table 2 — Comparison of monolayer adsorption capacity of MCHLAC with other magnetic adsorbents reported from the literature for the removal of lead(II) ions

Adsorbents	Adsorption capacity, q <sub>m</sub> (mg g <sup>-1</sup> )	Reference
Oak powder	54.95	[9]
<i>Saccharum officinarum</i> leaves	148.00	[10]
Oil Palm Empty Fruit Bunch	181.00	[11]
<i>Ceiba pentandra</i>	49.00	[12]
Aloe vera leaves	333.30	[13]
Pinewood	42.87	[18]
Rice husk biochars	129.00	[19]
Grape stalk	247.00	[36]
MCHLAC	345.65	(Present study)

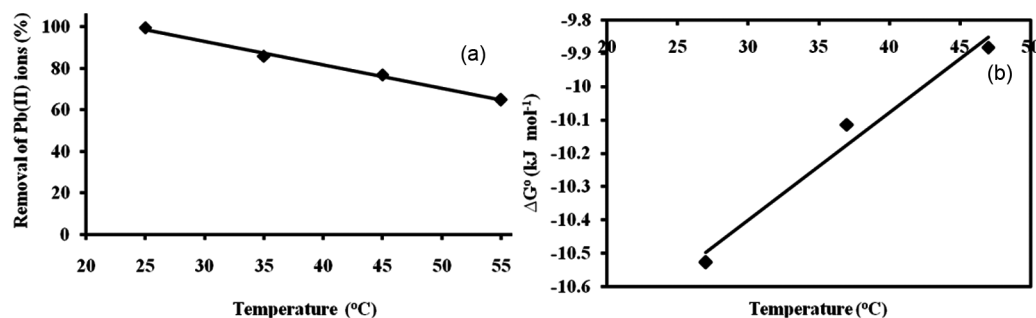


Fig. 5 — (a) Effect of temperature on the removal of lead(II) ions onto MCHLAC and (b) Gibbs free energy change versus temperature

change ( $\Delta H^\circ$ ) and entropy change ( $\Delta S^\circ$ ) values were estimated from the slope and intercept by plotting  $\Delta G^\circ$  versus  $T$  (Figure 5b) using the following equation<sup>37</sup>:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \dots (12)$$

The results of the thermodynamic parameters are given in Table 1. The negative value of Gibbs free energy replicates that the adsorption process was feasible and spontaneous in nature. The  $\Delta G^\circ$  value is more negative when decreasing the temperature, suggesting that lower temperatures favor the adsorption. The negative value of enthalpy indicates that the exothermic nature of adsorption and the entropy value used to describe the randomness at the MCHLAC-solution interface during the sorption.

#### Kinetic studies

The adsorbed amounts versus contact time experimental data and their prediction are aids in the design and modeling of adsorption systems, which in turn determine the mechanism and the potential rate-limiting steps. In the present study the pseudo-first order<sup>38</sup>, pseudo-second order<sup>39</sup> and elovich<sup>40</sup> equation was applied to analyse the equilibrium data.

The performance of kinetic studies were performed out by adding 0.1 g of MCHLAC with 100 mL of solution containing an initial concentration of 20, 30, 40 mg L<sup>-1</sup> lead(II) ions at an optimum pH of 6.0. Then the mixture of the solution was shaken in a rotary mechanical shaker for various times intervals at different temperatures (27, 37 and 47°C). The uptake of lead(II) ions at time  $t$ ,  $q_t$  was calculated as following equation:

$$q_t = \frac{(C_0 - C_t)V}{M} \quad \dots (13)$$

where  $C_t$  is the of lead(II) ion concentration at any time  $t$  (mg L<sup>-1</sup>).

The nonlinear forms of pseudo-first-order, pseudo-second-order and elovich equations are exposed in the following equation (14), (15) and (16) respectively.

$$q_t = q_e(1 - e^{-k_1 t}) \quad \dots (14)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad \dots (15)$$

$$q_t = (1 + \beta_E) \ln(1 + \alpha_E \beta_E t) \quad \dots (16)$$

where,  $k_1$  and  $k_2$  are the pseudo-first-order and second order constant;  $q_e$  and  $q_t$  are the sum of lead(II) ions adsorbed at equilibrium and at time  $t$ ;  $\alpha_E$  and  $\beta_E$  are the initial adsorption rate and desorption constant related to the extent of the surface coverage and activation energy for chemical adsorption.

The kinetic parameters namely equilibrium adsorption capacity, sum of squares error (SSE), correlation coefficients ( $R^2$ ), and root mean squared error (RMSE) are calculated as the MATLAB R2010b using the plot of  $q_t$  versus time are drawn in Figs 6 (a), (b) and (c). The kinetic parameters for the adsorption of lead(II) ions were listed in Table 3. As seen from Table 3 the correlation coefficient ( $R^2$ ) values for the pseudo-second-order model was higher than other two kinetic models. In addition to that, the calculated  $q_e$  value is found to be much closer to the experimental  $q_e$  value at different temperatures. These results confirm that the adsorption kinetics of Pb(II) ions onto MCHLAC is mainly governed by pseudo-second order equation and hence the rate-limiting step of Pb(II) ions onto MCHLAC may be chemisorptions.

#### Design of batch adsorption experiments

The best fit of the Langmuir isotherm model equation is used to predict the design of single-stage batch adsorber system<sup>41</sup>. The design objective is to reduce the initial Pb(II) ion concentration from  $C_0$  to  $C_e$  (mg L<sup>-1</sup>) of volume of solution  $V$  (L). The amount of MCHLAC adsorbent is  $M$  (g) and Pb(II) ions loading changes from  $q_0$  to  $q_e$  (mg g<sup>-1</sup>). At time  $t = 0$ ,  $q_0 = 0$  as



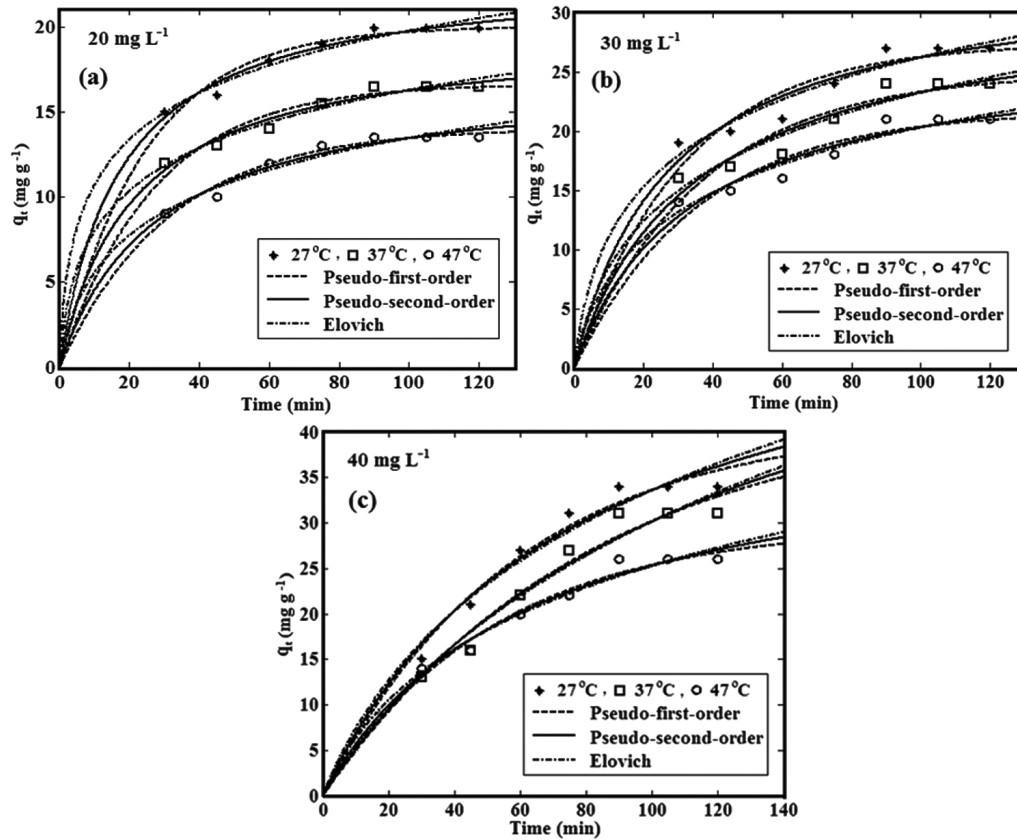


Fig. 6 — (a, b, c) Nonlinear kinetic models for the adsorption of lead(II) ions onto MCHLAC at different initial concentrations

Table 3 — Kinetic constants for the adsorption of lead(II) ions onto MCHLAC

Kinetic model	Parameters	20 mg L <sup>-1</sup>			30 mg L <sup>-1</sup>			40 mg L <sup>-1</sup>		
		27°C	37°C	47°C	27°C	37°C	47°C	27°C	37°C	47°C
Pseudo-first order	$k_1$ (min <sup>-1</sup> )	0.041	0.037	0.032	0.032	0.027	0.021	0.017	0.012	0.019
	$q_e$ cal (mg/g)	18.01	16.64	14.03	27.39	24.91	23.52	43.06	42.73	35.28
	$R^2$	0.930	0.909	0.945	0.824	0.852	0.897	0.940	0.950	0.960
	SSE	1.697	1.909	1.890	13.30	11.19	10.56	11.94	15.94	6.007
	RMSE	0.583	0.618	0.598	1.631	1.496	1.235	1.534	1.786	1.096
Pseudo-second order	$k_2$ (g/ mg/ min)	0.035	0.030	0.028	0.025	0.020	0.019	0.015	0.012	0.009
	$q_e$ cal (mg/g)	20.01	19.66	19.70	30.20	30.14	29.80	40.50	39.70	39.85
	$q_e$ exp(mg/g)	19.90	19.80	19.50	29.95	29.85	29.74	40.20	39.96	39.70
	$R^2$	0.990	0.991	0.990	0.988	0.990	0.992	0.990	0.994	0.996
	SSE	1.001	1.007	1.023	1.250	1.102	1.012	1.015	1.100	0.990
Elovich	RMSE	0.128	0.179	0.159	0.190	0.130	0.165	0.115	0.095	0.080
	a	1.752	1.12	0.509	0.170	0.094	0.057	0.006	0.002	0.015
	b	0.755	0.645	0.654	2.143	2.258	2.312	7.504	9.689	4.409
	$R^2$	0.950	0.955	0.916	0.906	0.908	0.912	0.939	0.942	0.955
	SSE	1.230	0.945	1.457	7.095	6.964	6.592	20.35	19.79	6.702
RMSE	0.496	0.435	0.540	1.191	1.118	1.110	2.017	1.989	1.158	

time proceeds, the mass balance equates the lead(II) ions removed from the aqueous solution to that picked by the MCHLAC. The mass balance for the single-stage batch adsorption system can be expressed as:

$$V(C_0 - C_e) = M(q_e - q_0) = Mq_e \dots \quad \dots (17)$$

$$\frac{M}{V} = \frac{C_0 - C_e}{q_e} = \frac{C_0 - C_e}{\frac{q_m K_L C_e}{1 + K_L C_e}} \dots \quad \dots (18)$$

From Fig. 7 shows that the plot between the calculated amount of MCHLAC required to remove Pb(II) ions containing an initial concentration of  $50 \text{ mg L}^{-1}$  for 80 %, 85 %, 90 % and 95 % removal of Pb(II) ions at different solution volume (1 to 10 L) for a single-stage batch adsorption system, for which the design procedure is outlined.

#### Lead(II) removal from real electroplating wastewater and desorption studies

Batch experiments with lead electro plating wastewater have been carried out to elucidate the applicability of the adsorbent under batch mode operations. The lead(II) wastewater was collected from local electroplating industry in near Perunduari in Erode district, Tamilnadu, India. As the wastewater having the concentration of  $128 \text{ mg L}^{-1}$  of lead(II) ions in 1 liter. The effect of MCHLAC dose for the removal of lead(II) ions in real wastewater sample were given in Fig. 8(a). It could be explored from the Fig. 8(a) the optimum MCHLAC dose of 0.6 g was required for the maximum Pb(II) removal of  $99.6 (\pm 0.4) \%$  in 1 liter wastewater containing  $128 \text{ mg L}^{-1}$  lead(II) ions. This indicates that the MCHLAC was more effective for the removal of lead(II) ions containing electroplating wastewater.

Disposal of spent adsorbent by conventional methods may not be ideal, i.e., sending to the landfill will cause the hazardous wastes to leach from the spent adsorbent, while incineration may lead to release of poisonous gases. Alternative method such as the use of regenerated spent adsorbent is not only esthetic, but also provided added value to the adsorbent in respect to its reusability. In adsorption studies the reusability of

activated carbon is one of the important parameter. The activated carbon (MCHLAC) was regenerated using 0.5 N HCl for seven cycles. The result obtained from the Fig. 8(b) showed that a slight increase in the sorption of Pb(II) could be observed after each and every cycle with MCHLAC, improving the recovery of Pb(II) ions. This increase in the sorption (99 -99.9 %) may occur because additional surface active sites present on the sorbent surface open after repeated regeneration cycles. However, the recovery of Pb(II) ions was not changed at the end of the seventh cycle. It could be concluded that the MCHLAC has a larger potential for repetitive use and recovery of lead(II) ions containing electroplating wastewater and 2.0 % attrition losses was determined at the end of the seventh series.

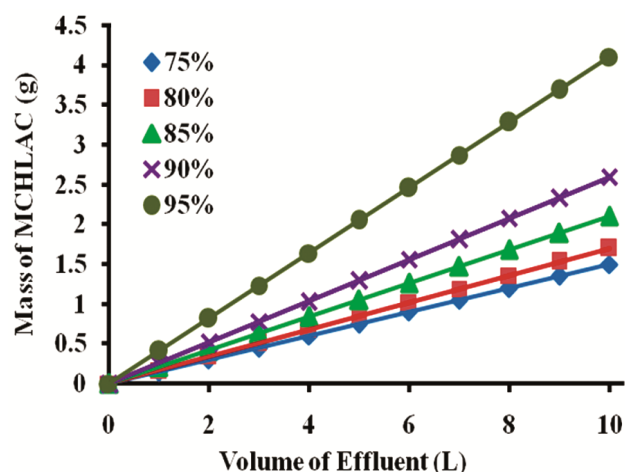


Fig. 7 — Batch design plot for the adsorption of lead(II) ions onto MCHLAC

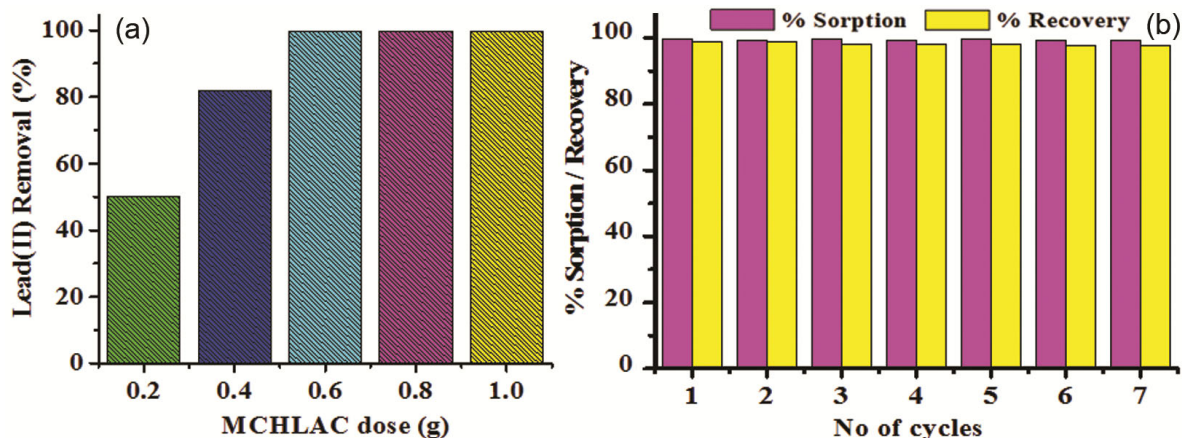


Fig. 8 — (a) Effect of MCHLAC dose for the removal of lead(II) ions from industrial wastewater and (b) The sorption-recovery of lead(II) ions onto MCHLAC with seven cycles

## Conclusion

The potential of Fe<sub>3</sub>O<sub>4</sub> loaded *Citrus hystrix* leaves activated carbon was used as a novel low cost adsorbent for the adsorption lead(II) ions from aqueous solution. The optimum metal ion concentrations, contact time, pH, adsorbent dose and temperature was 20 mg L<sup>-1</sup>, 90 min, 6.0, 0.1 g and 27°C respectively. The Langmuir isotherm model was fitted well with all experimental data and the maximum monolayer adsorption capacity was 345.65 mg g<sup>-1</sup> at 27°C. The negative value of ΔH° and ΔG° indicated that the adsorption process is exothermic and spontaneous in nature. The adsorption process could be fitted by pseudo-second order model at different temperatures. The MCHLAC could be effectively applied for industrial wastewater and exhibited a good reusability upto seven cycles. In the view of the present research results, it could be concluded that MCHLAC may be utilized as an efficient adsorbent for the removal and recovery of lead(II) ions from aqueous solution and wastewater.

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