

The Effect of Coke-Polymer Composite on Lead (II) Removal from Aqueous Solution

Lindani M. Mdlalose, Shivani B. Mishra, Bhekile B. Mamba

Abstract—The present study deals with the possible use of coke-polymer composite instead of raw coke in the removal of lead ions from aqueous solution. The composite preparation comprises modifying the surface properties of coke with hydrophilic polymers like polyvinyl alcohol (PVA), poly ethylene glycol (PEG) and poly vinyl pyrrolidone (PVP). Characterization of the obtained material in terms of morphology, surface area, pore volume and adsorptive properties of lead was done. The batch adsorption studies were carried out using variables such as pH, contact time and the initial concentration. The composite material was found to have better adsorption capacity when compared to raw coke. To understand the adsorption isotherm processes, Freundlich and Langmuir isotherm were analyzed. The monolayer adsorption capacity for lead ions removal was found to be 2.41 mg/g, 2.95 mg/g, 8.32 mg/g, 9.70 mg/g and 9.84 mg/g for raw coke, acid treated coke, PVA coated coke, PEG coated coke and PVP coated coke, respectively. Kinetic measurements showed that adsorption attained equilibrium in 600 min. and the model followed second order in nature.

Keywords—Adsorption, hydrophilic polymers, isotherms, polymer coating.

I. INTRODUCTION

HEAVY metals always find a way to get into our water streams as a result of their solubility nature in the aquatic environment. These originate from domestic and industrial activities such as mining, smelting operations and agriculture. Metals like cadmium (Cd), lead (Pb) and mercury (Hg) are found to be cumulative poison which do not break down easily in the environment and are said to be carcinogenic and mutagenic [1]. The accumulation of lead in the human body causes chronic poisoning which include mental retardation to infants and kidney problem to adults [2]. Till today, water treatment methods are still under examination since it is the major challenge for municipalities and industries to dispose polluted water on a daily basis. Industrial wastes are the major cause of health hazards in water pollution [3]. As a result, a number of researchers developed methods which involve filtration, ion exchange, membrane process, chemical precipitation, adsorption, etc for the removal of various pollutants like heavy metals in water [4]. Among other technologies adsorption has a wider

applicability in contaminated water control. It is well known that activated carbon is of great interest in terms of metal recovery in aqueous solutions by adsorption process. And coke has been found to be one of the precursors of activated carbon due to its high carbon content and the fact that it is already carbonized [5]. In spite of the efficacy of activated carbon in metal recovery, is not an economical option for large effluents as its processing costs are high. Therefore there is still a need of investigating effective adsorbents which are of cheap precursors, cheap preparation process and avoids activation. Petroleum coke is a readily available material and most abundant in Canada for bitumen upgrading [6]. As a result of high percentage of organic content on coke and abundance, it serves a possible option for aquatic reclamation. It has been shown that unmodified coke do have some adsorption strength to heavy metals, however its capacity is very low [7]-[8]. This also applies to when untreated coke powder was used to remove naphthenic acids together with total acid extractable organics from tailing water deposits, the adsorption strength was low [9]. Poor interaction between the metals and coke surface may be attributed to low contact ratio and limited active sites in coke which is again hydrophobic in nature. It has been reported that coke is made up of stable micrographitic (naphthalene, anthracene, pyrene etc.) structures and contain certain amount of minerals which are said to block coke pores [10]. However, the stability of coke could be disturbed through various treatment methods as coke is a carbonaceous material, incorporating functionality is much simpler. Polymer coating is another way of modifying the surface properties of carbonaceous materials specifically for adsorption purposes where the wettability of the material can be altered [11]. This method is practically straightforward and avoids complicated polymerization reactions. For materials which are rich in carbon and hydrophobic in nature (like coke), incorporating hydrophilic polymers to enable the particles to be stable in water is necessary. The drawback associated with hydrophilic polymers attached to the carbonaceous surface is that they tend to dissolve in water with time. However, when the material is cross-linked, water molecules will be absorbed and the composite swell but does not dissolve in water. Methods such as photocrosslinking, gamma irradiations, freeze-thaw cycles and electron beam are able to crosslink the polymers [12]. Poly vinyl alcohol, poly ethylene glycol and poly vinyl pyrrolidone have been used for many purposes especially in biomedical and pharmaceutical applications due to its low toxicity and biocompatibility. They

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have been incorporated in materials like glass, silica gel activated carbon etc. to enhance adsorption in aqueous solution and odour emissions through different preparation methods [13]-[16]. The present study deals with the uptake of lead ions in aqueous solutions by adsorption process using coke hydrophilic polymer composite. Based on the type of nature of the target impurity, coke surface was modified by chemical oxidation to introduce active groups like carboxyl and lactone. The oxidized coke material was further dispersed in to polymer solutions and an initiator was used as a form of a catalyst to crosslink the composite. In particular, focal areas of the present work were to investigate the properties of raw and functionalized coke based composites and its application towards adsorption properties.

II. EXPERIMENTAL

A. Instruments and Apparatus

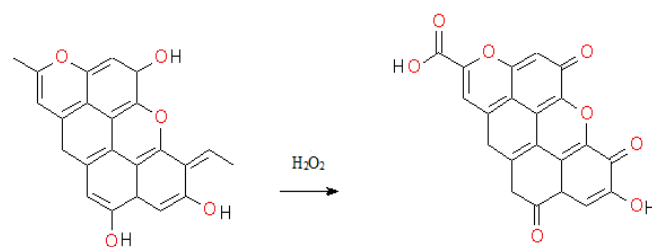
Lead ions were determined by Atomic Absorption Spectrometer (AAAnalyst 400 Perkin Elmer) The wavelength selected was 283.3 nm. The pH meter (Mettler Toledo) was used for pH adjustments. Specific surface area and pore volume of raw coke together with the polymer coated coke were measured by sorption of nitrogen at -196 °C on a Brunauer-Emmett-Teller (BET) Sorptometer. The morphology was examined using JEOL scanning electron microscope (SEM) under a 20 kV electron acceleration voltage. Raman spectra were measured using RamanMicro 200 Microscope where on a glass slide in a powder form without any solvent.

B. Reagents and Standard Solutions

All chemicals were of analytical grade. Coke sample was received from Macphail Coal Distributors in South Africa. PVA, PEG and PVP were purchased form Sigma Aldrich hydrogen peroxide, potassium persulphate, hydrochloric acid together with sodium hydroxide were procured from Merck. The stock standard solution of Pb(II) was prepared by dissolving Pb(NO₃)₂ with de-ionized water. Working standard solutions were prepared by diluting the stock solution with de-ionized water to get the required concentrations.

C. Sample Preparation

Coke powder was oxidized with hydrogen peroxide (32% v/v) for 3 hours at 323 K.. The obtained product was further introduced to hydrochloric acid to remove the mineral components found in coke. This was then filtered and washed thoroughly with de-ionized water until the pH of the filtrate was around 7 and dried for overnight.



Scheme 1: Chemical oxidation of coke

For coating of raw and functionalized coke particles, 5% (w/v) polymer solution was prepared. The raw and modified cokes were kept in contact with the polymer solution for 12 h to allow polymer chains to absorb onto coke particles. Potassium persulphate was added to the solution to induce crosslinking. This was stirred for 1 h at 50 °C in a nitrogen atmosphere. This was later filtered, washed gentle with de-ionized water and dried out in an oven at 353K.

D. Adsorption Experiments

Batch experiments were carried out using conical flasks of 100.0 mL capacity. The effect of medium pH, contact time and initial concentration were conducted on Pb(II). The effect of pH on adsorption was investigated at pH range 2.0-9.0 using either 0.1 M HCl or 0.1 M NaOH to adjust the pH at room temperature. For kinetic studies, 500 mg of the adsorbent was shaken with 200.0 mL of Pb(II) (25 ppm) and the filtered solution was taken at different time intervals. Contents were constantly agitated in a mechanical shaker at 160 rpm. Adsorption isotherm measurements were performed by agitating 50 mg of the adsorbent with 50.0 mL of varying Pb(II) concentrations from 2.0 to 70.0 ppm at an optimum pH of 6.0. At the end of each effect the adsorbent was filtered out and concentration in the supernatant was determined using flame Atomic Absorption Spectrometer (FAAS). The amount adsorbed was therefore determined from the difference in initial and residual concentration in the liquid phase using the formula:

$$qe = \frac{(Ci - Ce)V}{m} \quad (1)$$

Where: Ci (mg/L) is the initial concentration of Pb(II), Ce (mg/L) is the concentration at equilibrium, V (L) is the volume of the solution and m (g) is the mass of the adsorbent.

E. Limit of Detection Determination

This was calculated based on three times the standard deviation of blank solution tested in eight runs. overlap

III. RESULTS AND DISCUSSION

A. Characterization of Coke and Coke-Polymer Composite

The measured BET surface area of raw coke was 1.058 (m²/g) and upon treated with acid it went up by 8% to 1.152 (m²/g), which indicate the successful removal of minerals found in coke. And again this was also evidenced by coke calcination to obtain the ash content of coke which was originally 15% and dropped to 4.7% after being modified with an acid. Coating with polymer films decreased the surface area as well as the pore volume of the material as shown in Table I. This is attributed to polymers depositing to coke surface particles and filling up the small cavities that were present in coke. The scanning electron micrographs (SEMs) in Fig. 1 show that the coke particles were actually coated with polymers. Here it shows that the uncoated coke particles are likely to be rough, heterogeneous and have voids throughout, whereas on the other hand the coated particles are smooth and pores are slightly blocked. These findings accord the coating of coke particles with polymer films.

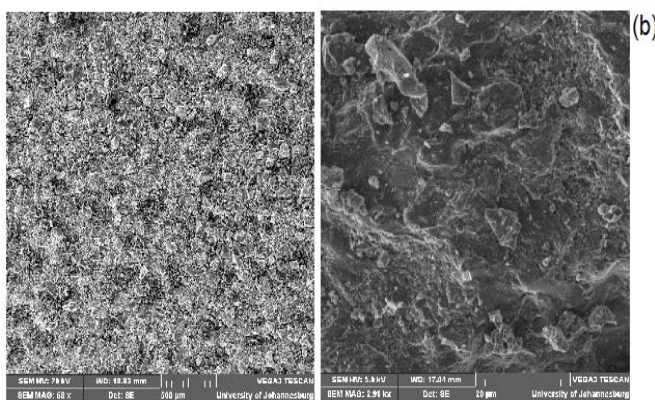
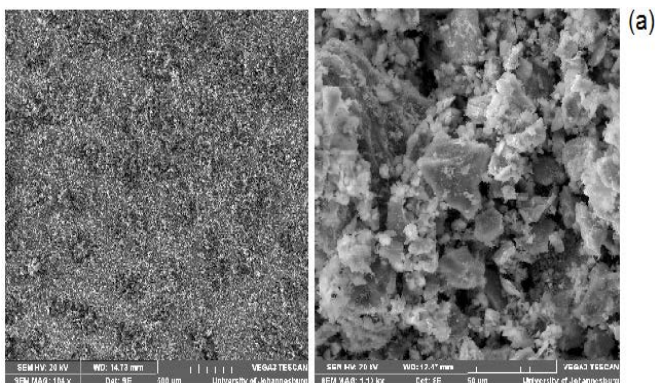


Fig. 1 Scanning electron micrographs of (a) uncoated raw coke and (b) poly vinyl pyrrolidone coated acid treated coke.

Conjugated carbon double bonds lead to high Raman intensity, therefore Raman serves as a best tool to understand the atomic ordering of a material. For carbonaceous materials, two predominant peaks appear on the spectra. Those are: D-band/peak which is likely visible at around (1355 cm⁻¹) and G-

band at (1580 cm⁻¹) [17]-[18]. Higher disorder (D-band) is as a result of six fold rings where as the gravitic nature (G-band) is associated with the in plane stretching bonds of sp² carbon atoms as shown in Fig. 2. Positions of the D-band and G-band are given in Table II with their corresponding intensity ratios. From the results it goes without any doubt that coke is amorphous or disordered. This is supported by the higher D-band in Fig.3 which is the distribution of vibrational modes that are amorphous in nature. Previously the difference between amorphous and graphitic was based on the note that graphite could be converted to gravitic acid by using oxidizing agents where as the amorphous carbon was known not to be affected in this regard [19]. However when amorphous materials were introduced to heating then the structure will be destructed [18]. So from the obtained results it shows that the atomic ordering of coke technically remained the same as there were insignificant changes upon acid treatment and polymer coating. Intensity ratio (I_D/I_G) approaching zero suggests the increase in graphitic mode which was contrary to the obtained results as the structure was amorphous.

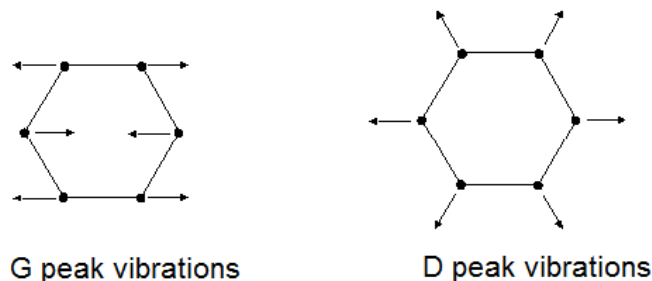


Fig. 2 Raman vibration modes [17].

TABLE I
SURFACE AREA AND PORE VOLUME CALCULATED BY BET EQUATION

Sample ID	Surface area (m ² /g)	Pore volume (cm ³ /g)
R-C	1.058	0.0458
F-C	1.152	0.0507
R-PVA	0.120	0.0139
F-PVA	0.193	0.0221
R-PEG	0.102	0.0137
F-PEG	0.158	0.0189
R-PVP	0.083	0.0137
F-PVP	0.194	0.0133

Where, R-C: Raw coke, F-C: Acid treated coke, R-PVA: PVA coated raw coke, F-PVA: PVA coated acid treated coke, R-PEG: PEG coated raw coke, F-PEG: PEG coated raw coke, R-PVP: PVP

B. Effect of pH

The degree of metal adsorption is technically related to the

pH in aqueous solution for the fact that the dissociation of adsorbent active sites as well as the speciation of metal ions in aqueous phase [20]. Hence the effect of hydrogen ion concentration in the study was examined at pH ranging from 2 to 9 as indicated in Fig. 4. Here it shows the summary of Pb (II) uptake at various pH values of which the same trend was followed for coke and its composites. Initially or at low pH values there is poor metal adsorption as a result of excess amount of hydronium ions (H_3O^+) than the metal ions present in the solution. Therefore these H_3O^+ take over on the adsorbent binding sites leading to metal ion being free in the solution. Increase of metal ions uptake is observed from pH 2 up to 6. This may be explained by the fact that increasing the pH of Pb (II) in solution results in various species being noticeably present. Like for example at pH 6, $Pb(OH)^+$ and Pb^{2+} are major ions in the solution, making it easier to be accessed or to interact with surface functional groups present in the adsorbent [21]. And once again in increasing the pH to higher values than 6, there is a formation of metal precipitation and the adsorbent weakened again. This drastic deteriorating was due to the change of species to a negatively charged ion $Pb(OH)_3^-$ which was now resisting on the surface active sites of the adsorbent [22].

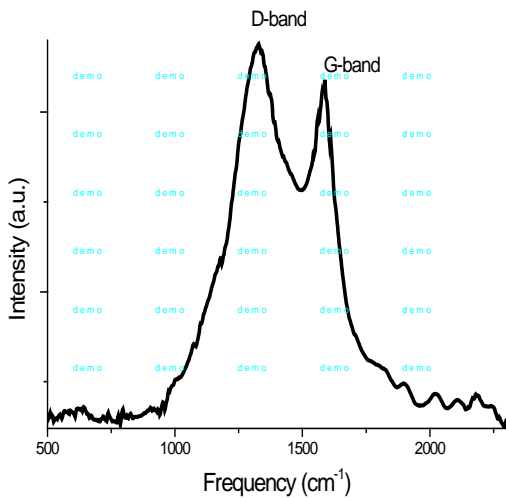


Fig. 3 Raman spectra of raw coke.

TABLE II
RAMAN PEAK POSITIONS AND INTENSITY RATIOS (I_D/I_G)

Sample ID	D-band (cm ⁻¹)	G-band (cm ⁻¹)	I_D/I_G
R-C	1344	1590	1.038
F-C	1350	1600	1.024
F-PVA	1344	1596	1.046
F-PEG	1350	1600	1.021
F-PVP	1346	1602	1.053

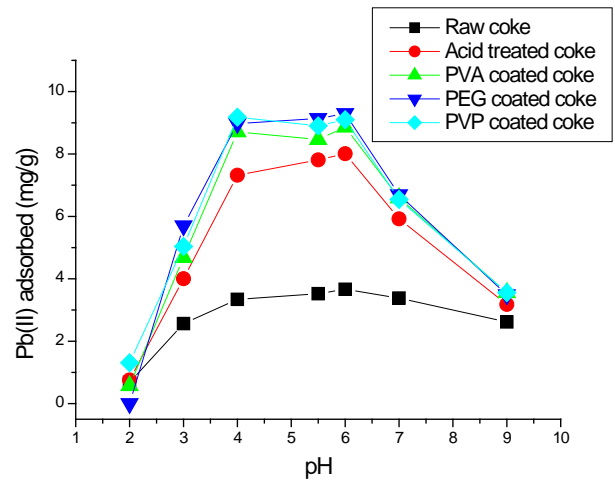


Fig. 4 Effect of pH on 25 mg/L Pb (II) solution, agitation speed = 160 rpm, temperature $\pm 25^\circ C$, contact time 120 min and adsorbent dosage = 0.05 g/20 mL.

C. Adsorption Kinetics

Time effect was conducted in order to measure the time taken to reach equilibrium. The presented plot in Fig. 4 reveals that the substantial removal was during the first 60 min and insignificant changes were noticed after that. This is probably associated with availability of surface active sites at an earlier stage of which with time it become exhausted leaving only the interior part of adsorbent to perform the up taking which is much slower. A close look on Fig.5 indicates that polymer composites were somehow slower that the as received coke and the acid treated coke. This delay may be due to different characteristics of the adsorbent like the degree or percentage amount of polymer coated with which may require longer period for mass transfer of the metal ions.

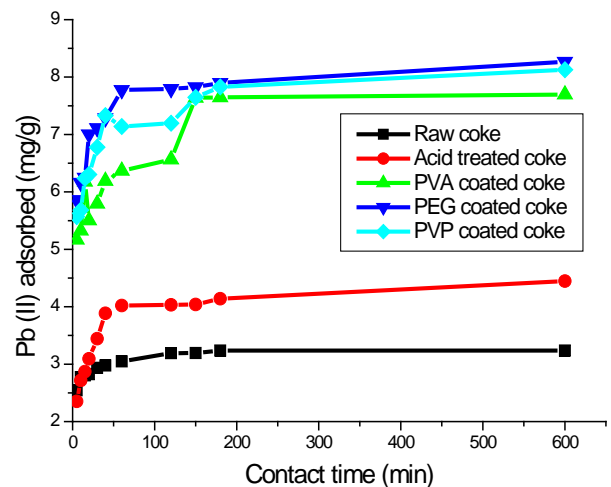


Fig. 5 Effect of contact time on 25 mg/L Pb (II) solution, agitation speed = 160 rpm, temperature $\pm 25^\circ C$, pH = 6 and adsorbent dosage = 0.5 g/200 mL.

The evaluation of adsorption kinetics in wastewater treatment is vital as it provides clear trails on reaction pathways and sorption reaction mechanisms as it explains the solid uptake rate as well as controlling the adsorbent resident time on a solid-solution interface [23]. Therefore, having an idea of the pollutant rate removal makes it possible to create an appropriate adsorption treatment plant. Here two models have been looked at to investigate the sorption mechanism that is pseudo-first order equation (based on solid capacity) and pseudo-second order (based on solid phase), respectively [23]. Integrated equations are shown in equation (2) and (3):

$$\log(qe - qt) = \log qe - \frac{k_1}{2.303} t \quad (2)$$

$$\frac{t}{qt} = \frac{1}{k_2 q^2} + \frac{1}{qe} t \quad (3)$$

where: q_e and q_t are adsorbed amount in mg/g at equilibrium and at time t . k_1 and k_2 are pseudo first and second order adsorption models measured in min^{-1} .

According to the results summarized in Table III, the study belongs to second order model as in first order the calculated q_e was not correlating with experimental q_e . Therefore, first order could not comply in the system. So what this basically means is that the adsorption was associated with two sites possession. One great benefit with second order model is to directly get the equilibrium capacity from the measurements [24].

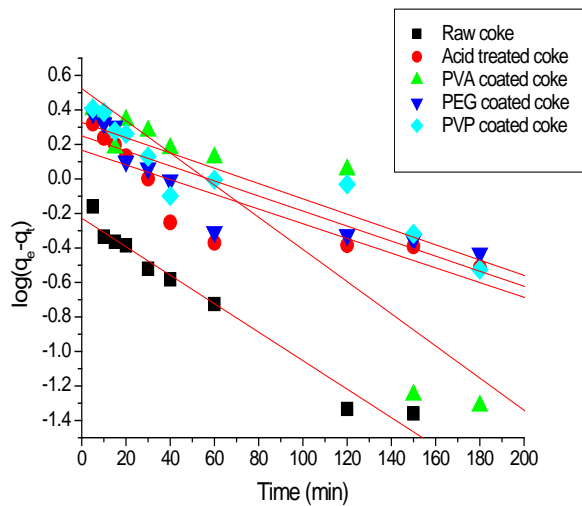


Fig. 6 Pseudo-first order kinetic plot

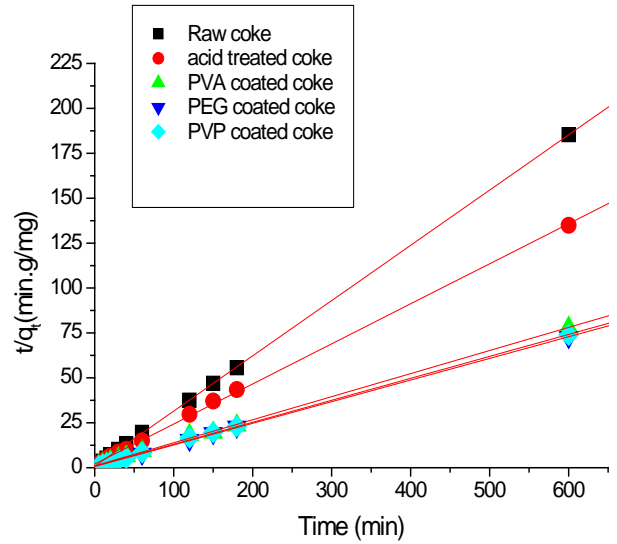


Fig. 7 Pseudo-second order kinetic plot

D. Effect of Initial Metal Concentration

Various metal concentrations were measured to conduct the driving force of mass transfer between the solution and solid phases. The observations reveal that, the amount of metal ion adsorbed increased with the increase in the concentration of Pb(II) from 2 ppm to 70 ppm as shown in Fig. 8. Here, it was indicated that the adsorption process on different coke materials was dependent on the amount of Pb(II) ion present in the solution.

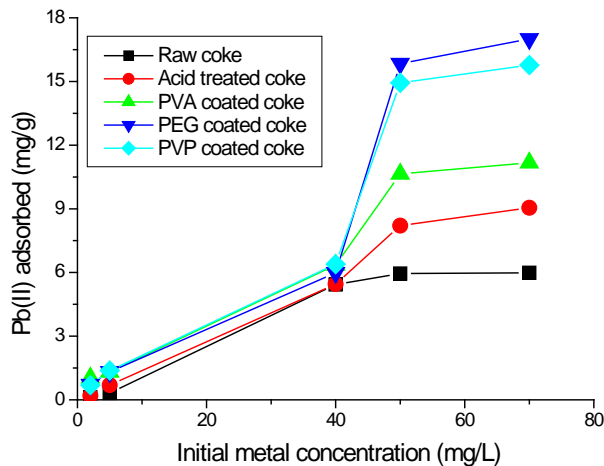
The other important physiochemical characteristic for adsorption assessment other than kinetics is the equilibrium of adsorption. Equilibrium is capable of revealing the capacity of the adsorbent [25]. The relationship between equilibrium and the adsorbent is well described by the implication of isotherms. The two isotherms reported in the study were: Langmuir and Freundlich isotherms as expressed equations (4) and (5).

$$\frac{1}{qe} = \frac{1}{K_L} \frac{1}{Ce} + \frac{1}{q \max} \quad (4)$$

Where: q_e is the amount adsorbed at equilibrium (mg/g)
 q_{\max} maximum adsorption capacity of the adsorbent (mg/g)

TABLE III
 LAGERGREN KINETIC PARAMETERS

Sample ID	q _e (exp.) (mg/g)	First order kinetic model			Second order kinetic model		
		k ₁ (L/min)	q _e (cal.) (mg/g)	R ²	k ₂ (g/mg.min)	q _e (cal.) (mg/g)	R ²
Raw coke	3.2374	0.0183	0.2274	0.9732	0.1194	3.2531	1.0000
Acid treated coke	4.4467	0.0099	0.1667	0.7567	0.0243	4.4863	0.9994
PVA coated coke	7.6948	0.0214	0.5239	0.8263	0.0157	7.7882	0.9988
PEG coated coke	8.2680	0.0101	0.2499	0.8039	0.0092	8.3056	0.9998
PVP coated coke	8.1272	0.0101	0.3280	0.8503	0.0177	8.1833	0.9995


 Fig.8 Effect of initial metal concentration on optimum pH = 6, agitation speed = 160 rpm, temperature $\pm 25^{\circ}\text{C}$, contact time 120 min and adsorbent dosage = 0.05 g/20 mL.

The overall obtained adsorption isotherm data (Table IV) fitted both the Langmuir and Freundlich isotherm equations as typical linearized graphical representations are shown in Fig. 9 to 12, respectively.

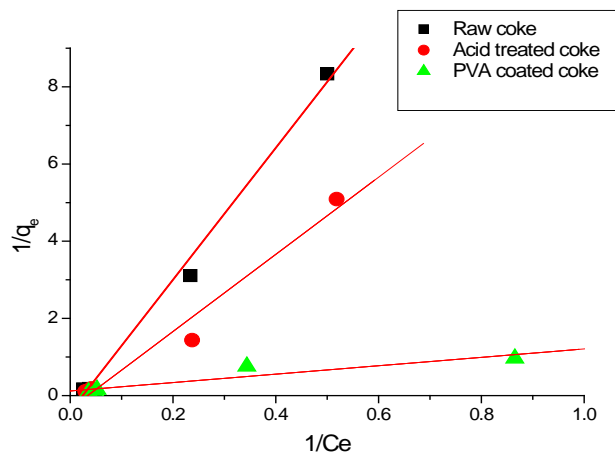


Fig. 9 Plot of Langmuir adsorption isotherm on raw coke, acid

This is supported by the correlation coefficient (R^2) of > 0.9 . Parameters such as q_{max} (in Langmuir) and n (in Freundlich) which are connected to adsorption capacity increased upon coke modification, from the demineralized coke as well as on coke fused with hydrophilic polymers.

E. The detection Limit and Instrumental precision

Following the procedure on the International Union of Pure and Applied Chemistry,[26] detection limit was the product of three times the standard deviation of data obtained from eight runs of the blank solution. The detection limit was found to be 0.183 mg/L and the standard deviation was 2.67 revealing the precision of results on Pb(II) analysis.

$$\log qe = \log K_F + \frac{1}{n} \log C_e \quad (5)$$

C_e is the equilibrium concentration of pollutant (mg/L)

K_L is the Langmuir constant

K_F and n are the parameters of Freundlich related to adsorption capacity

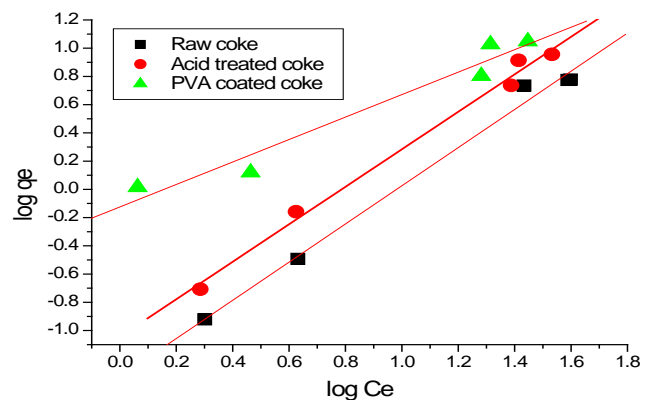


Fig. 10 Plot of Freundlich adsorption isotherm on raw coke, treated coke and PVA coated coke

TABLE IV
PARAMETERS OF LANGMUIR AND FREUNDLICH ADSORPTION ISOTHERM MODELS

Sample ID	Langmuir			Freundlich		
	q_{max}	K_L	R^2	n	K_F	R^2
Raw coke	2.4091	0.0243	0.9939	0.7395	0.0471	0.9922
Acid treated coke	2.9455	0.0340	0.9752	0.7531	0.0903	0.9926
PVA coated coke	8.3195	0.1011	0.8691	1.2574	0.7511	0.9559
PEG coated coke	9.6993	0.8563	0.9923	1.7388	2.6626	0.9478
PVP coated coke	9.8425	0.8167	0.9946	1.7787	2.5735	0.9564

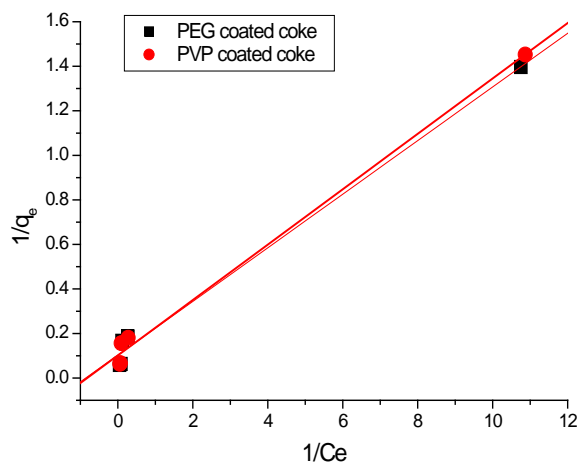


Fig. 11 Plot of Langmuir adsorption isotherm on PEG coated coke and PVP coated coke.

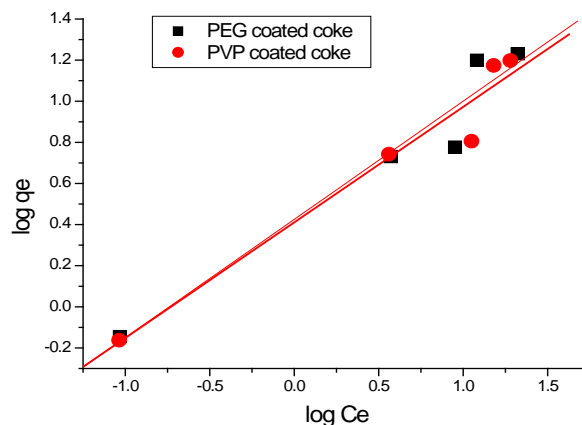


Fig.12 Plot of Freundlich adsorption isotherm on PEG coated coke and PVP coated coke.

IV. CONCLUSION

Isotherm parameters fitted both Langmuir and Freundlich models however in PVA coated coke only the Freundlich was favored. This may due to heterogeneous interactions between lead ions and PVA coke composite. For the kinetic measurements, pseudo-second order correlated very well with the experimental results. In addition, adsorption mechanism is most likely to be a chemisorption reaction.

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