



## Adsorption Study of Lead(II) Ions on Poly(methyl methacrylate) Waste Material

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The sorption of Pb<sup>2+</sup> from solution by poly(methyl methacrylate) (PMMA) waste has been investigated. The morphological characterization of the collected PMMA polymer were studied by scanning electron microscopy. Equilibrium, kinetics and thermodynamic batch adsorption experiments of Pb<sup>2+</sup> on the PMMA waste samples were carried out. This study enabled the determination of the concentration, time and temperature effects, respectively on the adsorption properties of the PMMA polymer. The morphological image of the PMMA polymer showed the presence of irregular small size particles that indicated a high surface which is therefore possible to facilitate sorption. The reaction kinetics of the adsorption studies of Pb<sup>2+</sup> by the polymer followed a second-order rate process. The results indicated that the adsorbent, PMMA, proved to be an effective material for the treatment of lead contaminated water solution. The thermodynamic studies suggested a reaction that favoured a relatively low temperature (low energy) sorption that is exothermically controlled with a physisorption mechanism.

**Keywords:** Sorption, Poly(methyl methacrylate) waste, Adsorbent, Heavy metals, Polymer.

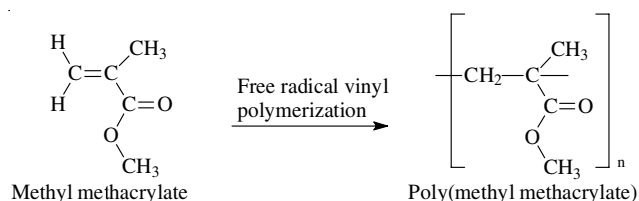
### INTRODUCTION

It is known that chemical substances especially lead, if present in certain concentrations in water, wastewater and the environment constitute a danger to human health and other organisms. Lead discharged by several industrial and commercial activities is found in the environment, such that its removal, from water and wastewater has become a challenge to researchers [1,2].

The most conventional and applied methods of removal of heavy metals like lead from waste water which include precipitation, flocculation, filtration, ion exchange, reverse osmosis, *etc.*, are very much capital intensive. In the recent past, renewable materials are being identified for the removal of metals from effluents which include biomasses like Nipa palm [3], Manihot sculenta Cranz. [4], sea weed [5] and *Medicago sativa* [6]. A new low-cost or less capital intensive and more effective adsorbents are required for wastewater treatments leading researchers to engage in the search for a low-cost and possibly, a locally available material that could be used as adsorbent providing maximum adsorption capacities.

Poly(methyl methacrylate) (PMMA) produced from the polymerization of methyl methacrylate is a transparent thermo-plastic which is often used as a light weight or shatter-resistant

alternative material. It has moderate properties, easy handling as well as processing and has a low cost. The non-modified PMMA is brittle under an impact force and more prone to scratching. However, the modified PMMA achieves very high scratch and impact resistance. It has good impact strength higher than both glass and polystyrene. Poly(methyl methacrylate) is soluble in dichloromethane or trichloromethane. It has a maximum water absorption ratio of (0.3-0.4) % by weight [7].



Poly(methylmethacrylate) has numerous applications such as in residential aquariums, submarines, lenses of exterior lights of vehicles and other means of transport, windows of air crafts because of this usage [8]. It is also used for furniture, picture framing, CDs, DVDs, plastic optical fiber, intraocular lenses, contact lenses and in cosmetic surgery and dental fillings [9]. The low levels of recycling and biodegradation of poly(methyl methacrylate) has resulted in much of it ending in landfills and as a pollutant in the outdoor environment, predominantly

along shores, waterways and waste dumps, due to its variety of uses [7].

In this study, we present the use of poly(methyl methacrylate), waste materials obtained from the environment in the Niger Delta region of Nigeria as adsorbent material for the sorption of lead ions in water solution. The poly(methyl methacrylate) polymer material is characterized by FTIR, XRD, SEM and EDS.

## EXPERIMENTAL

Poly(methyl methacrylate) (PMMA) polymer materials were acquired from the discarded bins and thoroughly washed with the deionized water and dried in oven at 30 °C. The dry samples were crushed, milled and passed through the 100-mesh partitioning panels using a Wiley mill. These particle sizes were then washed twice with 0.01 M HCl to eliminate any metal and other hard trash fragments that might be in the polymer prior to experimental metal ion exposure. The acid washed PMMA polymer samples were washed twice again with deionized water to remove acid and then oven dried at 30 °C to constant weight.

**Characterization of polymer sample:** The morphological depictions of the polymer were analyzed by different techniques such as FE-SEM, HR-TEM, EDS, XRD and FTIR. The outward morphology and EDS measurements were recorded with a JEOL 7500F Field Emission scanning electron microscope. The HR-TEM images of the sample were obtained by a CM 200 electron microscope operated at 100 KV. Powder X-ray diffraction configurations were assembled with a Bruker AXS D8 Advanced diffractometer operated at 45kV and 40 mA with monochromated copper K $\alpha$ 1 radiation wavelength ( $\lambda = 1.540598$ ) and K $\alpha$ 2 radiation wavelength ( $\lambda = 1.544426$ ). Scan speed of s/step and step size of 0.03°. The Fourier transform infrared spectra were recorded on a Perkin-Elmer spectrometer 400 FTIR/FT-NIR spectrometer in the range 4000-400 cm<sup>-1</sup>.

### Batch adsorption experiment

**Concentration effect:** 0.2 g of the polymer sample was weighed and placed in pre-cleaned test tubes. Six Pb<sup>2+</sup> ion solutions with standard concentrations of 21.8, 48.0, 72.3, 97.7, 120.9 and 141.5 mg/L were made from spectroscopic grade standards of Pb<sup>2+</sup> [from Pb(NO<sub>3</sub>)<sub>2</sub>]. 10 mL of each lead ion solution were added to each tube comprising the PMMA polymer sample and equilibrated for 1 h by shaking at 29 °C. The polymer particle colloidal suspensions were centrifuged for 5 min at 2500 rpm. The supernatants were analyzed as stated in metal analysis. The amount of Pb<sup>2+</sup> removed from the system was estimated using eqn. 1.

**Time dependent studies:** 0.2 g of the polymer sample was weighed and placed in five pre-cleaned test tubes. The Pb<sup>2+</sup> ion solution with standard concentration of 72.3 mg/L was made from spectroscopic grade standard of Pb<sup>2+</sup> [from Pb(NO<sub>3</sub>)<sub>2</sub>]. 10 mL of the Pb<sup>2+</sup> ion solution was added to each tube containing the polymer sample and equilibrated for each time intervals of (5, 10, 20, 40 and 60) min, respectively by shaking at 29 °C. The polymer suspensions were centrifuged for 5 min at 2500 rpm. The supernatants were analyzed as

stated in metal analysis section. The amount of lead metal ion removed from the solution was processed using eqn. 1.

**Temperature effect:** 0.2 g of the polymer sample was weighed and placed in four pre-cleaned test tubes. Metal ion solution with standard concentration of 72.3 mg/L was made from spectroscopic grade standard of Pb<sup>2+</sup>. 10 mL of the metal solution was added to each tube containing the polymer sample and equilibrated for 1 h by shaking at temperatures of (28, 40, 60 and 80) °C, respectively using a Compenstat Gallenham water bath. The polymer suspensions were centrifuged for 5 min at 2500 rpm. The supernatants were evaluated as stated in the metal analysis. The amount of lead metal ion removed from solution was calculated using eqn. 1.

**Metal analysis:** The metal analysis was performed by AAS using a Buck Scientific Atomic Absorption/Emission spectrophotometer 200A (AAES). Controls of one of the metal solution were run to detect any possible metal precipitation or contamination.

**Data analysis:** Data interpretation utilizing different equilibrium, kinetic and thermodynamic simulations were employed to interpret the data and establish the extent of adsorption. The amount of metal uptake was computed using the material balance equation for batch dynamic studies eqn. 1 [5].

$$q_e = \frac{V}{M}(C_o - C_e) \quad (1)$$

where  $q_e$  is metal uptake capacity (mg/L) polymer at equilibrium,  $C_e$  is metal ion concentration in solution (mg/L) at equilibrium,  $C_o$  is the initial metal ion concentration in solution (mg/L),  $V$  is the volume of solution in litres and  $M$  is the dry weight of polymer used in grams.

Langmuir plots were carried out using eqn. 2:

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (2)$$

where  $q_e$  is the amount of Pb<sup>2+</sup> adsorbed in mg/g of adsorbent,  $C_e$  is the residual concentration of adsorbate in mg/L,  $K_L$  is the Langmuir constant and  $q_m$  is the maximum amount of adsorbate adsorbed in mg/g, obtained from the slope and intercepts of the plots, respectively.

The essential characteristics of the Langmuir isotherm were expressed in terms of a dimensionless separation factor or equilibrium parameter  $S_f$  [10].

$$S_f = \frac{1}{(1 + K_L C_o)} \quad (3)$$

where  $C_o$  is the initial concentration of Pb<sup>2+</sup> in solution. It has been shown by mathematical calculations that the magnitude of the parameter  $S_f$  provides a measure of the type of adsorption isotherm [10]. If  $S_f > 1.0$ , the isotherm is unfavourable;  $S_f = 1.0$  (linear);  $0 < S_f < 1.0$  (favourable) and  $S_f = 0$  (irreversible).

The adsorption intensity of Pb<sup>2+</sup> was assessed from the Freundlich plots using the eqn. 4:

$$q_e = K_F C_e^{1/n} \quad (4)$$

where  $K_F$  and  $n$  are Freundlich constants and  $1/n$  is approximately equal to the adsorption intensity.

The linearity of heat of adsorption with the surface coverage of  $\text{Pb}^{2+}$  on the adsorbent was assessed from the Temkin plot using eqn. 5:

$$q_e = \frac{RT}{b_T} \ln(K_T C_e) \quad (5)$$

where  $K_T$  is the Temkin isotherm constant ( $\text{dm}^3 \text{g}^{-1}$ ) and  $b_T$  is the adsorption potential of the adsorbent ( $\text{J mol}^{-1}$ ).

The fraction of polymer surface covered by  $\text{Pb}^{2+}$  was computed using eqn. 6:

$$\theta = 1 - \frac{C_e}{C_o} \quad (6)$$

where  $\theta$  is the degree of surface coverage.

The predominant form of adsorption was evaluated using Dubinin-Radushkevich equation (eqn. 7).

$$q_e = q_D \exp(-B_D [RT \ln(1 + 1/C_e)]^2) \quad (7)$$

The mean free energy of sorption  $E$ , is related to the constant  $B_D$  by eqn. 8:

$$E = \frac{1}{\sqrt{2B_D}} \quad (8)$$

The prevalent sorption process between monolayer and multilayer was assessed by the Redlich-Peterson and the Sip's isotherms as given in eqns. 9 and 10, respectively.

$$q_e = \frac{k_{RP} C_e}{1 + a_{RP} C_e^g} \quad (9)$$

$$q_e = \frac{Q_S K_S C_e^{n_s}}{1 + K_S C_e^{n_s}} \quad (10)$$

The effectiveness of adsorbent (polymer) was assessed by the number of cycles of equilibrium sorption process required to reduce the levels of  $\text{Pb}^{2+}$  in solution according to the value of distribution (partition) coefficient ( $K_d$ ) in eqn. 11 [11].

$$K_d = \frac{C_{aq}}{C_{ads}} \quad (11)$$

where  $C_{aq}$  is the concentration of  $\text{Pb}^{2+}$  in solution ( $\text{mg/L}$ );  $C_{ads}$  is the concentration of  $\text{Pb}^{2+}$  in adsorbent in ( $\text{mg/L}$ ).

The heat of adsorption ( $Q_{ads}$ ) was obtained using the following Suzuki equation [12]:

$$\ln \theta = \frac{\ln K_o C_o}{T^{0.5}} + \frac{Q_{ads}}{RT} \quad (12)$$

where  $T$  = solution temperature (K);  $K_o$  = constant and  $R$  = gas constant ( $8.314 \text{ J/Kmol}$ ).

The linear form of the modified Arrhenius expression was applied to the experimental data to evaluate the activation energy ( $E_a$ ) and sticking probability  $S^*$  as shown in eqn. 13 [13].

$$\ln(1 - \theta) = S^* + \frac{E_a}{RT} \quad (13)$$

The apparent Gibbs free energy of sorption  $\Delta G^\circ$  which is a fundamental criterion for spontaneity, was evaluated using the following equation:

$$\Delta G^\circ = -RT \ln K_o \quad (14)$$

where  $K_o$  is obtained from the Suzuki equation (eqn. 12).

The experimental data was further subjected to thermodynamic treatment in order to evaluate the apparent enthalpy ( $\Delta H^\circ$ ) and entropy ( $\Delta S^\circ$ ) of sorption using eqn. 15:

$$\ln K_o = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (15)$$

To evaluate the packing of  $\text{Pb}^{2+}$  on the polymer surface, thermodynamic analysis of adsorption density ( $\rho$ ) was carried out with the following equation:

$$\rho = ZrC_e e^{-(\Delta H^\circ/RT)} \quad (16)$$

where  $Z$  is the valency of  $\text{Pb}^{2+}$ ,  $\rho$  is the effective radius of  $\text{Pb}^{2+}$  in cm and  $C_e$  is the equilibrium concentration in  $\text{mol/cm}^3$ .

The relationship between the number of hopping ( $n$ ) and that of the surface coverage ( $\theta$ ) as shown in eqn. 17 was applied to the experimental data.

$$n = \frac{1}{(1 - \theta)\theta} \quad (17)$$

Other thermodynamic parameters such as adsorption potential ( $A$ ) was tested by applying eqn. 18:

$$A = -RT \ln \frac{C_o}{C_e} \quad (18)$$

where  $C_o$  and  $C_e$  = initial and equilibrium concentrations, respectively in  $\text{mol/cm}^3$ ,  $R$  = gas constant and  $T$  = solution temperature in K.

The kinetic performance of the sorption process was investigated by testing the data using the first, second, pseudo-first and pseudo-second order kinetic models as presented in eqns. 19-22.

$$q_t = q_o e^{-k_1 t} \quad (19)$$

$$q_t = \frac{q_o}{1 + q_o k_2 t} \quad (20)$$

$$q_t = q_e (1 - e^{-k_1 t}) \quad (21)$$

$$q_t = \frac{q_e^2 k_2 t}{1 + k_2 q_e t} \quad (22)$$

where  $q_t$  is the quantity of  $\text{Pb}^{2+}$  on polymer ( $\text{mg/g}$  or  $\text{mmol/g}$ ) at time  $t$ ,  $q_o$  is the amount of  $\text{Pb}^{2+}$  on polymer at time  $t_o$ ,  $k_1$  and  $k_2$  are the first and second order rate constant, respectively.

## RESULTS AND DISCUSSION

**Characterization studies:** Fourier transform infrared (FTIR) spectroscopy was extensively used to study the environment of chemical bonds of polymers and the supramolecular interactions between molecules through the characterization of their vibrational types [14-20]. FTIR spectroscopic study of the polymer was conducted to ascertain the active functional groups on the polymer accountable for attaching of  $\text{Pb}^{2+}$  from solution. Fourier transform infrared spectrum of poly(methyl methacrylate) in the wavenumber range of  $4000\text{--}400 \text{ cm}^{-1}$  is presented in Fig. 1. The weak band observed at  $3491 \text{ cm}^{-1}$  is due to hydrogen bonded O-H stretching vibration resulting

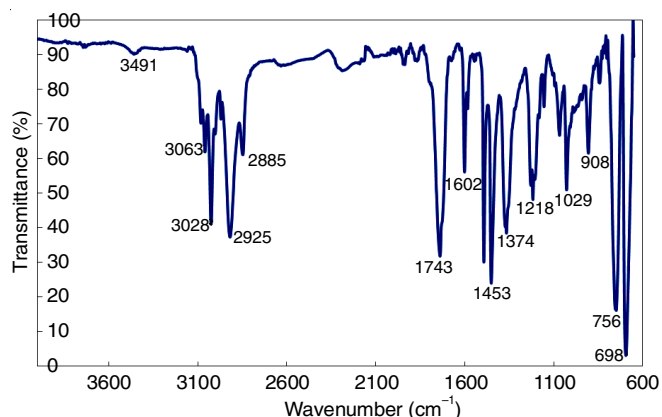


Fig. 1. Fourier transform infrared (FTIR) spectrum of poly(methyl-2-methacrylate) sample

from environmental dilapidation of the polymer material. The peaks at 2925 and 2885  $\text{cm}^{-1}$ , respectively emanate from the presence of  $\text{CH}_2$  asymmetric and symmetric stretching vibrations of the methylene group. The absorption band at 1743  $\text{cm}^{-1}$  is a CO stretching vibration of the poly(methyl methacrylate) [21]. The absorption bands at 1453, 1374, 1218, 1029 and 908  $\text{cm}^{-1}$  are due to bending deformation,  $\text{CH}_3$  symmetric deformation, wagging deformation, twisting deformation and wagging deformation vibrations. The C–O–C symmetric stretching vibration and the O– $\text{CH}_3$  deformation vibrations which are the fingerprint vibrations of PMMA are observed at 908 and 1374  $\text{cm}^{-1}$ , respectively. Poly(methyl methacrylate) is a saturated polymeric ester ( $-\text{COOR}$ ) that yields an intense peak at 1743  $\text{cm}^{-1}$  due to the symmetrical stretching vibration of the carbonyl group [22,23]. The absorption bands observed in 756–698  $\text{cm}^{-1}$  region due to the presence of bending, ring out of plane or rocking deformation vibrations of poly(methyl methacrylate). The presence of these absorption bands indicates that no functional group have played a major role in the sorption process.

X-ray diffraction outlines of the poly(methylmethacrylate) used in this study is presented in Fig. 2. X-ray powder diffraction is employed to show the crystallite size, phase and the stress or strain of the polymer. The crystalline morphology of the polymer species will have a unique X-ray diffraction pattern when investigated. With a diffraction pattern, an examiner can identify an unknown species or reveal the atomic scale structure

of an already recognized substance. Fig. 2 gives the diffractogram of the poly(methyl methacrylate) polymer sample. Poly(methylmethacrylate) is categorized as a polymer material that comprises mainly of an amorphous and a crystalline region in different proportions. The XRD pattern show notable high intensity Bragg diffraction peaks at  $2\theta = 9.16^\circ$  and  $19.12^\circ$ . These peaks are characteristic XRD peaks of poly(methyl methacrylate) [16]. The intense peak at  $2\theta = 19.12^\circ$  indicates the crystallinity of the poly(methylmethacrylate) polymer sample while the peak at  $2\theta = 9.16^\circ$  indicates that the polymer is amorphous in nature. A  $2\theta$  value of  $8.10^\circ$  has been reported for PMMA [21]. The weak background hump around  $2\theta = 42^\circ$  has been observed in other works [2,22]. This  $2\theta$  value is also indicative of the amorphous nature of the material.

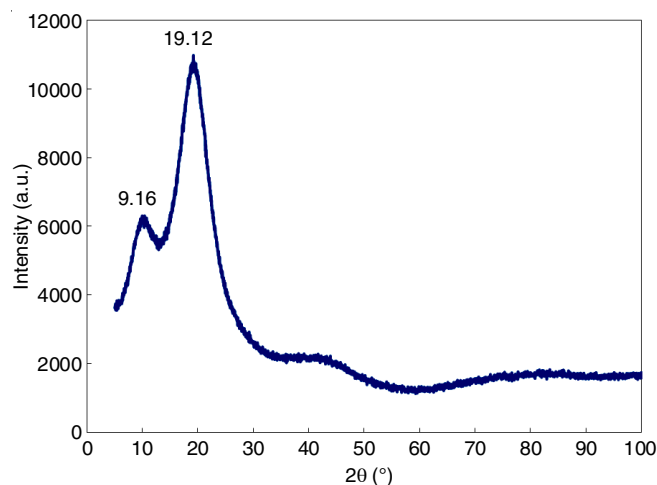


Fig. 2. X-ray diffraction (XRD) pattern of poly(methyl methacrylate) sample

Energy dispersive X-ray (EDX) was engaged for elemental analysis of the polymer samples. The EDX spectrum presented in Fig. 3 confirmed sharp peaks due to the following elements: C (93 %), Al (2 %) and O (5 %) in addition to hydrogen. The occurrence of these elements will generate charges on the surface of the polymer and create electrostatic forces of attraction between the sample and  $\text{Pb}^{2+}$  in solution.

To define the morphology of the polymer, scanning electron microscope (SEM) image of the sample was taken at magnifi-

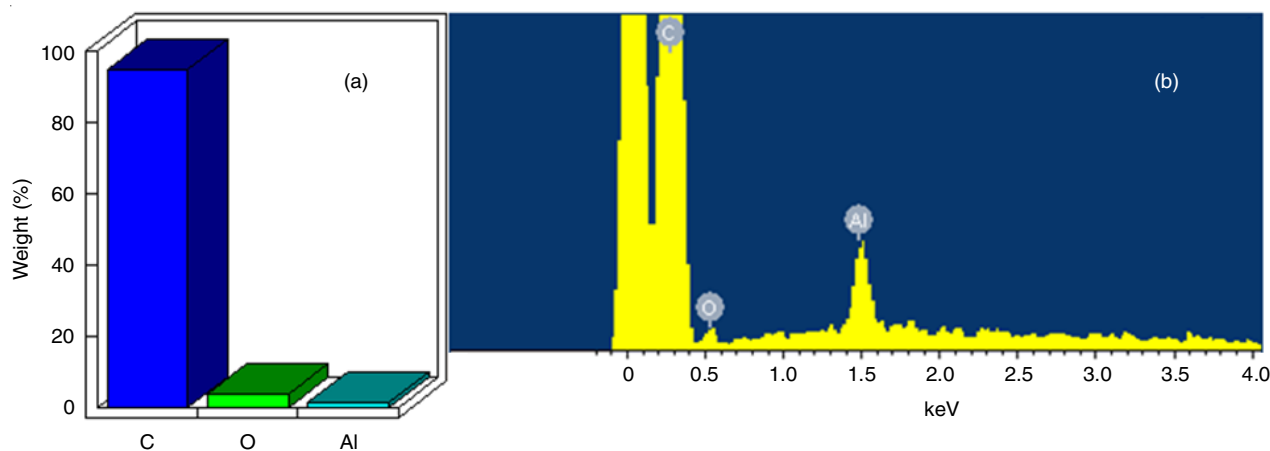


Fig. 3. Energy dispersive X-ray (EDX) of poly(methyl methacrylate) sample (a) quantitative result and (b) spectrum



cation x270. The SEM image shows that the surface of the polymer sample had irregular small size particles which indicated a high surface area and porous nature (Fig. 4). The presence of substantial surface area of any adsorbent facilitates extreme adsorption [12].

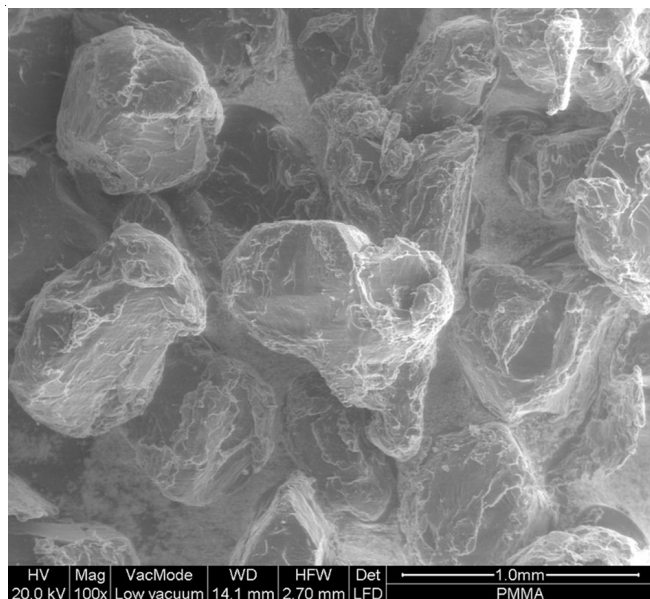


Fig. 4. Scanning electron microscope (SEM) image of poly(methyl methacrylate) sample

**Sorption equilibrium studies:** The percentage of sorption of  $Pb^{2+}$  by PMMA at different concentrations of  $Pb^{2+}$  is presented in Fig. 5. The maximum adsorption of 60 % took place at equilibrium concentration of 20 mg/L  $Pb^{2+}$ . This is because at lower concentration more polymer pore spaces were available for  $Pb^{2+}$ , but as the concentration of  $Pb^{2+}$  increased, the adsorption capacity of the polymer diminished considerably due to reduced availability of free pore spaces. The results indicated that the sorption of  $Pb^{2+}$  were considerably dependent on the concentration of  $Pb^{2+}$ .

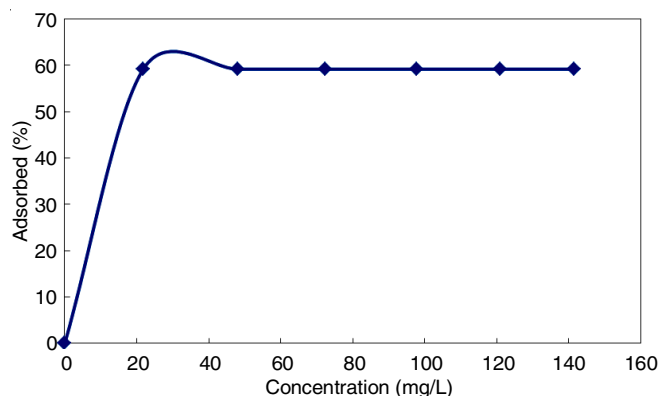


Fig. 5. Effect of initial concentration of  $Pb^{2+}$  on the sorption by poly(methyl methacrylate) sample

The extent of adsorption of lead ions onto the waste material can be compared by means of an isotherm. Efforts were made to fit the data obtained from the adsorption experiments into several adsorption isotherms. Langmuir and Freundlich isotherm models for the sorption of  $Pb^{2+}$  by PMMA show the

linear plots. The linear plots established the application of the Langmuir and Freundlich isotherm models to the adsorption of  $Pb^{2+}$  by the polymer (figures not shown). The gradients and intercepts were used to compute the Langmuir constants and adsorption capacity. The linear isotherm parameters of the adsorption are given in Table-1.

TABLE-1  
LINEAR ISOTHERM PARAMETERS OF  
 $Pb^{2+}$  SORPTION BY PMMA

Isotherm	Parameter	Value
Langmuir	$q_{max}$ (mg/g)	10,000
	$K$ (L/g)	0.00000725
	$R^2$	1.0000
	$\chi^2$	$4.40569 \times 10^{-6}$
	SSE	$1.59 \times 10^{-5}$
Freundlich	$K_F$ (mg/g)	0.07243
	$n$	1.0003
	$R^2$	1.0000
	$\chi^2$	$4.0895 \times 10^{-6}$
	SSE	$1.4668 \times 10^{-5}$
Temkin	$B$	1.8556
	$K_T$	0.6887
	$R^2$	0.9319
	$\chi^2$	0.6169
	SSE	0.6062
Dubinin-Radushkevich	$q_D$ (mg/g)	3.1277
	$B_D$ (mol <sup>2</sup> kJ <sup>-2</sup> )	0.00001
	$E$ (kJ/mol)	223.606
	$R^2$	0.840
	$\chi^2$	1.0478
	SSE	2.845073

These linear plots confirmed the application of the isotherm models to the adsorption of  $Pb^{2+}$  by the polymer. All the linear isotherm plots gave coefficients of determination ( $R^2$ ) of 1. The high linear correlation coefficients of both isotherms imply that chemisorption and physisorption occurred simultaneously. The value of the Freundlich adsorption intensity parameter,  $n$  of 0.9997 also gave indication of a favourable adsorption. Values of  $n$  between 0 or 1 and 10 have been shown to be beneficial adsorption [17-19]. The  $n$  value of this adsorption lies within range and hence it is favourable.

Non-linear forms of the applied isotherms were also used to show the closeness and hence validity of the parameters obtained in the linear models. The non-linear parameters are shown in Table-2. The values of the non-linear isotherm parameters are consistent with those of the linear parameters, for the Freundlich and Temkin isotherms. The non-linear plot of the Langmuir isotherm positions  $q_{max}$  at 156.65 mg/g of adsorbent and this is not close to that of the linear value.

To identify the best fit model between the Langmuir and the Freundlich, as well as show the validity of the parameters of the applied models; two three-parameter non-linear isotherms, namely; Redlich-Peterson and Sip's were applied to the adsorption data. The respective isotherm models are given in eqns. 9 and 10 and the parameters are shown in Table-2. The relationship with the non-linear models of Langmuir, Freundlich and Temkin are shown in Fig. 6. The Redlich-Peterson model is one that incorporates the terms in the Langmuir and the Freundlich isotherms. It proposes that the equation reduces to the

TABLE-2  
NON-LINEAR ISOTHERM PARAMETERS OF  
Pb<sup>2+</sup> SORPTION BY PMMA

Isotherm	Parameter	Value
Langmuir	q <sub>max</sub> (mg/g)	156.654
	K <sub>L</sub> (L/g)	0.0004728
	R <sup>2</sup>	0.9998
	χ <sup>2</sup>	0.0007528
	SSE	0.001358315
Freundlich	K <sub>F</sub> (mg/g)	0.07243
	n	0.9996
	R <sup>2</sup>	0.9999
	χ <sup>2</sup>	4.0895 × 10 <sup>-6</sup>
	SSE	1.46676 × 10 <sup>-05</sup>
Temkin	B	1.8556
	k <sub>T</sub> (J/mol)	0.1314
	χ <sup>2</sup>	0.3031
	R <sup>2</sup>	0.9319
Redlich-Peterson	K <sub>RP</sub>	0.03788
	a <sub>RP</sub>	0.03455
	g	1.0006
	R <sup>2</sup>	0.9999
	χ <sup>2</sup>	4.0861 × 10 <sup>-6</sup>
	SSE	1.4666 × 10 <sup>-5</sup>
Sip's	Q <sub>s</sub>	0.7663
	k <sub>s</sub>	-0.00365
	n <sub>s</sub>	1.0127
	R <sup>2</sup>	0.9999
	χ <sup>2</sup>	4.0856 × 10 <sup>-6</sup>
	SSE	1.4666 × 10 <sup>-5</sup>

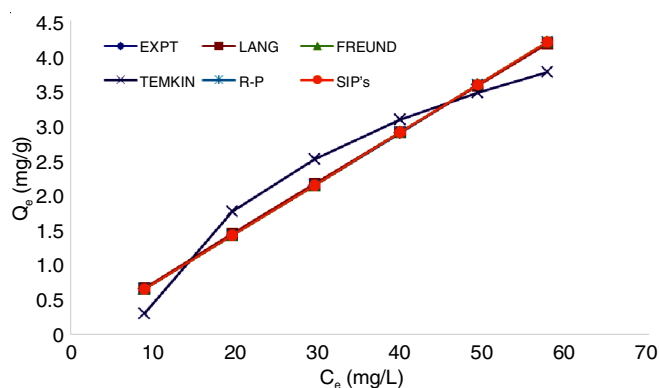


Fig. 6. Non-linear isotherm plots for the sorption of Pb<sup>2+</sup> by the polymer sample

Langmuir when the parameter  $g = 1$  and becomes Freundlich with  $g = 1$  and the denominator product  $a_{RP}C_e \gg 1$ . The product  $a_{RP}C_e$  is less than 1 for the first two values of  $C_e$  while the rest higher concentrations have product values greater than 1. The variation in these values could mean that the sorption tends more to the Freundlich which approximates multilayer physisorption, as the residual adsorbate concentration increase with the quantity adsorbed. The value of the  $g$  term of the equation, though slightly greater than 1 (1.0006406) is closer and could enhance the chemisorption process, but with a higher number of the product  $a_{RP}C_e$  greater than 1, the physisorption process could be assumed to predominate.

The Sip's isotherm is another model that incorporates the terms of both the Langmuir and Freundlich isotherms and it provides that the equation becomes Langmuir, if the parameter  $n_s = 1$  and reduces to the Freundlich as  $k_s$  tends to zero. Though

the  $n_s$  value is slightly greater than 1 ( $n_s = 1.01269$ ),  $k_s$  value is more on the side of zero than 1, it is obvious then that the equation reduces to the Freundlich; in which case, physisorption becomes more dominant.

A further test of best-fit between Langmuir and Freundlich models was the use of chi-squared ( $\chi^2$ ) test as recommended by Tran *et al.* [20]. The test showed that the Freundlich model to be closer to zero than the Langmuir, hence the Freundlich modelled the sorption better than the Langmuir. The chi-squared ( $\chi^2$ ) value of the Freundlich data was about the same with those of Redlich-Peterson and Sip's (Table-2). Though monolayer and multilayer adsorption occurred simultaneously, the multilayer process seemed to be prevalent, based on the predictive values of the parameters and tests measurements. It is worth noting here that SSE value (Table-2) of Langmuir plot was also far higher than that of Freundlich.

The fraction of the polymer surface enveloped by Pb<sup>2+</sup> is given as 0.592 (Table-3). This value alludes to the fact that over 59 % of the pore spaces of the polymer surface were masked by Pb<sup>2+</sup>, which means moderately high degree of adsorption.

TABLE-3  
EQUILIBRIUM PARAMETERS

Surface coverage ( $\theta$ )	Separation factor ( $S_f$ )	Sorption coefficient ( $K_d$ )	Adsorption capacity (mg/g)
0.592	0.951	0.689	10000

The favourability or otherwise of the adsorption was determined by the dimensionless constant separation factor term  $S_f$  (eqn. 3). The result ( $S_f = 0.951$ ) was less than one and greater than zero, which showed that sorption of Pb<sup>2+</sup> onto the polymer was favourable.

The effectiveness of the polymer as an adsorbent for Pb<sup>2+</sup> from solution was appraised through the sorption distribution or partition coefficient  $K_d$  presented in Table-3. The value of  $K_d$  (0.689) suggests that the polymer is a relatively effective adsorbent and that an insufficient number of cycles of equilibrium sorption process will be required to reduce the levels of Pb<sup>2+</sup> in solution.

**Adsorption kinetics and diffusion:** Time dependency studies of the polymer sample show the aggregate time needed for maximum adsorption to ensue. The disparity in the percentage removal of Pb<sup>2+</sup> ions in solution with time is shown in Fig. 7. This indicates that a minimum of 59 % removal of Pb<sup>2+</sup> was observed in 5 min and continued constant afterwards. The relatively short contact time required to attain equilibrium implies that a rapid uptake of Pb<sup>2+</sup> by the polymer occurred to fill some of the unoccupied pores in the polymer and subsequently, the remaining spaces were difficult to be occupied due to repellent forces between Pb<sup>2+</sup> ions.

The kinetic behaviour of the Pb<sup>2+</sup> ions towards the adsorbent was evaluated using the non-linear first, second, pseudo-first order rate and the pseudo-second models which take the form of eqns. 19-22, respectively. These were plotted with the experimental to see which correlated best. The non-linear kinetic plots for the first, second, pseudo-first and pseudo-second order kinetic models rate models are given in Fig. 8. It can be seen from the plot that the first-order model followed

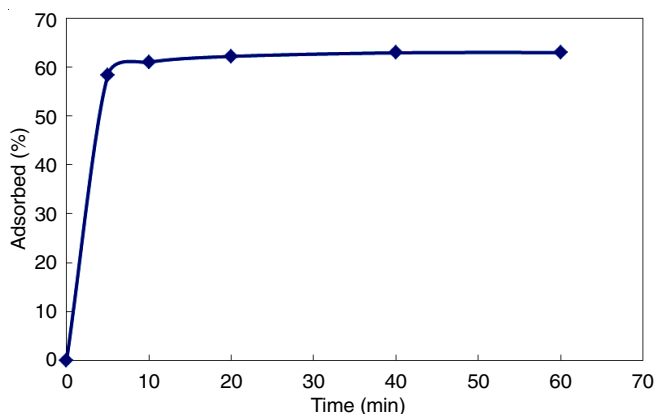


Fig. 7. Effect of contact time on the sorption of  $Pb^{2+}$  by the poly(methyl methacrylate) sample

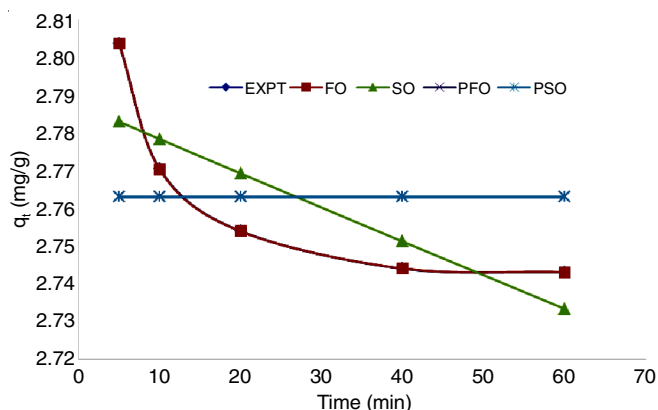


Fig. 8. Non-linear kinetic plot for the sorption of  $Pb^{2+}$  by the poly(methyl methacrylate) sample

the experimental data more than the other kinetic models. Thus, the controlling kinetic mechanism for this sorption was the first order. The non-linear kinetic parameters are given in Table-4. Diffusion models for adsorption were applied to the data to determine the rate limiting mechanism. The sorption diffusion mechanism that best fitted experimental data was estimated using the intra-particle diffusion or pore diffusion. This is given by eqn. 23

$$R = k_{id} t^a \quad (23)$$

TABLE-4 NON-LINEAR KINETIC AND DIFFUSION PARAMETERS OF $Pb^{2+}$ SORPTION BY PMMA		
Type	Parameter	Value
First order	$q_0$ (mg/g)	2.7874
	$K_1$	0.000326
	$R^2$	0.6564
	$\chi^2$	$7.7172 \times 10^{-9}$
	SSE	$2.136 \times 10^{-8}$
Second order	$q_0$ (mg/g)	2.7876
	$K_2$	0.0001186
	$R^2$	0.6584
	$\chi^2$	0.000315
	SSE	0.000873
Intraparticle diffusion (pore)	$K_{id}$	57.4499
	$a$	0.02398
	$R^2$	0.9336
	$\chi^2$	0.013058
	SSE	0.792376

where  $R$  is the percent adsorbed,  $k_{id}$  is the intraparticle diffusion constant, ' $a$ ' is a constant and  $t$  is the time in minutes. The plot given in Fig. 9 shows that the model followed close to the experimental data, hence the controlling diffusion mechanism is the pore diffusion. The parameters are also given in Table-4.

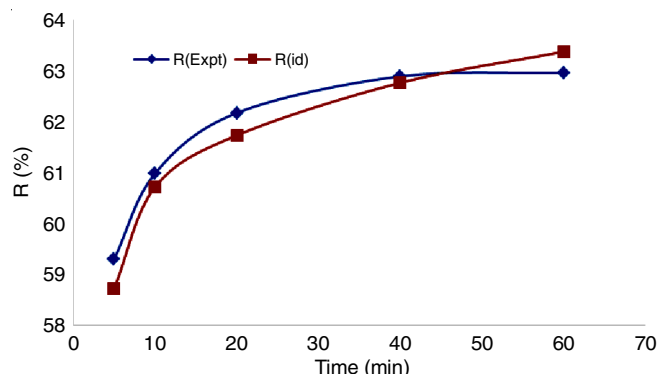


Fig. 9. Intraparticle diffusion (pore diffusion) plot for the adsorption of  $Pb^{2+}$  by polymer

**Adsorption thermodynamics:** Fig. 10 presents the plot of percentage adsorption of  $Pb^{2+}$  by PMMA at varying temperatures with optimum sorption of 49 % occurring at 30 °C. The plot showed that additional increase in temperature resulted in a minor decrease in adsorption. This is in harmony with the general principle that physical adsorption declines with increase in temperature, *i.e.* molecules adsorbed earlier on a surface tend to desorb from it at elevated temperatures [11,24]. This behaviour might be attributed to the dwindling of attractive forces between the polymer and  $Pb^{2+}$ , increased kinetic energy of  $Pb^{2+}$  and decrease in the stiffness of the boundary layers of polymer due to the higher tendency of  $Pb^{2+}$  to escape from the polymer.

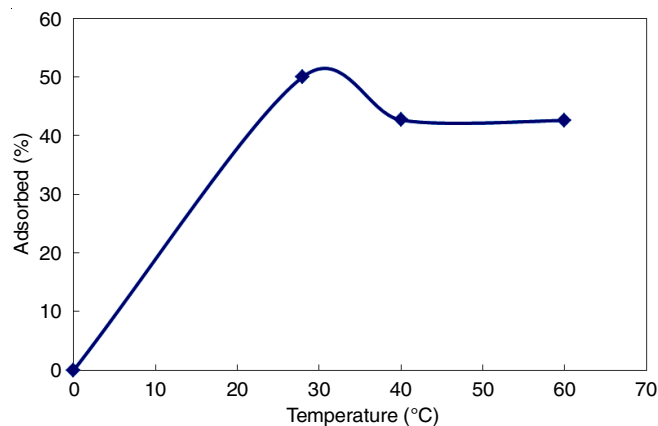


Fig. 10. Effect of temperature on the sorption of  $Pb^{2+}$  by poly(methyl methacrylate) sample

To estimate the heat of adsorption ( $Q_{ads}$ ) for the sorption of  $Pb^{2+}$  onto the polymer, eqn. 12 was used. The value of  $Q_{ads}$  (-1.34 KJ/Kmol) is negative as given in Table-5, which indicates that the adsorption was exothermic *i.e.* low temperatures support the adsorption of  $Pb^{2+}$  by the PMMA polymer and implied a diffusion controlled second order kinetic process. Temperature increase did not boost the sorption process.

TABLE-5  
RESULTS OF THERMODYNAMIC PARAMETERS

Heat of adsorption ( $Q_{ads}$ ) (KJ/Kmol)	Sticking probability ( $S^*$ )	Activation energy ( $E_a$ ) (J/Kmol)	Gibbs free energy of adsorption ( $\Delta G^\circ$ ) (KJ/mol)	Apparent entropy ( $\Delta S^\circ$ ) (J/Kmol)	Apparent enthalpy ( $\Delta H^\circ$ ) (J/mol)	Adsorption density ( $\rho$ ) (mol/cm <sup>2</sup> )	Hopping number (n)	Adsorption potential (A) (KJ/mol)
-1.34	0.654	-62.73	-0.799	4.99	-16.00	$5.9 \times 10^{-6}$	4	1.51

The plot of  $\ln(1-\theta)$  versus  $1/T$  using eqn. 13 showed a linear line (Fig. 11). The activation energy ( $E_a$ ) and the sticking probability ( $S^*$ ) were assessed from the slope and intercept correspondingly. The value of  $E_a$  and  $S^*$  were shown in Table-5 as -62.73 J/Kmol and 0.654, respectively. The relatively small and negative  $E_a$  value indicates that low temperature or energy supports the sorption. The adsorption process is therefore exothermic. Relatively low value of  $E_a$  also implies that the sorption process is diffusion controlled. The sticking probability ( $S^*$ ) indicates the measure of the potential of an adsorbate to remain on the adsorbent. It is often interpreted as  $S^* > 1$  (no sorption),  $S^* = 1$  (mixture of physisorption and chemisorption),  $S^* = 0$  (indefinite sticking – chemisorption),  $0 < S^* < 1$  (favourable sticking – physisorption). The significance of  $S^*$  obtained for the sorption of  $Pb^{2+}$  by polymer was between zero and one, which indicates that adsorption was favourable and obeyed a physisorption mechanism.

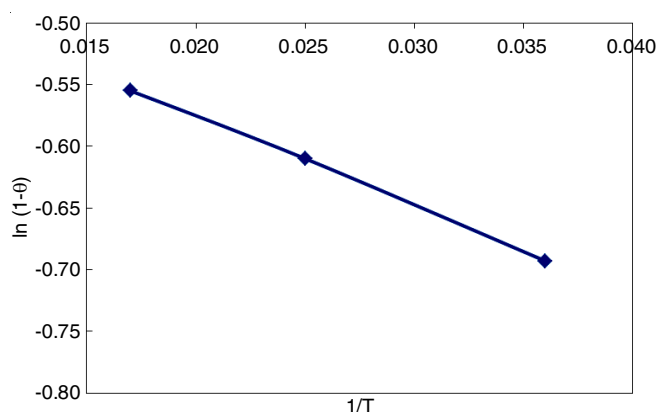


Fig. 11. Plot of  $\ln(1-\theta)$  versus  $1/T$  for the sorption of  $Pb^{2+}$  by the poly(methyl methacrylate) sample

Table-5 also presents the Gibbs free energy ( $\Delta G^\circ$ ) for the sorption of  $Pb^{2+}$  by the polymer which was calculated from eqn. 14. Gibbs free energy is the fundamental criterion of spontaneity. The  $\Delta G^\circ$  value of -0.799 KJ/mol was negative indicating that the sorption process was spontaneous. The value obtained for  $\Delta G^\circ$  was also less than -20 KJ/mol suggesting a spontaneous process in which there was electrostatic interaction between  $Pb^{2+}$  and the polymer to support a physisorption mechanism.

The plot of  $\ln K_o$  versus  $1/T$  from eqn. 15 produced a straight-line graph (Fig. 12), with the slope and intercept equal to  $-\Delta H^\circ/R$  and  $\Delta S^\circ/R$ , respectively. The value of the enthalpy change ( $\Delta H^\circ$ ) calculated from the slope was -16.00 J/mol. A negative  $\Delta H^\circ$  suggests that sorption proceeded favourably at a lower temperature and the sorption mechanism was exothermic. The value of the entropy change computed from the intercept was 4.99 J/Kmol and presented in Table-5. A positive

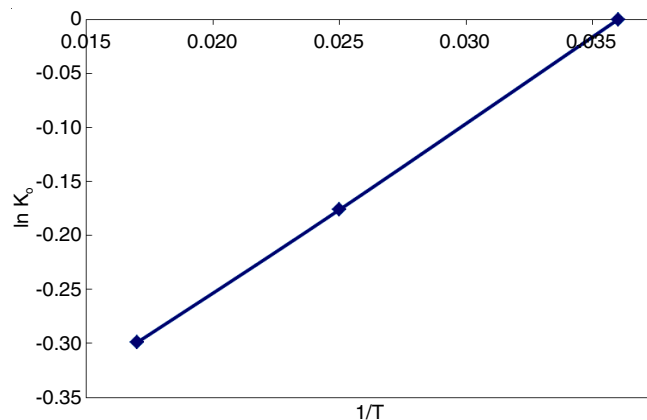


Fig. 12. Plot of  $\ln K_o$  versus  $1/T$  for the sorption of  $Pb^{2+}$  by the poly(methyl methacrylate) sample

$\Delta S$  suggests that freedom of the adsorbed  $Pb^{2+}$  was not restricted in the polymer, indicating that physisorption mechanism predominates.

The packing of  $Pb^{2+}$  in the polymer was assessed using eqn. 16 and results presented in Table-5. The adsorption density ( $\rho$ ) obtained was  $5.9 \times 10^{-6}$  mol/cm<sup>2</sup>. The change in the chemical potential that occurred as  $Pb^{2+}$  moved from the solution to the surface of the polymer was calculated using eqn. 18. Table-5 gives the adsorption potential as 1.51 KJ/mol.

The possibility of  $Pb^{2+}$  finding unoccupied site on PMMA polymer exterior throughout the sorption process was correlated by the number of hopping (n) done by  $Pb^{2+}$ . The hopping number was found to be 4. The lesser the hopping numbers the quicker the adsorption [23,24]. The small value of n obtained suggests that the adsorption of  $Pb^{2+}$  on polymer was very fast and efficient.

## Conclusion

The equilibrium, kinetic and thermodynamic studies recorded a comparatively rapid uptake of  $Pb^{2+}$  by the polymer poly(methyl methacrylate) which was a diffusion controlled in a first-order process. The adsorption was supported by low temperature and energy which was exothermic with a physisorption mechanism. The result of this study has shown that the polymer PMMA, is an efficient adsorbent for the removal of  $Pb^{2+}$  from water solution. The calculations obtained from this study will be constructive in the production or formulation of a novel filtration technology material, which is effective and environment responsive for the removal and recovery of toxic metals such as lead from water solution. The high adsorption capacity of the polymer indicates that it can replace some of the most conventional relatively expensive water treatment techniques presently in use, which is not reasonably viable for small scale industries due to enormous capital investment.



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