

# Comparative Study of Polystyrene and Polymethylmethacrylate Wastes as Adsorbents for Sorption of Pb<sup>2+</sup> from Aqueous Solution

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A comparative study of the sorption of  $Pb^{2+}$  from aqueous solution using polystyrene and polymethylmethacrylate wastes was investigated. The morphological features of the polymer samples were studied using the energy dispersive X-ray spectroscopy, scanning electron microscopy, X-ray diffraction spectroscopy and Fourier transform infrared spectroscopy. Equilibrium, kinetic and thermodynamic batch adsorption experiments were carried out by the concentration, time and temperature effects respectively. The morphological images of the polymers showed irregular small size particles which indicated a high surface area and porosities that facilitated sorption. The adsorption studies recorded relatively rapid uptake of  $Pb^{2+}$  by the polymers which were mainly diffusion controlled and followed second order kinetic process. The thermodynamic studies suggested relatively low temperature (low energy) favoured sorption which was exothermic with physisorption mechanisms for both polymers.

Keywords: Sorption, Polystyrene, Polymethylmethacrylate waste, Adsorbent, Heavy metals.

#### **INTRODUCTION**

Lead contamination is known as one of the most pervasive and elusive environmental health threats, as considered by the fact that exposure to it has been associated with death and diseases in humans, birds and other animals<sup>1,2</sup>. The conventional methods of removal of heavy metals such as Pb<sup>2+</sup> from waste water which include precipitation, flocculation, filtration, ion exchange, reverse osmosis, etc., are very much capital intensive. However, low-cost and renewable materials have been used for the removal of metals from effluents which include biomasses like Nipa palm, Manihotsculentacranz, Sea weed and Medicago sativa<sup>3-6</sup>. But in recent years the surge of industrial activities has intensified more environmental problems as, for example in the deterioration of several ecosystems due to the accumulation of dangerous pollutants such as lead<sup>7</sup>. There is, therefore, the need for the removal of these toxic metal ions from municipal, commercial and industrial effluents before discharge into our environment. This has led to a further search for more low-cost and locally available adsorbent materials with maximum adsorption capacity.

Information on the uses of polystyrene and poly(methyl methacrylate) wastes for the removal of metal ions from solutions is very scanty which has necessitated the present comparative study. Poly(1-phenylethene-1, 2-diyl), also known as

polystyrene or thermocole is an aromatic polymer made from the monomer, styrene.



Poly(1-phenylethene-1, 2-diyl) is one of the most widely used plastics, the scale being several billions kilograms per year. It is used for example in disposable cutlery, plastic models, CD and DVD cases and smoke detector housings. Foamed polystyrene are used for ubiquitous products such as packing materials, insulators and foam drink cups<sup>8</sup>.

Poly(methyl 2-methylpropenoate), commonly called poly-(methyl methacrylate) (PMMA), a synthetic resin produced from the polymerization of methyl methacrylate is a transparent thermoplastic often used as a lightweight or shatter-resistant alternative to glass and is sometimes referred to as acrylic glass. It has moderate properties, easy handling and processing and of 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. PMMA is soluble in di- or tri-chloromethane. It has a maximum water absorption ratio of 0.3-0.4 % by weight<sup>8</sup>.



Poly(methylmethacrylate) is a versatile material and has been used in a wide range of fields and applications such as in residential aquariums, submarines, lenses of exterior lights of automobiles, aircraft windows<sup>9</sup>. It is also used for furniture, picture framing, CDs, DVDs, plastic optical fiber, intraocular lenses, contact lenses and in cosmetic surgery and dental fillings<sup>10</sup>.

The low levels of recycling and biodegradation of both polymers have resulted in much of them ending in landfills and so often abundant as a forms of pollution in the outdoor environment, particularly along shores and waterways and waste dumps, due to their variety of uses<sup>8</sup>.

# **EXPERIMENTAL**

**Sample preparation:** Polymer samples were obtained from the waste bins and thoroughly washed with the deionized water and oven dried at 30 °C. The dry samples were ground and passed through the 100-mesh screens using a Wiley mill. These particle sizes were then washed twice with 0.01 M HCl to remove any metals and debris that might be in the polymer prior to experimental metal ion exposure. The acid washed 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 features of the polymer samples were analysed by FE-SEM, HR-TEM, EDS, XRD and FTIR. The surface morphology and EDS measurements were recorded with a JEOL 7500 F field emission scanning election microscope. The HR-TEM images of the samples were obtained by a CM 200 election microscope operated at 100 KV. Powder X-ray diffraction (PXRD) patterns were collected with a bruker AXS D8 Advanced diffractometer operated at 45 kv 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°. IR spectra were recorded using Perkin-Elmer spectrum 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 samples were weighed and placed in pre-cleaned test tubes. Six Pb<sup>2+</sup> 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 metal solution were added to each tube containing the polymer sample and

equilibrated for 1 h 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. The amount of metal uptake was computed using eqn. 1.

**Time dependent studies:** 0.2 g of the polymer samples were weighed and placed in five pre-cleaned test tubes. The Pb<sup>2+</sup> 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 metal 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. The amount of metal uptake was computed using eqn. 1.

**Temperature effect:** 0.2 g of the polymer samples were weighed and placed in four pre-cleaned test tubes. The Pb<sup>2+</sup> solution with standard concentrationof 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 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 gallenhamp water bath. The polymer suspensions were centrifuged for 5 min at 2500 rpm. The supernatants were analysed as stated in metal analysis. The amount of metal uptake was computed 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:** Various equilibrium, kinetic and thermodynamic models (equations) 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)<sup>5</sup>.

$$q_e = \frac{v}{M}(C_o - C_e) \tag{1}$$

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

Langmuir plots were carried out using the linearized eqn. 2 below.

$$\frac{M}{X} = \frac{1}{abC_e} + \frac{1}{b}$$
(2)

where is the amount of Pb<sup>2+</sup> adsorbed per mass of polymer in mg/L, a and b are the Langmuir constants obtained from the slope and intercepts of the plots.

The essential characteristics of the Langmuir isotherm were expressed in terms of a dimensionless separation factor or equilibrium parameter  $S_f^{11}$ .

$$S_{f} = \frac{1}{(1 + aC_{o})}$$
(3)

where is the initial concentration of  $Pb^{2+}$  in solution. Poot *et al.*<sup>11</sup> have shown by mathematical calculations that the magnitude

of the parameter provides a measure of the type of adsorption isotherm. If > 1, the isotherm is unfavourable;  $S_f = 1$  (linear);  $0 < S_f < 1$  (favourable) and  $S_f = 0$  (irreversible).

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

$$\ln\frac{X}{M} = \frac{1}{n}(\ln C_e) + \ln K$$
(4)

where K and n are Freundlich constants and  $\frac{1}{n}$  is approximately equal to the adsorption capacity.

The fraction of polymer surface covered by the Pb<sup>2+</sup> was computed using eqn. 5

$$\theta = 1 - \frac{C_e}{C_o} \tag{5}$$

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

The effectiveness of the adsorbent (polymer) was assessed by the number of cycles of equilibrium sorption process required to reduce the levels of  $Pb^{2+}$  in solution according to the value of the distribution *i.e.*, partition coefficient (K<sub>d</sub>) in eqn. 6<sup>12</sup>.

$$K_{d} = \frac{C_{aq}}{C_{ads}}$$
(6)

where  $C_{aq}$  is concentration of Pb<sup>2+</sup> in solution, mg/L;  $C_{ads}$  is concentration of Pb<sup>2+</sup> in polymer in mg/L.

The heat of adsorption  $(Q_{ads})$  was obtained using the following Suzuki equation<sup>13</sup>.

$$\ln \theta = \frac{\ln K_o C_o}{T^{0.5}} + \frac{Q_{ads}}{RT}$$
(7)

where T is solution temperature (K);  $K_0$  a constant and R gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>).

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 equation  $8^{14}$ .

$$\ln(1-\theta) = S^* + \frac{E_a}{RT}$$
(8)

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

$$\Delta G^{\circ} = -RT \ln K_{\circ} \tag{9}$$

where  $K_0$  is obtained from the Suzuki equation (eqn. 7).

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. 10.

$$\ln K_{o} = \frac{\Delta S^{o}}{R} - \frac{\Delta H^{o}}{RT}$$
(10)

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

$$\rho = ZrC_e e^{-\left(\frac{\Delta G^\circ}{RT}\right)}$$
(11)

where Z is the valency of the  $Pb^{2+}$ , r the effective radius of the  $Pb^{2+}$  in cm and C<sub>e</sub> the equilibrium concentration in mol/cm<sup>3</sup>.

The expression relating the number of hopping (n) and that of the surface coverage ( $\theta$ ) as shown in eqn. 12 was applied to the experimental data.

$$\mathbf{n} = \frac{1}{(1-\theta)\theta} \tag{12}$$

Other thermodynamic parameters such as adsorption potential (A) was tested by applying eqn. 13

$$A = -RT \ln \frac{C_o}{C_e}$$
(13)

with  $C_o$  and  $C_e$  as initial and equilibrium concentrations in, mol/cm<sup>3</sup> R, the gas constant and T, the solution temperature in K.

The kinetic behaviour of the sorption process was investigated by testing the data using the second order kinetic model expressed in eqn. 14.

$$\frac{1}{q_{t}} = \frac{1}{q_{o}} + K_{2}$$
(14)

where  $q_t$  is the amount of Pb<sup>2+</sup> on the polymer (mg/g or mmol/g at time t,  $q_o$  is the amount of Pb<sup>2+</sup> on the polymer at time  $t_o$  to and  $k_2$  is the second order rate constant.

### **RESULTS AND DISCUSSION**

Fourier transform infrared (FT-IR) spectroscopic study of the polymer was carried out to determine the active functional groups responsible for the binding of Pb<sup>2+</sup> from solution. FTIR spectrum of polystyrene and poly(methyl methacrylate) wastes are presented in Fig. 1a,b. The sharp peaks at 3000-



Fig. 1. Fourier transform infrared (FTIR) spectra of polymer samples,(a) polystyrene and (b) poly(methyl methacrylate)

2800 cm<sup>-1</sup> due to the aromatic C-H stretching, 1700-1500 cm<sup>-1</sup> due to the C = C aromatic stretching , 4000-3900 cm<sup>-1</sup> due to the aliphatic C-H stretching for PS and 3000-2800 cm<sup>-1</sup> due to the alkane C-H stretching, 1600-1300 cm<sup>-1</sup> due to the aliphatic C-H bending and 1750-1735 cm<sup>-1</sup> due to the ester (carbonyl) C=O stretching for polystyrene and PMMA indicate that no functional groups may have played a major role in the sorption process.

X-ray powder diffraction is a powerful tool for characterizing a solid state sample. Each crystalline species has a unique X-ray diffraction pattern. With a diffraction pattern an investigator can identify an unknown specie or characterize the atomic scale structure of an already identified substance. The XRD diffractogram of polystyrene and poly(methyl methacrylate) waste materials are presented in Fig. 2a,b. The most prominent peak in the polymer waste are observed at  $2\theta = 9.51$  and  $18.88^{\circ}$  for polystyrene and for poly(methyl methacrylate), 9.16 and  $19.12^{\circ}$ . The presence of the peaks at  $2\theta = 9.51$  and 9.16 are indications for the presence of amorphous material in the polymer samples while the peaks at 18.88 and 19.12 indicate the presence of crystalline polymer material.



Fig. 2. Powder X-ray diffractogram (XRD) of polymer samples, (a) polystyrene and (b) poly(methyl methacrylate)

Energy dispersive X-ray was applied for elemental analysis of the polymer samples. The EDX spectrum presented in Fig. 3 confirmed sharp peaks due to the following elements: C (95), Al (2) and Ag (3 %), for PS and C (93), Al (2) and O (5 %) for PMMA in addition to hydrogen. The presence of these elements will produce charges on the surfaces of the polymers and create electrostatic forces of attraction between the samples and Pb<sup>2+</sup> in solution.



Fig. 3. Energy dispersive X-ray (EDX) of polymer samples showing quantitative results and spectra for (a) polystyrene and (b) poly(methyl methacrylate)

In order to determine the morphology of the polymers, scanning electron microscope (SEM) images of the samples were taken at magnification  $\times$  270. The SEM images show that the surfaces of the polymer samples had irregular small size particles which indicated a high surface areas and porous nature as shown in Fig. 4. Large surface area of any adsorbent facilitates maximum adsorption<sup>14</sup>.

The percentage sorption of  $Pb^{2+}$  by the polymer samples at different concentrations of the  $Pb^{2+}$  are presented in Fig. 5. The maximum adsorption of 73 % took place at equilibrium concentration of 20 mg/L  $Pb^{2+}$  for PS and of 60 % at equilibrium concentration of 20 mg/L  $Pb^{2+}$  for PMMA. This is because at lower concentration more polymer pore spaces were available for the  $Pb^{2+}$ , but as the concentration of  $Pb^{2+}$  increased, the adsorption capacity of the polymers decreased due to reduced availability of free pore spaces. The results indicated that the sorption of  $Pb^{2+}$  were very much dependent on the concentration of the  $Pb^{2+}$ .

Time dependency studies show the amount of time needed for maximum adsorption to occur. The variation in percentage removal of Pb<sup>2+</sup> with time has been presented in Fig. 6. It indicates that a maximum of 70 % removal of Pb<sup>2+</sup> was observed in 5 min and remained constant afterwards for PS and 58 % within 5 min for PMMA. The relatively short contact times required to attain equilibrium suggest that rapid uptake of Pb<sup>2+</sup> by the polymer occurred to fill some of the vacant pores in the polymers and after which the remaining spaces were difficult to be occupied due to repulsive forces between the Pb ions.





Fig. 4. Scanning electron microscope images of polymer samples, (a) polystyrene and (b) poly(methyl methacrylate)



Fig. 5. Effect of initial concentration of Pb<sup>2+</sup> on the sorption by polymer sample: ◆ polystyrene and ■ poly(methylmethacrylate)



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60 Adsorbed (%) 50 40 30 20 10 0 0 10 30 70 20 40 50 60 Time (min) Fig. 6. Effect of contact time on the sorption of Pb<sup>2+</sup> by the polymer sample:

polystyrene and poly(methylmethacrylate)

Fig. 7 presents the plot of percentage adsorption of Pb<sup>2+</sup> by the polymer at varying temperatures with optimum sorption of 58 % occurring at 28 °C for the PS and 50 % at 28 °C for PMMA. The plots showed that further increase in temperature resulted in a slight decrease in adsorption. This is in agreement with the general principle that physical adsorption decreases with increase in temperature, *i.e.*, molecules adsorbed earlier on a surface tend to desorb from it at elevated temperatures<sup>15</sup>. This behaviour could be attributed to the weakening of the attractive forces between the polymers and Pb<sup>2+</sup>, the increased kinetic energy of the Pb<sup>2+</sup> and the decrease in the thickness of the boundary layers of the polymers.



Fig. 7. Effect of temperature on the sorption of Pb<sup>2+</sup> by polymer sample:

♦ polystyrene and ■ poly(methylmethacrylate)

The extent of adsorption can be correlated by means of an isotherm. Attempts were made to fit the data obtained from the adsorption experiments into various adsorption isotherms. The linear plots of the Langmuir and Freundlich isotherm models for the sorption of  $Pb^{2+}$  by the polymer are presented in Figs. 8 and 9. These straight line plots confirmed the application of the Langmuir and Freundlich isotherm models to the adsorption of  $Pb^{2+}$  by the polymers. The slopes and intercepts were used to compute the Langmuir constants and adsorption capacity.

The fraction of the polymer surface covered by the  $Pb^{2+}$  is given as 0.730 for PS and 0.592 for PMMA (Table-1). These values indicate that over 70 and 59 % of the pore spaces of the PS and PMMA surfaces respectively were covered by the  $Pb^{2+}$ , which means higher degree of adsorption with the polystyrene.



Fig. 8. Langmuir isotherm plot for the sorption of Pb<sup>2+</sup> by the polymer samples, (a) polystyrene and (b) poly(methyl methacrylate)



Fig. 9. Freundlich isotherm plot for the sorption of Pb<sup>2+</sup> by polymer sample, (a) polystyrene and (b) poly(methylmethacrylate)

In order to determine the nature of the adsorption process, whether favourable or unfavourable, the dimensionless constant separation  $S_f$  term was investigated (eqn. 3). The result ( $S_f = 0.678$ ) for PS and ( $S_f = 0.951$ ) for the PMMA, in Table-1 were less than one and greater than zero which showed that the sorption of Pb<sup>2+</sup> onto the polymers was favourable.

TABLE-1 EQUILIBRIUM AND KINETIC PARAMETERS							
Polymer waste	Surface coverage $(\theta)$	Separation factor $(S_f)$	Sorption coefficient (K <sub>d</sub> )	Adsorption capacity (mol/g)			
PS	0.730	0.678	0.374	1.00			
PMMA	0.592	0.951	0.689	1.00			

The effectiveness of the polymer as an adsorbent for  $Pb^{2+}$  from solution was assessed through the sorption distribution or partition coefficient (k<sub>d</sub>) presented in Table-1. The value of (0.374) for PS and (0.689) for PMMA suggest that polystyrene is a more effective adsorbent than poly(methylmethacrylate) and that a few number of cycles of equilibrium sorption process will be required to reduce the levels of  $Pb^{2+}$  in solution.

From the Freundlich plot (Fig. 9), the adsorption capacities of the polymers were calculated to be 1 mol/g for PS and 1 mol/g for PMMA.

In order to calculate the heats of adsorption ( $Q_{ads}$ ) for the sorption of Pb<sup>2+</sup> onto the polymers, eqn. 7 was used. The value of (-0.123 KJ mol<sup>-1</sup> K<sup>-1</sup>) for PS and (-1.34 KJ mol<sup>-1</sup> K<sup>-1</sup>) for PMMA are negative as presented in Table-2, which indicate that the adsorptions were exothermic *i.e.*, low temperatures favour the adsorption of Pb<sup>2+</sup> by the polymers and also suggested diffusion controlled second order kinetic processes. Temperature increase did not enhance the sorption processes.

The plots of  $\ln(1 - \theta)$  versus 1/T using eqn. 8 yielded straight lines as presented in Fig. 10. The activation energies  $E_a$  and the sticking probabilities S\* were calculated from the slopes and intercepts, respectively. The values of  $E_a$  and S\* were shown in Table-2 as PS (-156.0 J k<sup>-1</sup>mol<sup>-1</sup>), PMMA (-62.73 J k<sup>-1</sup>mol<sup>-1</sup>) and PS (0.819), PMMA (0.654), respectively. The relatively low and negative  $E_a$  values indicate that low temperature or energy favours the sorption and the adsorption processes were exothermic. Relatively low values of  $E_a$  also suggest that the sorption processes were 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



Fig. 10. Plot of ln(1-θ) versus 1/T for the sorption of Pb<sup>2+</sup> by the polymer sample: ◆ polystyrene and ■ poly(methyl methacrylate)

TABLE-2 THERMODYNAMIC PARAMETERS									
Polymer waste	Heat of adsorption (Q <sub>ads</sub> , KJ/mol K)	Sticking probability (S*)	Activation energy (E <sub>a</sub> , JK mol)	Gibbs free energy of adsorption (ΔG°, KJ/mol)	Apparent entropy (ΔS°, J/mol K)	Apparent enthalpy (ΔH°, J/mol)	Adsorption density (P, mol/cm <sup>2</sup> )	Hopping number (n)	Adsorption potential (A, KJ/mol)
PS	-0.123	0.819	-156.0	-0.840	1.67	-155.9	$5.60 \times 10^{-5}$	4	1.92
PMMA	-1.340	0.654	-62.73	-0.799	4.99	-16.0	$5.90 \times 10^{-6}$	4	1.51

and chemisorption),  $S^* = 0$  (indefinite sticking - chemisorption),  $0 < S^* < 1$  (favourable sticking - physisor-ption). The values of  $S^*$  obtained for the sorption of  $Pb^{2+}$  by the polymer were between zero and one which indicate that the adsorption was favourable and followed a physisorption mechanism.

Table-2 also presents the Gibbs free energy ( $\Delta G^{\circ}$ ) for the sorption of Pb<sup>2+</sup> by the polymers which was calculated from eqn. 9. Gibbs free energy is the fundamental criterion of spontaneity. The  $\Delta G^{\circ}$  value of -0.840 KJ/mol for PS and -0.799 KJ/mol for PMMA were negative indicating that the sorption processes were spontaneous. The values obtained for  $\Delta G^{\circ}$  were also less than -20 KJ/mol suggesting electrostatic interactions between the Pb<sup>2+</sup> and the polymers which supported physisorption mechanisms.

The plots of lnK<sub>o</sub> versus 1/T from eqn. 10 were linear as presented in Fig. 11, with the slopes and intercepts equal to - $\Delta$ H°/R and  $\Delta$ S°/R, respectively. The values of the enthalpy changes ( $\Delta$ H°) calculated from the slopes were PS (-155.9 J/ mol) and PMMA (-16 J/mol). The negative  $\Delta$ H° values suggest that sorption proceeded favourably at a lower temperatures and the sorption mechanisms were exothermic. The values of the entropy changes computed from the intercept were PS (1.67 J/mol K), PMMA (4.99 J/mol K) and presented in Table-2. The positive  $\Delta$ S values obtained suggest that the freedom of the adsorbed Pb<sup>2+</sup> were not restricted in the polymers, indicating that physisorption mechanisms predominate.

The packing of  $Pb^{2+}$  in the polymer was assessed using eqn. 11 and results presented in Table-2. The adsorption densities,



sample:  $\blacklozenge$  polystyrene and  $\blacksquare$  poly(methylmethacrylate)

 $\rho$ , obtained were 5.6 × 10<sup>-5</sup> and 5.9 × 10<sup>-6</sup> for PS and PMMA, respectively.

The changes in the chemical potentials that occurred as the Pb<sup>2+</sup> moved from the solution to the surfaces of the polymers were calculated using eqn. 13. Table-2 give the adsorption potentials as PS (1.92 KJ/mol) and PMMA (1.51 KJ/mol).

The probability of  $Pb^{2+}$  finding vacant site on the polymer surfaces during the sorption was correlated by the number of hopping (n) done by the  $Pb^{2+}$ . The hopping numbers presented in Table-2 were 4 and 4 for PS and PMMA, respectively. The lower the hopping number the faster the adsorption<sup>14</sup>. The low values of n obtained for both PS and PMMA suggest that the adsorption of  $Pb^{2+}$  on that polymers were very fast.

The rate at which sorption takes place in a batch adsorption process is very important in designing batch sorption systems. Consequently, it was important to establish the time dependence of such system under various process conditions. In an attempt to understand the sorption process, the second order kinetic rate expression model was applied to the experimental data. The second order kinetic model was applicable to the experimental data because linear relationships were obtained by the plots of *versus* for the PS and PMMA as presented in Fig. 12.



Fig. 12. Second order kinetic plot for the sorption of Pb<sup>2+</sup> by the polymer sample: ◆ polystyrene and ■ poly(methylmethacrylate)

#### Conclusion

The equilibrium, kinetic and thermodynamic studies recorded relatively rapid uptake of  $Pb^{2+}$  by the polymers which were diffusion controlled second order processes. The adsorptions were favoured by low temperature and energy which were exothermic with physisorption mechanisms. The polymers were effective adsorbent for the removal of  $Pb^{2+}$  from aqueous solution. The results from this study will be useful for a novel

filtration technology which is effective and environment friendly to remove and recover heavy metals from aqueous solutions. This will replace the most conventional relatively expensive treatment techniques presently in existence, which are not economically viable for small scale industries due to huge capital investment.

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