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Removal studies of lead onto activated carbon derived from lignocellulosic *Mangifera indica* seed shell

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ABSTRACT

A novel material *Mangifera Indica* seed shell was used as an adsorbent after converting into activated carbon via acid activation for the removal of Pb(II) from aqueous solution. The effects of pH, contact time, adsorbent dose were also investigated. The sorption interaction of Pb(II) onto the activated carbon was found to obey the first-order rate equation and intra-particle diffusion model. Moreover, the experimental data showed a good fit with Langmuir, Freundlich and Temkin isotherm models. The maximum adsorption capacity of 122 mg g^{-1} was achieved under optimized conditions using Langmuir model. The thermodynamic values obtained in the study revealed that the adsorption process was endothermic and spontaneous. Furthermore, the study also confirmed the presence of surface functional groups and other surface properties of the proposed adsorbent by FTIR, SEM and EDS. The obtained experimental data thus demonstrated *M. indica* seed shell to be suitable sorbent material for removing lead from wastewater.

Keywords: Adsorption; Characterization; Activated carbon; *Mangifera indica*

1. Introduction

Heavy metal pollution has been of concern for several decades [1–3]. The most common toxic heavy metals in wastewater are arsenic, lead, mercury, cadmium, chromium, copper, nickel, zinc, etc. These heavy metals are extremely toxic to the organisms in water and also to their consumers. These pollutants have several sources; e.g. vehicular traffic, industrial and mining activities and non-regulated disposal of solid waste [4]. The major sources of heavy metals are industrial effluents; notably, from metal plating, mining operations and tanneries. Lead poisoning is very common among the Pakistani population [5]. In Pakistan, wastewater is normally contaminated from lead in the range of 200–500 mg L^{-1} of Pb(II) which is far greater than the WHO acceptable limit (0.05–0.01 mg L^{-1}). Lead is a well-known neurotoxin. Lead exposure can cause hyperactivity, anaemia, brain damage and mental retardation; adults may suffer hypertension, hearing and vision impairment, and nerve damage. Children are particularly vulnerable to lead exposure, since developing brains are more sensitive to its harmful effects.

Techniques for the removal of toxicants include chemical precipitation, ion exchange, membrane processes, and electrolytic methods [6]. Adsorption

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onto carbonaceous material is popular because of the extended surface area, micro-porous structure, high adsorption capacity and high degree of surface reactivity. Among resources available for the preparation of carbon-based adsorbents, adsorbents based on agricultural waste are attractive because of their low to nil cost. They are also as effective as adsorbents prepared from conventional sources [7]. These wastes include soybean hulls, peanut hulls, almond hulls, cottonseed hulls, apricot stone and corncobs [2,8].

Chemical activation of activated carbon is preferable to physical activation. The chemical option requires lower temperatures and takes less time to prepare. Acid activation followed by thermal treatment increases the adsorption capacity further to an extended surface area and pore volume [6]. The raw material of the prepared adsorbent usually contains lignin in high percentage. During aggressive acid activation, all organic compounds including lignin ultimately carbonize and convert into activated carbon.

There is always a need for novel raw materials for the preparation of activated carbon. The criteria for this selection are better efficiency and availability. A *Mangifera Indica* (mango) seed shell (MISS) fulfilled both criteria. Raw Mango seeds were used for adsorption of dyes and heavy metal [9] previously, but the acid-activated MISS has not been used for sorption. This is what makes the prepared material novel [10,11]. Pakistan is the third largest producer of mangoes in the world (about 1.75 million tonnes) and so the seed shell of *M. indica* (MI) is abundantly available. In order to optimize the sorption, conditions like pH and characterization of prepared activated carbon were also investigated. The study also examined some important kinetics and adsorption models connected with the adsorption process.

2. Materials and methods

Seed shells of *M. indica* were collected from the fruit juice maker of the local market, and washed with tap water to remove the flesh completely. They were then rinsed with distilled water, dried in sunlight and crushed to powder using a high speed crusher. Later, a fraction of the powder with particle size less than 180 µ was selected, treated with concentrated sulphuric acid (S.G. 1.84) in a beaker, and heated at 150˚C for 24 h using an electric oven [12]. A quantity of 4.0 g of sulphuric acid was used with each gram of raw material for this purpose. The activated carbon, thus obtained, was washed a number of times with distilled water using a filtration assembly. The adsorbent was dried in an oven at 80˚C, pulverized using mortar and pestle, and sieved again. The fraction of adsorbent passed through the sieve (BS 410, mesh number 85, 180 mics., 0.0071 ins.) was selected for further studies.

The stock solution of Pb (1,000 mg L^{-1}) was prepared using Pb(II) nitrate (extra pure, Merck) and working solutions of required concentrations were prepared by dilution.

The Pb concentration was determined using an atomic absorption spectrophotometer, Perkin Elmer 2380. The instrument was optimized as per instruction manual. The pH of the solution was adjusted using a Precisa (pH 900) pH meter.

Moisture [13], ash [14], volatile matter [15] and gross calorific value [16] were determined by using the ASTM method. The Elemental analysis (C, H, N and S) was carried out in a Perkin–Elmer, PE–2400 analyzer (Table 1). The specific surface area (SSA) of acid-activated carbon was estimated by the adsorption of methylene blue (MB) dye [17] and the iodine number was determined according to the standard procedure [18].

For the IR studies, the material was oven dried at 105˚C for 1 h to remove moisture from the material. The FTIR spectrum was recorded on a Thermo Nicolete 380 spectrophotometer using EZ Omnic software within the range of 4,000–500 cm^{-1}.

The SEM (scanning electron microscope) images and EDS (energy dispersive spectroscopy) spectra were collected using a JEOL JSM—6380 microscope.

Batch experiments were arranged to gauge the effect of various parameters like pH, agitation time, adsorptive concentration and ionic strength on the adsorption of lead on the activated carbon. For each

Table 1
Data of chemical and physical properties of acidically activated MISS

Proximate analysis (wt. %)	
Moisture	15.36
Volatile matter	19.02
Ashes	0.765
Fixed carbon	64.85
Elemental analysis (wt. % of dried material)	
C	65.77
H	4.75
N	1.87
S	0.62
O	26.22
Physical parameters	
Average pore size (from SEM)	1.26 µm
Gross calorific value	4,219 kcal kg^{-1}
Specific surface area	94.13 m^2 g^{-1}
Iodine number	77.14 mg g^{-1}
Colour	Black

batch run, 0.04 g of adsorbent and 50 mL of adsorptive solution were taken in a 250 mL Erlenmeyer flask and agitated using an orbital shaker (VRN-360) at 125 rpm.

The effect of pH on the process was studied in a pH range of 1.0–5.0. The initial pH of the solution was adjusted using either 0.1 mol L^{-1} HNO_3 or NaOH. The pH drift method was applied to determine the pH point of the zero charge (pHPZC) [19]. For this purpose, the pH of test solution was adjusted with 0.5 mol L^{-1} HCl or NaOH in the range 2.85–10.20 having 5×10^{-3} mol L^{-1} sodium chloride. A quantity of 0.05 g of adsorbent was taken into 20 mL of pH adjusted solution in a capped vial and equilibrated for 24 h at 25˚C. The pH at which curve cuts the pH initial = pH final line was considered as pHPZC.

Adsorption equilibrium studies were performed at 293 K in the range of 50–800 mg L^{-1} of Pb(II) solution.

The kinetic data of an adsorbed amount of metal at the time t, q_t (in mg g^{-1} of adsorbent), were calculated by the mass balance equation (1),

$$q_t = \frac{[(C_0 - C_t)V]}{m} \quad (1)$$

where q_t is adsorbed metal (mg g^{-1}) on the sorbents, m is the mass of sorbents (g), V is the volume of metal solution (mL), C_0 and C_t are the initial and final metal concentrations (mg L^{-1}) at any time.

Kinetic studies were investigated at 308, 318 and 328 K temperatures under optimized conditions. The effect of ionic strength was investigated at pH 3.0 and 32 ± 1˚C in the range of 0.1–0.5 mol L^{-1} of potassium nitrate with 0.04 g of adsorbent and 100 mg L^{-1} of Pb(II) ions.

The surfactant effect on the process was also investigated in the range of 0.00–0.05% of N-dodecyl pyridinum chloride (NDPC), sodium dodecyl sulphate (SDS) and Triton X-100 surfactants with 0.04 g of adsorbent at pH 3.0 and 32 ± 1˚C temperature.

Finally, the regeneration of adsorbent was carried out with 0.1 mol L^{-1} HNO_3. This process was performed in five cycles by treating the spent material with 50 mL of regenerating solution each time.

3. Results and discussion

3.1. Characterization of the adsorbent

The characteristics of activated MISS are shown in the Table 1. Proximate analysis comprises moisture, volatile matter, ash and fixed carbon. Determination of the SSA of activated adsorbent was carried out by adsorption of MB that can be adsorbed only on the negatively charged surface of the adsorbent. It has been found that the MB adsorption method has priority over the BET method. In the BET method, N_2 molecules could not penetrate into the inner layers; whereas, the MB method affects the total surface area, both external and internal [20].

The adsorbent was further analysed by SEM, using an acceleration voltage of 20 kV with 4,500× magnification.

It is evident from Fig. 1(a) that the substrate lacks the porosity that is crucial for high surface area. Acid activation increased the porosity of the parent material. The adsorbent acquired a well-defined open porous structure with an enhanced surface area having an average 1.26 μm pore size as evident from its SEM, shown in Fig. 1(b). The EDS was used for elemental analysis of the activated carbon after adsorption of Pb (II) ions as shown in Fig. 1(c).

Functional groups play an important role in the sorption process. The FTIR spectrum (Fig. 2) illustrated the oxygen containing functional group on the adsorbent surface.

The absorption with maxima 3,423 cm^{-1} showed O–H characteristic of the adsorbent. The bands at 2,374 and 2,291 cm^{-1} were due to the presence of carbon dioxide. IR absorption bands in the range of 2,800–2,930 cm^{-1} are associated with stretching of sp3 hybridized C–H bond. The band observed at 1,697 cm^{-1} was assigned to a carbonyl band (C=O) of unionized carboxylate stretching of carboxylic acid, while the band at 1,625 showed carboxyl group and 1,562 cm^{-1} attributed to C=O stretching of carboxylic acid with inter-hydrogen bond or ionized carboxyl group. IR absorption bands at 1,159 and 1,384 cm^{-1} correspond to the presence of sulphonate group introduced by the high temperature activation with conc. sulphuric acid. The IR spectra confirmed the bands corresponding to the carboxylic, hydroxyl of phenolic groups and sulphonate groups as active centres on the adsorbent for metal interaction [21].

The per cent ionization of the carboxyl and hydroxyl groups is a highly pH dependent phenomenon. The negatively charged groups on the adsorbent surface are responsible for the electrostatic attraction of cation towards the surface. The hydroxyl groups also take part in the ion-exchange process, but this may lead to a significant decrease in the pH of the solution [8].

The pH_{PZC} of non-activated and activated MISS samples were found to be 7.0 and 2.8, respectively (Fig. 3). This described the condition when the electric charge density on the surface was zero. The PZC expresses the disability of the adsorbent for the divalent metal attraction. Below this pH, the surface became positively charged and metal ions removal was not feasible. As the pH values increased above the PZC value, the adsorbent surface became predominantly negatively charged; there was an enhanced electrostatic attraction between the surface and lead cation.

3.2. Effect of pH

Adsorption of metal on activated carbon is known to be a pH-dependent process [22]. Thus, the pH effect of the lead adsorption on the activated carbon was studied in the range from 1.00 to 4.52 pH. It was observed that, for pH range 1.0–3.0, the adsorption capacity of adsorbent increased with the increase in pH. From pH 3.0 onward no significant increase in the adsorption capacity was observed (Fig. 4). This behaviour can be explained using Eqs. (2) and (3) [23]. As shown in these equations protons appear as product species and according to Le Chatelier's principle decrease in pH would shift the process to reactants side and hence the less amount of Pb(II) ions gets adsorbed onto the surface. Fig. 4 summarized the competition between Pb(II) and H^+ ions for the active sites. The protons remain dominant until pH 3.0, however, Pb(II) ions dominated from pH 3.0 onward in their competition for the active sites.

$$\text{R-COOH} + \text{Pb}^{2+} \rightleftharpoons \text{R-COOPb}^{+} + \text{H}^{+} \tag{2}$$

$$\text{R-COOH} + \text{Pb}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{R-COOPbOH} + 2\text{H}^{+} \tag{3}$$

The pH range in this study was restricted to pH 5.0 because with the increase in pH removal of Pb^{2+} takes place through precipitation of various types of lead hydroxides rather than adsorption, causes secondary problem. Results showed that the metal uptake was favoured at pH 3.0 and there was no appreciable increase in the sorption of lead at pH higher than 3, pH 3 was adopted for further studies.

3.3. Effect of adsorbent amount

The effect of adsorbent dose ranging from 0.02 to 1.00 g on the removal of Pb was studied as shown in Fig. 5. It was observed that the percentage removal of Pb increased from 23.0 to 76.84%. It was obvious that at a low amount of adsorbent all available binding sites on the adsorbent surface were exposed for sorption; thus, saturation is achieved at a low initial percentage removal. As the amount of adsorbent is increased, the total number of available binding sites also increased. Consequently, almost all the adsorptive was adsorbed; hence the percentage removal of metal ion increased. On the contrary, the adsorption capacity for the Pb ion decreased from 10.25 to 6.63 mg g^{-1} with the increase in adsorbent dose from 0.02 to 1.00, respectively, as shown in Fig. 5.

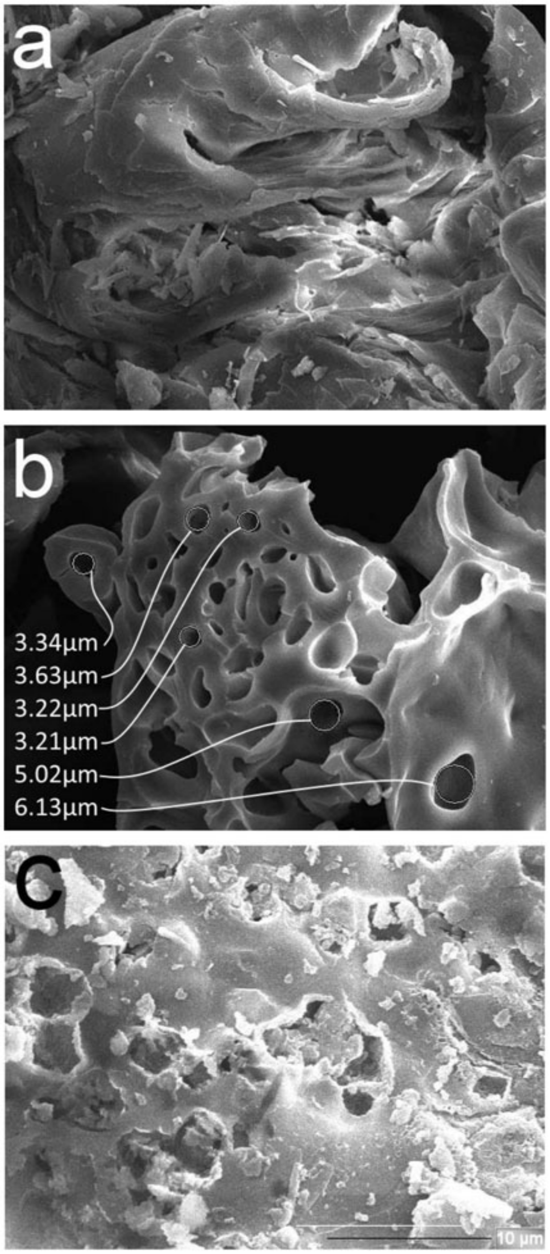
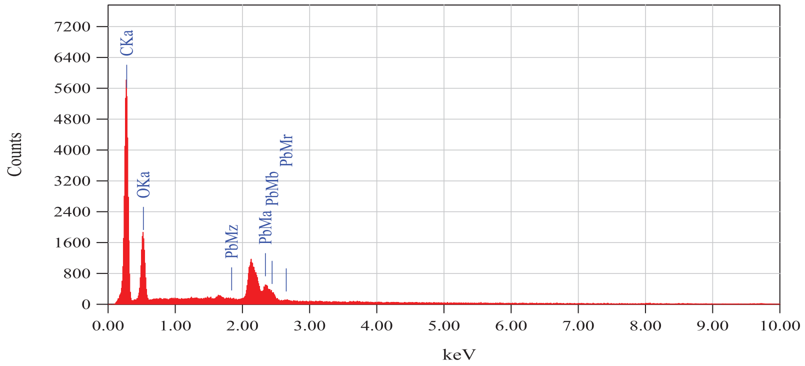


Fig. 1. Representative SEM micrograph and EDS analysis of the adsorbent *Mangifera indica* seed shell (MISS) (a) SEM of MISS substrate, (b) SEM of activated carbon, and (c) SEM of activated carbon after adsorption of metal ions.



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ZAF Method Standardless Quantitative Analysis

Fitting Coefficient : 0.3247

Element          (keV)    mass%   Error%      At%  Compound    mass%  Cation          K

 C K             0.277    58.15     0.06    69.77                               57.0096

 O K             0.525    32.87     0.33    29.61                               30.8470

Pb M             2.342     8.98     0.77     0.62                               12.1433

Total                    100.00            100.00
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Fig. 1. (*Continued*).

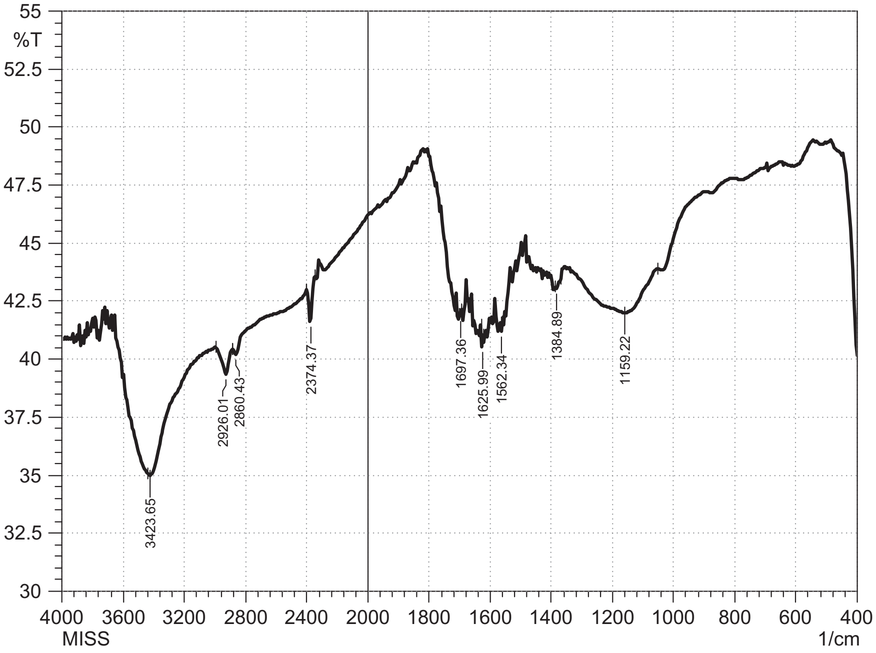

Fig. 2. The FTIR spectrum of *Mangifera indica* seed shell.

3.4. *Effect of shaking frequency*

The effect of agitation frequency was also studied in the range of 75–200 rpm. Observations showed that percentage sorption increased with increased shaking speed and reached its maximum at 150 rpm. A speed of 125 rpm was selected for further work; it can provide sufficient energy for lead removal (Fig. 6).

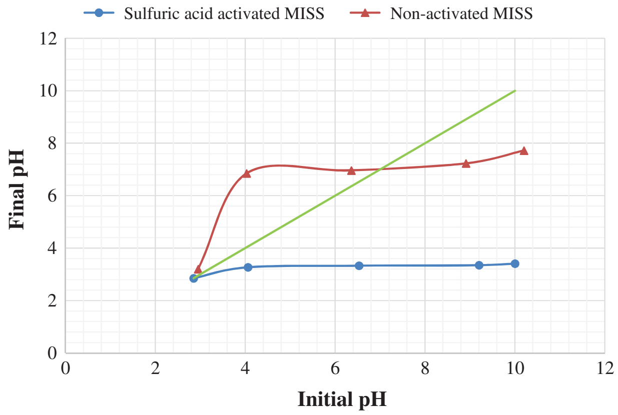

Fig. 3. The variation in equilibrium pH of *Mangifera indica* seed shell.

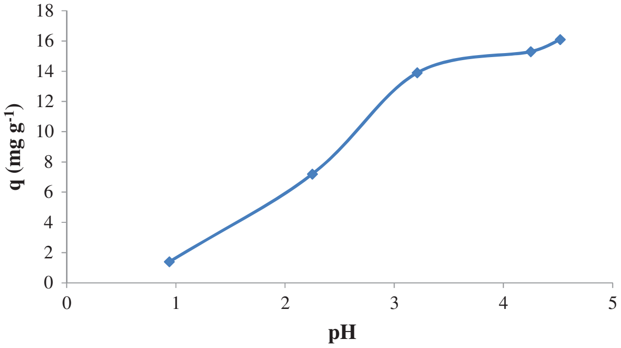

Fig. 4. Effect of initial pH on sorption of Pb(II) by MISS (initial Pb(II) conc. = 20 mg L^{-1}, adsorbent dose = 0.05 g, agitating rate = 125 rpm, contact time = 60 s, temperature = 32˚C).

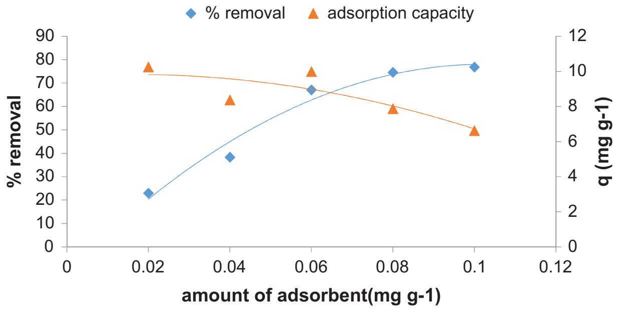

Fig. 5. Effect of adsorbent amount on sorption of Pb(II) by MISS (initial Pb(II) conc. = 20 mg L^{-1}, pH = 3.0, agitating rate = 125 rpm, contact time = 60 s, temperature = 32˚C).

3.5. Effect of contact time

The influence of contact time on the adsorption of Pb(II) on MISS was investigated from 30–600 s at 125 rpm. The percentage adsorption rose with an increasing agitation period (Fig. 7). Finally, 420 s of an agitation time was found suitable for maximum adsorption and used in all subsequent runs.

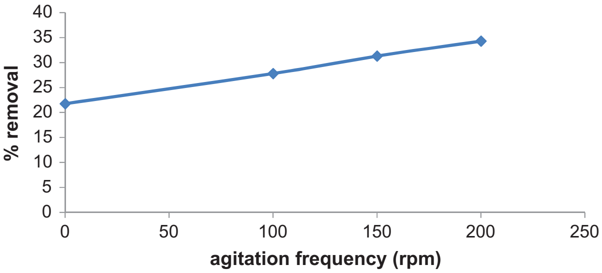

Fig. 6. Effect of shaking frequency on sorption of Pb(II) by MISS (initial Pb(II) conc. = 20 mg L^{-1}, adsorbent dose = 0.05 g, pH = 3.0, contact time = 60 s, temperature = 32˚C).

3.6. Adsorption dynamics

In order to investigate the controlling mechanism of the sorption process, kinetic modelling was carried out. Pseudo-first and pseudo-second-order kinetic models were tested for lead adsorption onto treated MISS. The Lagergren rate equation is the most widely used model for the sorption of a solute from a liquid solution. The first-order rate expression (Eq. (4)) and pseudo-second-order kinetic equations (Eq. (5)) of Lagergren [24] are shown as follows.

$$\ln(q_{\mathrm{e}} - q_t) = \ln q_{\mathrm{e}} - k_1 t \tag{4}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_{\mathrm{e}}^2} + \frac{1}{q_{\mathrm{e}}} t \tag{5}$$

where q_t and q_{e} (mg g^{-1}) are the amount adsorbed at time t (s) and at equilibrium, respectively. k_1 (min^{-1})

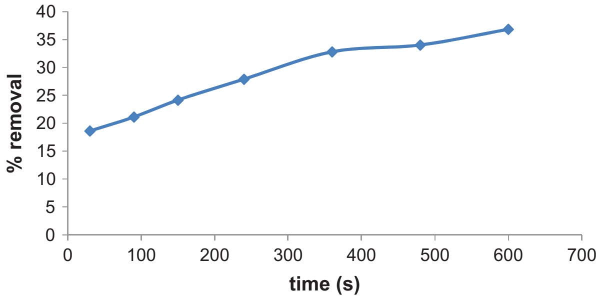

Fig. 7. Effect of contact time on sorption of Pb(II) by MISS (initial Pb(II) conc. = 20 mg L^{-1}, adsorbent dose = 0.05 g, pH = 3.0, agitating rate = 125 rpm, temperature = 32˚C).

and k_2 (g mg^{-1} min^{-1}) are the rate constants of the first-order and pseudo-second-order kinetics equations, respectively. Experimental data showed that the Pb(II) sorption process followed the pseudo-first-order kinetics (Table 2).

The values of sorption rate constant k_1, at different temperatures were used in the Arrhenius plot to determine activation energy, and found to be 9.36 kJ mol^{-1}. The controlling mechanism of Pb(II) sorption was explored by fitting experimental data into first- and second-order models at different temperatures. An evaluation of the coefficients of determination indicated that Pb(II) sorption on the MISS was better described by the pseudo-first-order model (Table 2).

According to the intra-particle diffusion model of Weber and Morris [25], the plot of q_t vs. $t^{1/2}$ should be linear if there is intra-particle diffusion in the sorption process. In case of the line passing through the origin, then intra-particle diffusion is the rate controlling step. The initial linear portion ($r^2 = 0.999$) represented the intra-particle diffusion while the plateau ($r^2 = 1$) corresponded to equilibrium as shown in Fig. 8. The values of coefficient of determination showed a good fit for both portions. The intra-particle diffusion rate constant, $k_{\text{int},1}$ (9.8×10^{-2} mg g^{-1} s$^{-1/2}$) represented the first linear portion while the $k_{\text{int},2}$ (0.20×10^{-2} mg g^{-1} s$^{-1/2}$) represented the equilibrium portion.

3.7. Adsorption isotherms

Capacity studies of adsorbent reveal significant information regarding the distribution of metals between adsorbent and the aqueous phase. When adsorbent is exposed to aqueous phase containing metal ions a rapid distribution of metal ions takes place at the surface of adsorbent until dynamic equilibrium is achieved. The increase in initial concentration of metal ions decreases the removal efficiency of ions. This is related to the limited capacity of adsorbent to accommodate metal ions. Adsorbent is effective until it has sufficient active sites left after adsorption. Increase in the initial concentration of metal ions decrease the number of available sites left for adsorption, ultimately, a point reach where further increase in initial concentration levels off. This is attributed to the saturation of adsorbent. The mathematical models of Langmuir, Freundlich and Temkin were applied to understand the sorption mechanism and surface characteristics of MISS.

The Langmuir isotherm assumes [26] that there are finite number of binding sites distributed homogeneously over the surface of the adsorbent. Eq. (6) is the mathematical representation of this isotherm.

$$q = \frac{q_m bC}{1 + bC} \tag{6}$$

where q_m and b are the Langmuir constants, representing the maximum sorption capacity for the solid phase loading and the energy constant related to the heat of sorption, respectively.

Values of Langmuir constants (q_m and b) were calculated from the slope and intercept of the plot. Adsorption capacity (122 mg g^{-1}) and coefficient of determination value ($r^2 = 0.968$) substantiated the fact that the lead—MISS sorption follows the Langmuir model.

The Freundlich isotherm [27] was applied to study the adsorption behaviour. This isotherm assumes a heterogeneous surface of the adsorbent and the general form of the model is obtained using Eq. (7).

$$q = K_F C^{1/n} \tag{7}$$

where $1/n$ and K_F are the Freundlich constants, and measure the sorption intensity of metal ions on activated MISS and sorption capacity of adsorbent, respectively.

The isotherm data closely fitted the Freundlich model ($r^2 = 0.982$), where $1/n$ and K_F are 0.2434 and 29.873, respectively, evaluated from the plot between log q and log C at 20°C (Table 3). Since the value of $1/n$ is less than one, this indicated a favourable sorption and formation of relatively stronger bonds between Pb(II) and the active sites of the adsorbent.

Table 2
Kinetic Studies of lead adsorption on activated MISS

Temperature (K)	Rate constant (k) First-order	Coefficient of determination (r^2) First-order	 Second-order
308	0.0120	0.9698	0.9382
318	0.0139	0.9643	0.9276
328	0.0150	0.9747	0.9315

Table 3
Isotherm constants for adsorption of Pb(II) onto activated MISS

Langmuir		Freundlich		Temkin	
q	122 (mg g^{-1})	K_F	29.873	K_T	0.827
b	0.062 (L mg^{-1})	$1/n$	0.2434	b_T	110.440 (kJ mol^{-1})
r^2	0.968	r^2	0.982	r^2	0.979

The Temkin isotherm [28] describes sorption potentials of sorbent for sorbate. According to this model, the heat of sorption of the molecules in the layer decreases linearly with coverage. The Temkin isotherm assumes that the fall in the heat of sorption is linear rather than logarithmic. The expression that explains Temkin isotherm model is shown in Eq. (8).

$$q = \frac{RT}{b_T}\ln(K_T C) \tag{8}$$

where K_T (dm^3 g^{-1}) is the Temkin sorption potential and b_T (kJ mol^{-1}) is the heat of sorption. The experimental data fitted well in the Temkin isotherm model ($r^2 = 0.979$) where the values of K_T and b_T are 0.827 and 110.440 kJ mol^{-1}, respectively. The value of $b_T > 8$ verified the presence of the stronger bond between lead and activated carbon [29].

High values of coefficient of determination between sorbate and sorbent systems for Langmuir, Freundlich and Temkin models (>0.968) indicated the applicability of MISS for Pb(II) removal in monolayer sorption, heterogeneous and non-uniform surface conditions.

A comparison of the maximum adsorption capacities for Pb(II) removal using a variety of adsorbents is reported in the literature and is summarized in Table 4. The value found in this study is in good agreement with the reported values.

3.8. Thermodynamic studies

A Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were determined by using Eqs. (9) and (10) [30]:

$$\ln b = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{9}$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \tag{10}$$

where R is the gas constant (8.314 J K^{-1} mol^{-1}), T is the temperature in Kelvin and b is the Langmuir constant related to the affinity of binding sites. The plot of ln b vs. $1/T$ yielded a straight line through which ΔH° and ΔS° were calculated. The value of r^2 was found to be 0.952. The calculated values of ΔH°, ΔS° and ΔG° were 94.56 kJ mol^{-1}, 0.357 kJ mol^{-1} K^{-1} and −10.743 kJ mol^{-1}, respectively.

The positive value of ΔH° implied that the sorption process was endothermic in nature. However, positive ΔS° reflected an increase in the randomness at the solid/solution interface during the sorption process. The negative value of ΔG° supported the spontaneous nature of sorption process. It can be concluded that the overall process is entropy driven rather than enthalpy driven.

3.9. Effect of ionic strength

The ionic strength is another important factor influencing aqueous phase equilibrium. Generally, adsorption decreases with the increasing ionic strength of the aqueous solution. The effect of the interfering ion KNO_3 was evaluated. The results showed that due to the increased charge density, there was a decrease in Pb(II) uptake capacity 13.5–9.5 mg g^{-1} for the range of (0.1–0.5 mol L^{-1}) KNO_3 ionic concentration.

3.10. Interference effect

Interference by other ions may have a detrimental effect on the uptake of lead by MISS. To examine the competition among metal ions which may hinder the Pb(II) binding ability of the adsorbent, the efficiency was studied for Pb(II) removal in the presence of Cd (II), Ni(II) and Cu(II) ions. It was observed that the percentage of Pb(II) adsorption decreased by 2.65, 11.39 and 40.50% for Cd(II), Ni(II) and Cu(II), respectively, due to the preferential sorption of these metal ions onto the active centre of the adsorbent.

3.11. Surfactant effect

The surfactants can play a leading role in modifying the adsorption behaviour of ionexchangers [31]. To study the effect of surfactants, three types were tested: i.e. cationic (NDPC), non-ionic (Triton X-100) and anionic (SDS) surfactants were tried. All surfactants were used within the range of 0–0.05%. It was observed that N-dodecyl pyridinium chloride (NDPC) decreased the percentage of Pb(II) removal from 27.1 to 0.20, with an increase in NDPC concentration. This was due to the formation of the layer of counter ions possibly via electrostatic attraction [32]. In contrast, triton X-100 had no significant effect on the percentage

Table 4
Comparision of $q_{\max}$ values of various sorbents for Pb(II) removal

Sorbent	Reported $q_{\max}$ (mg g^{-1})	References
S. cumini L. leaves biomass	32.4	[33]
Euphorbia rigida	279.7	[34]
Penicillium simplicissimum	152.6	[35]
Siderite	12.4	[36]
Saw dust activated carbon	116	[37]
Date pits carbon	30.6	[38]
Mangifera Indica seed shell	122	This study

of Pb(II) removal. But, SDS increased 87.6% removal of Pb(II) from the aqueous solution. This enhancement was due to the existence of sparingly soluble metal—surfactant species either as a separate phase or on the surface of adsorbent [32]. Hence, SDS was chosen for the experiment.

3.12. Column studies

To initiate the column study, dry activated MISS (1.00 g) was packed in a column with an approximate packing density of 1.0 g cm^{-3}. The column was slowly flooded with water followed by the lead solution from the top at 7 min/200 mL flow rate, until the sorption reached its point of saturation. To examine the adsorbed amount of lead onto spent adsorbent after repeated cycles, SEM micrograph and EDS analysis were carried out. They clearly indicated the presence of lead in significant quantity (Fig. 1).

Regeneration of the spent adsorbent was considered as most important to the development of a new adsorbent. In the present investigation, 0.1 mol L^{-1} HNO_3 has been scrutinized for Pb(II) desorption from the activated carbons. The percentage recovery was found to be approximately 90%. The mechanism behind desorption of Pb(II) was the preferential ion-exchange process in which Pb(II) ions were replaced by the hydrogen ions. The process followed first-order kinetics.

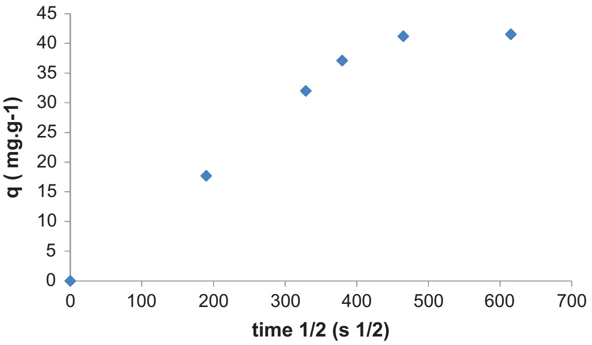

Fig. 8. Intra-particle diffusion kinetics for the adsorption of Pb(II) on MISS.

4. Conclusion

In this study, we present an inexpensive, effective and adequately available material MISS for the removal of lead from aqueous solution after converting into activated carbon via an acid activation process. Sorption data of Pb(II) follows Langmuir, Freundlich and Temkin isotherm models. Analysis shows that the process followed first-order kinetics. Thermodynamic parameters show the spontaneity and the endothermic nature of the process. MISS exhibits 122 mg g^{-1} maximum adsorption capacity under optimal conditions. It is concluded that under optimized conditions there was 100% removal of Pb(II) after adsorption, which successfully meets the WHO standards. Thus, a proposed adsorbent with excellent regeneration capability has the potential to be used as an environment friendly and economical material for the removal of lead from wastewater.

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