ADSORPTION KINETICS OF Pb²⁺, Ni²⁺ AND Cd²⁺ ONTO POWDERED EGGSHELLS

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ABSTRACT

In this paper, the removal of lead, nickel and cadmium from aqueous solution by adsorption was studied. Chicken's eggshells were collected, washed with distilled water, air dried, pulverized, sieved into different particle sizes and stored for use. Powdered eggshells (PES) were separated, its properties were determined and used as an adsorbent to remove each of these selected metals from aqueous solution individually, multi-component synthetic wastewater and from natural water in a batch process. Effects of initial concentration of the metals, initial pH of the solution and particle size of PES on the adsorption capacities of these selected metals onto PES were monitored. Estimated cost of producing PES was conducted under two major sources of power supply in Nigeria. The study revealed that PES contained calcium, aluminum, and iron as part of its major components. There were slight reductions in the adsorption of Pb²⁺, Ni²⁺ and Cd²⁺ onto the larger particle size of PES. Higher adsorption occurred when the initial concentrations and the pH values were increased, but the adsorption capacities were not affected. Cost of PES producing was found to be lower (0.43USD) than the cost of producing other adsorbents. It was concluded that PES could be used as an adsorbent to remove Pb²⁺, Ni²⁺ and Cd²⁺ from aqueous solutions and raw water.

Keywords: Adsorption, Eggshells, Heavy Metal, Synthetic Wastewaters, Natural Water, Isotherm .

INTRODUCTION

The presence of heavy metals such as lead (Pb²⁺), nickel (Ni²⁺) and cadmium (Cd²⁺) coupled with their effects on the environment have been documented in the literature. The sources of these heavy metals are well known to be wastewaters. Wastewater and water treatment techniques can be classified into the following groups: physical, chemical, biological, electrical, membrane and irradiation. The methods applied for the removal of heavy metals from wastewater include chemical precipitation (Otun *et al.,* 2006 a and b; Krishnan and Anirudhan, 2003), solvent extraction, ultrafiltration, biochemical treatment, ion exchange and adsorption. Out of these methods, adsorption, which is considered as a third stage of wastewater treatment has been preferred over other wastewater and water treatment techniques because of its cheapness and the high-quality treated effluents it produces. Adsorption is a process by which a solid adsorbent can attract a component from the aqueous phase to its surface and form an attachment through a physical or chemical bond, thereby removing the component from the aqueous phase. Over the years the role of adsorption in wastewaters and water treatment has not been underestimated. Adsorption of pollutant by a number of materials (low cost materials) such as carbon from palm kernel shells (Ogedengbe *et al.,* 1985; Adewumi, 1999) , leaf mould (Sharma and Forster, 1994), activated groundnut husk carbon (Srinivassan *et al.,* 1991;Periasamy *et al.,* 1991), coconut husk and palm pressed fibres (Tan *et al.,* 1993), coconut shell activated carbon (Erhan *et al.,* 2004), coconut shell, wood and dust coal activated carbons (Selomulya *et al.,* 1999), coconut jute carbon (Chan *et al.,* 1994), coconut tree sawdust carbon (Selvi *et al.,* 2001), sawdust and used tyres carbon (Hamadi *et al.,* 2001), activated carbon (Chan *et al.,* 1994) , chitosan (Schmub *et al.,* 2001), hazelnut shell carbon (Kobya, 2004) and carbon slurry (Singh and Tiwari, 1991) have been reported in the literature. Ho (2007) reported that about 9058 articles had been published on adsorption of materials and Erhan *et al.* (2004) listed 37 carbon materials as low cost adsorbents that had been studied. Additional information on adsorption can be found in literature such as Otun *et al.* (2006 a and b); Adie *et al.* (2010); Ismail *et al.* (2009); Olarinoye *et al.* (2012). It can then be

summarised that common adsorbent materials are activated carbon, synthetic resins, activated alumina agricultural solid wastes and natural adsorbents. The main objective of this study was to test the effectiveness of a solid waste (powdered egg shell) towards adsorption of Pb^{2+}, Ni^{2+} and Cd^{2+} from synthetic wastewaters (either in individual or multi-component systems) and from raw water with particular attention to its adsorption kinetics.

MATERIALS AND METHODS

As a follow-up to previous studies on powdered eggshells (PES) by several authors (Otun *et al.*, 2006 a and b); Oke *et al.*, 2008), chicken eggshells were collected at the old Buka, Obafemi Awolowo University, Ile-Ife, Nigeria. These eggshells were washed with distilled water, air-dried, ground into powder and classified using British Standard (BS) sieve. Powdered eggshell with sieve sizes of 75 μm (PES_1), 150 μm (PES_2), 212 μm (PES_3) and 300 μm (PES_4) were separated and stored in desiccators. Selected properties (physical and chemical) of the powdered eggshell were determined using standard methods.

Moisture Content Determination

A well mixed sample of PES was evaporated in weighed dishes to a constant weight in an oven at 105°C (APHA, 1998). The decrease in the weight of the PES represents the moisture content (M_c) defined as:

$$M_c \,(\%) = \ 100\left(\frac{W_1 - W_2}{W_1}\right) \qquad (1)$$

Where M_c is moisture contents; W_1 and W_2 are initial and final weight of PES after oven dry at 105°C

Volatile Solid and Ash Content Determination

Known masses of dried samples used for moisture content determination were placed in crucibles and transferred into a muffle furnace. The furnace was heated to 550°C for 2 hours (APHA, 1998). The samples were cooled in desiccators and the final weights were measured. Volatile solid (VS) and ash content (Ash) of PES were calculated as follows (APHA, 1998):

$$VS \,(\%) = \ 100\left(\frac{W_2 - W_3}{W_2}\right) \qquad (2)$$

$$Ash \,(\%) = \ 100\left(\frac{W_3}{W_1}\right) \qquad (3)$$

Where; W_3 is final weight of PES after 2 hours incineration in the furnace at 550°C.

Water and Acid Solubilities Determination

Known dried masses (5 gram) of the samples were soaked in 300 mL of distilled water and in 300 mL of 0.25 M of HCl for 24 h separately. The samples were filtered using pre-dried and weighed filter papers (number 1). The samples and the filter papers were dried in the oven at 105° C for 24 h, cooled in desiccators to balance the temperature and the final weights were measured. Water soluble (Ws) and acid solubilities (As) of PES were calculated as follows (APHA, 1998):

$$WS \,(\%) = \ 100\left(\frac{W_2 - W_4}{W_2}\right) \qquad (4)$$

$$AS \,(\%) = \ 100\left(\frac{W_2 - W_5}{W_2}\right) \qquad (5)$$

Where W_4 and W_5 are dry weights of PES after soaked in water and acid respectively.

Metal Concentrations Determination

Known mass (1.0 g) of the PES was digested using nitric acid digestion method and chemical components of the adsorbent were determined using standard methods (APHA, 1998). Specifically, 1.0 gram of PES was digested using nitric acid and total metal concentrations (M_{cc}) were determined using spectormetry method. Metal concentrations were computed as follows:

$$M_{cc} \,(mg\,/\,L) = \ \left(\frac{A*B}{W_1}\right) \qquad (6)$$

Where; B is dilution factor; A is concentration of the metals (mg/L).

Micrograph structure of PES was conducted using electron Microscope facility available in the Materials Science and Engineering Department of the Obafemi Awolowo University, Ile-Ife, Nigeria. Adsorption capacities of PES were examined on synthetic wastewaters prepared by dissolving individually known masses of Pb^{2+} (1.598 g of $Pb(NO_3)_2$) in 100 ml of distilled water and was made up to 1000 ml mark with distilled water, Ni^{2+} (1.735 g of nickel chloride) in 200 ml of distilled

water and was made up to 1000 ml mark with distilled water and Cd^{2+} (2.74 g of $Cd(NO_3)_2$ - $4H_2O$) in 100 ml of distilled water and was made up to 1000 ml mark with distilled water (APHA, 1998). Known masses of the adsorbent were added into beakers containing 300 ml of a known concentration of the pollutants. The mixtures were stirred at 60 revolutions per minutes (rpm) for 3 minutes and allowed to stand for 18 hours (a time at which equilibrium concentration might have been reached). The supernatants were filtered through a filter paper Number 40 (Whatman) to remove suspended solids and to prevent interference of turbidity. Pb^{2+}, Ni^{2+} and Cd^{2+} concentrations in the filtrates were determined. In multi component synthetic wastewaters 1.598 g of $Pb(NO_3)_2$, 1.735 g of nickel chloride and 2.74 g of $Cd(NO_3)_2$ - $4H_2O$ were dissolved in 100 ml of distilled water and was made up to 1000 ml mark with distilled water. The procedures for the treatment of mono component (individual) wastewaters were repeated for raw water collected and for multi-component synthetic wastewater prepared. The amounts of solute removed (adsorbed) at equilibrium and at any time were computed using equations (7) and (8) respectively.

$$q_t = \frac{(C_o - C_t)}{M}V \qquad (7)$$

$$R_t = 100\left(\frac{(C_o - C_t)}{C_0}\right) \qquad (8)$$

Where; q_t is the adsorption capacity at time t (mg/g),; C_0 is initial concentration of lead in the solution (mg/l); C_t is experimental concentration in the solution at time t (mg/l) and R_t *is* the per cent pollutant adsorbed (%)

The laboratory analysis of heavy metal concentrations in both synthetic wastewaters and raw water were carried out as specified in APHA(1998) using the Alpha 4 Atomic Absorption Spectrophotometer (AAS) (Chem Techn Analytical) at the Central Science Laboratory, Obafemi Awolowo University, Ile-Ife, Nigeria. The adsorption kinetics of the adsorbent was analyzed through the use of graphical

methods for standard kinetics models. The kinetic data were further analyzed using the kinetic expression given by Boyd *et al.* (1947) to check whether sorption proceeds through external diffusion or intraparticle diffusion mechanism. These kinetics models were evaluated statistically using total errors, coefficient of determination (CD) and model of selection criterion (MSC). Estimated production costs (environmental economics analysis) were conducted. Total error (Err^2) can be computed using equation (9) as follows (Oke, 2007; Babatola *et al.,*2008)

$$Err^2 = \sum_{i=1}^{n}\left(Y_{obsi} - Y_{cali}\right)^2 \qquad (9)$$

Where; Y_{obsi} is observed concentration and Y_{cali} is calculated concentration and n is the number of samples.
CD can be expressed as follows:

$$CD = \frac{\sum_{i=1}^{n}\left(Y_{obsi} - \overline{Y_{cali}}\right)^2 - \sum_{i=1}^{n}\left(Y_{obsi} - Y_{cali}\right)^2}{\sum_{i=1}^{n}\left(Y_{obsi} - \overline{Y_{cali}}\right)^2} \qquad (10)$$

Where; $\overline{Y_{obsi}}$ is the average of observe concentration and $\overline{Y_{cali}}$ is the average of calculated concentration MSC can be computed using equation (11) as follows:
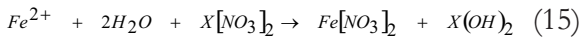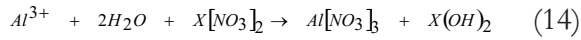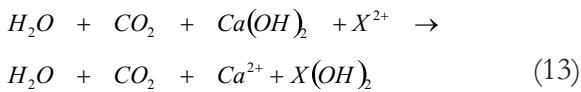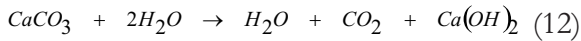
$$MSC = \ln\frac{\sum_{i=1}^{n}\left(Y_{obsi} - \overline{Y_{obs}}\right)^2}{\sum_{i=1}^{n}\left(Y_{obsi} - Y_{cali}\right)^2} - \frac{2p}{n} \qquad (11)$$

Where; p is number of parameters and n is the number of samples

RESULTS AND DISCUSSION
Properties of Powdered Eggshells
Result of the digestion indicates that one gram of PES contained iron, aluminium and calcium (Table 1). It is well known that eggshell contains $CaCO_3$ as the major components (up to 95% $CaCO_3$). It has been postulated that in the presence of water, inorganic salts undergo displacement reactions as indicated in equations 12-15. This shows that the PES underwent reactions in equations 15-19 with selected heavy metal ions, which can reduce the pH and the end product reacted with metallic ions to precipitate the pollutant.

$$CaCO_3 + 2H_2O \rightarrow H_2O + CO_2 + Ca(OH)_2 \quad (12)$$

$$H_2O + CO_2 + Ca(OH)_2 + X^{2+} \rightarrow$$
$$H_2O + CO_2 + Ca^{2+} + X(OH)_2 \quad (13)$$

$$Al^{3+} + 2H_2O + X[NO_3]_2 \rightarrow Al[NO_3]_3 + X(OH)_2 \quad (14)$$

$$Fe^{2+} + 2H_2O + X[NO_3]_2 \rightarrow Fe[NO_3]_2 + X(OH)_2 \quad (15)$$

By expressing the mass of PES in terms of Fe^{2+}, Ca^{2+} and Al^{3+} contents, 0. 1716 mole of Ca^{2+}, 4.0 x 10^{-2} mole of Fe^{2+} and 5.24 x 10^{-2} mole of Al^{3+} could be found in one hundred (100) grams of PES. Figure 1 presents the micrograph of PES.

Table 1 Chemical and Physical Properties of PES

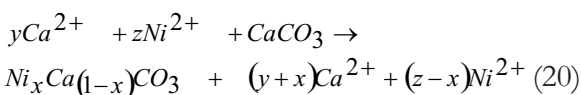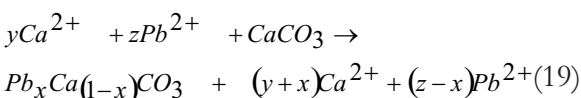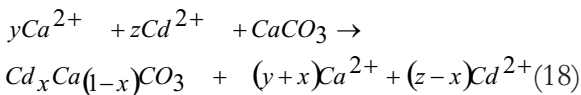| Description	Ash (%)	Moisture content (%)	Calcium (as Ca^{2+} mg/g)	Aluminium (as Al^{3+} mg/g)	Iron (as Fe^{2+} mg/g)	Volatile solids (%)	Water solubility (mg/g)	Acid solubility (mg/g)
Mean	97.58	1.06	407.44	13.45	27.6	2.31	0.64	2.96
Standard deviation	1.84	0.36	0.032	0.001	0.002	0.42	0.07	0.72

Ion Exchange Model

PES contains 2.31% volatile solids (Table 1), which indicates that powdered eggshells are partially cellulose-based adsorbents, which contain polar functional groups that can be involved in chemical bonding and are responsible for the cation exchange capacity of the PES. Thus, the PES and Pb^{2+}, Ni^{2+} and Cd^{2+} reactions may be represented in two ways (Ho, 1998; 2006; Ho and Mckay, 1999; 2003):

$$2PESc^- + X^{2+} \rightleftharpoons XPESc_2 \quad (16)$$

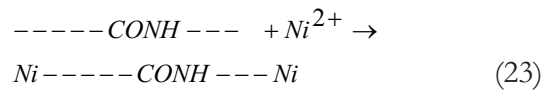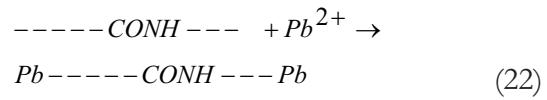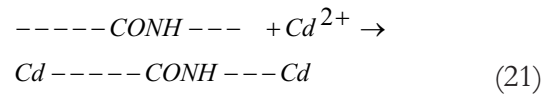$$2HPESc + X^{2+} \rightleftharpoons XPESc_2 + 2H^+ \quad (17)$$
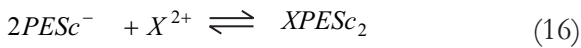
Where $PESc^-$ and $HPESc^-$ are the polar sites on the PES surface and X is the pollutant. The literature reported that removal of heavy metals such as lead, nickel cadmium in the presence of $CaCO_3$ can be represented as (Kohler *et al.,* 2007):

$$yCa^{2+} + zCd^{2+} + CaCO_3 \rightarrow$$
$$Cd_xCa_{(1-x)}CO_3 + (y+x)Ca^{2+} + (z-x)Cd^{2+} (18)$$

$$yCa^{2+} + zPb^{2+} + CaCO_3 \rightarrow$$
$$Pb_xCa_{(1-x)}CO_3 + (y+x)Ca^{2+} + (z-x)Pb^{2+} (19)$$

$$yCa^{2+} + zNi^{2+} + CaCO_3 \rightarrow$$
$$Ni_xCa_{(1-x)}CO_3 + (y+x)Ca^{2+} + (z-x)Ni^{2+} (20)$$

Also, Zou *et al.* (2008) reported that eggshell membrane is a unique cell surface with various functional groups, providing the potential for bio-sorption of metal species. Detailed information on functional groups in eggshell membrane can be found in Zou *et al.* (2008). Reactions between the functional groups and the pollutants can be expressed as follows:

$$-----CONH--- + Cd^{2+} \rightarrow$$
$$Cd-----CONH---Cd \quad (21)$$

$$-----CONH--- + Pb^{2+} \rightarrow$$
$$Pb-----CONH---Pb \quad (22)$$

$$-----CONH--- + Ni^{2+} \rightarrow$$
$$Ni-----CONH---Ni \quad (23)$$

From these equations above, it can be explained that higher values of hydrogen concentration will lower the formation of $XPESc_2$. This indicates that increasing pH value will not favour X^{2+} adsorption. Also, decreasing the pH either through addition of hydroxyl ions (OH) or otherwise will increase adsorption of X^{2+}. This phenomenon can be attributed to more charges, disassociation of more anions which will attract X^{2+}, higher attraction forces and formation of $X(OH)_2$ which will be precipitated or fill the pores. These observations agree with Jalili *et al.* (2008) on adsorption of palladium and platinum onto eggshell membrane, quality and ultra structure of eggshell studied and documented by Krystianik *et al.* (2005) and morphology properties presented in literature such as Lui *et al.* (2004).

Mechanism of Adsorption

Figures 2 and 3 show the mechanism of adsorption of lead, nickel and cadmium onto the PES. From the figures it can be seen that 89.4%,

89.4 % and 70.6 % of initial pollutant's concentrations were removed in mom-component synthetic wastewater of lead, cadmium and nickel respectively. In multi component synthetic wastewater 80.4%, 62.8% and 36.8% of initial concentration of the pollutant were adsorbed from lead, cadmium and nickel wastewaters respectively. The drop in the concentration of pollutants adsorbed can be attributed to competitive adsorptions by these cations. From the figures also, it can be seen that the curves in all cases are in two parts. The first parts (exponential) of the curves are attributed to mass transfer effects, which take place with boundary layer diffusion, while the final parts (linear) indicate intraparticle diffusion. The slope indicates that the pores are micro-pores and the intraparticle diffusional resistance is due to micro-pores only. From the figures the mechanism of adsorption of lead, nickel and cadmium onto PES as an adsorbent follows two-steps, namely pore diffusion and intraparticle transport. This result is the general observation for batch reactor, while for a continuous flow system film diffusion is likely to be included and as the limiting step. It is well known that there is a high possibility for pore diffusion to be the rate-limiting step in a batch process and that the adsorption rate parameter, which controls the batch process for most of the contact time is the intraparticle diffusion (Saswati and Ghosh, 2005).

Adsorption Kinetics of Pb^{2+}, Ni^{2+} and Cd^{2+} onto PES

Adsorption dynamics describes the solute uptake rate, which controls the residence time of adsorbate uptake at the solid- solution interface. It is well known that reaction order and rate constant must be determined by experiments. In order to establish kinetic of lead, nickel and cadmium adsorption, adsorption dynamics of PES were investigated by using pseudo first-order, pseudo second-order, Elovich and intraparticle diffusion kinetic models. The pseudo first-order equation has been well documented and is generally expressed as follows (Oke $et\,al.$, 2008):

$$\frac{dq}{dt} = k_i (q_e - q_t) \qquad (24)$$

Where; q_e is equilibrium solid-phase concentration of sorbate (mg/mg); t is the time and k_i is the rate

constant of pseudo first-order adsorption.

After integration and applying boundary conditions $t = 0$ to $t = t$ and $q_t = 0$ to $q_t = q_t$, the integrated form of equation (21) becomes (Erhan $et\,al.$, 2004; Oke $et\,al.$, 2008):

$$\log_e (q_e - q_t) = \log_e (q_e) - \frac{k_i}{2.303} t \qquad (25)$$

The values of $log_e\,(q_e - q_t)$ were linearly correlated with time. The plot of $log_e\,(q_e - q_t)$ $against$ time should give a linear relationship from which k_i and q_e can be determined from the slope and intercept of the respectively. Figure 4 shows graphical method for the parameter estimate. Tables 2, 3, 4 and 5 show the pseudo-first order model and their values respectively. The pseudo second-order adsorption kinetic rate equation is expressed as shown in equation (26):

$$\frac{dq}{dt} = k_2 (q_e - q_t)^2 \qquad (26)$$

Where k_2 is the rate constant of pseudo second-order adsorption. Integrating equation (24) and rearranging same gives equation (27) and let h (mg/g· h) is $h = k_2\,(q_e)^2$

$$\left(\frac{t}{q_t}\right) = \frac{1}{h} + \frac{1}{q_e} t \qquad (27)$$

The plot of (t/q_t) against $t\,in$ equation (27) should give a linear relationship from which h, q_e and k_2 can be determined from the slope and intercept of the plot respectively. Figure 5 shows graphical method for the parameter estimated. Tables 2, 3, 4 and 5 show more about the model.

The Elovich model equation is generally expressed as indicated in equation (28):

$$\frac{dq_t}{dt} = \alpha \exp(-\beta q_t) \qquad (28)$$

Where β is the desorption constant during any one experiment and is the initial adsorption rate Erhan $et\,al.$ (2004) simplifies Elovich equation as shown in equation (29)

$$q_t = \frac{1}{\beta} \log_e (\alpha\beta) + \frac{1}{\beta} \log_e (t) \qquad (29)$$

If lead, cadmium and nickel adsorption fits the Elovich model, a plot of q_t against logarithms to base e the time should yield a linear relationship with a slope of $(1/\beta)$ and an intercept of $(1/\beta)$ $\log_e(\alpha\beta)$. Figure 6 shows graphical method for the parameter estimated. Tables 2 to 5 present more on this dynamic model.

The intraparticle diffusion model is expressed as equation (30)

$$R = k_{id}(t)^a \qquad (30)$$

Where; R is the per cent pollutant adsorbed (%); a is the gradient of linear plots and k_{id} is the intraparticle diffusion rate constant (/h).

A linearised form of the equation is followed by $\log R = \log k_{id} + a \log(t)$. Literature (Oke et al., 2008; Erhan et al., 2004) reported that " a" depicts the adsorption mechanism and k_{id} may be taken as a rate factor (per cent pollutant adsorbed per unit time). Higher values of k_{id} illustrate an enhancement in the rate of adsorption, whereas larger k_{id} values illustrate a better adsorption mechanism, which is related to an improved bonding between pollutant and the adsorbent particles. Figure 7 shows graphical method for the parameter estimated. Tables 2 to 5 show more on this dynamic model. The intraparticle diffusion model based on the theory proposed by Weber and Morris (1963) was tested to identify the diffusion mechanism. It is an empirical functional relationship, common to the most adsorption processes, where the uptake varies proportionally with $t^{0.5}$ rather than with the contact time t. According to this theory (Edson et al., 2011):

$$R = k_p(t)^{0.5} \qquad (30a)$$

According to equation (30a) a plot of R versus $t^{0.5}$ should be a straight line with a slope k_p when the adsorption mechanism follows the intraparticle diffusion process. Such types of plots may present multi-linearity, implying that two or more steps occur (Edson et al., 2011). The sharp first-stage portion is the external surface adsorption stage. The second portion is the gradual adsorption stage, where the intraparticle diffusion is rate-limited. From the Figure (Figure 10b), it is noted that the sorption process tends to be controlled by the two or more phases. The slope of the second linear portion of the plot has been defined as the intraparticle diffusion parameter k_p (Edson et al., 2011). The calculated intraparticle diffusion coefficient values were given as 1.24, 1.91, 2.31, and 4.42 mg. g⁻¹ hr⁰·⁵ for an initial Pb²⁺ concentration of 0.13, 0.25, 15.02, and 20.45 mg.g⁻¹ respectively. At various mass adsorbent at a fixed particle size and pH, calculated intraparticle diffusion coefficient values were given by 2.37, 3.46 and 5.42 mg. g⁻¹ hr⁰·⁵ for an initial adsorbent mass of 0.3, 0.5, and 1.0.g per 500 ml respectively. For various particle sizes of adsorbent at a fixed mass and pH, calculated intraparticle diffusion coefficient values were given by 0.66, 1.46; 3.44 and 5.11 mg. g⁻¹ hr⁰·⁵ for an absorbent mass with particle size of 0.300 mm, 0.212 mm; 0.150 mm and 0.075 mm respectively. At various pH of 3, 4.5, 7.6 and 11.7 (value at fixed particle sizes of adsorbent at a fixed mass of adsorbent) calculated intraparticle diffusion coefficient values were given by 3.44, 3.99; 4.21 and 4.39 mg. g⁻¹ hr⁰·⁵ respectively for lead concentration. The values of the k_p increased with increasing initial Pb²⁺ concentration, mass of adsorbent, with decreasing particle size and pH value, which can indicate increase in the diffusion rate of the Pb²⁺ onto the adsorbent particle, mass of adsorbent, particle size of adsorbent and pH.

Applicability of the Adsorbent

Applicability of the process was tested on raw water samples and the results are as presented in Figures 8 to 10. Tables 2 to 5 show the kinetic parameters. From Table 3, it can be seen that in all cases the values of correlation coefficient vary from Pseudo second-order, Intraparticle diffusion, Elovich model to Pseudo first-order for the three metals. On the average, correlation coefficient increases from intraparticle diffusion (0.958) through Pseudo first (0.968) and Pseudo second (0.968) to Elovich (0.979). This indicates that adsorptions of Pb²⁺, Ni²⁺ and Cd²⁺ onto PES follow Elovich than any other model. From Tables 4, 5 and 6, the Coefficient of Determination (R^2) followed the same order as in the case of Table 3. The results indicate that Pb²⁺, Ni²⁺ and Cd²⁺ adsorptions onto PES fitted well into Pseudo second-order kinetics. The amounts of Pb²⁺, Ni²⁺ and Cd²⁺ adsorbed decrease as the

pH decreases toward 7.6. The variation in adsorption capacity in this pH range is largely due to the influence of pH on the adsorption characteristics of the powdered eggshell, which indicates that the adsorption capacity of the adsorbent is clearly pH dependent. Figure 11a reveals that optimum q_e occurs between 4.6 and 7.6 pH values. This indicates that PES will be effective in that pH range. From Figure 11b, it can be seen that amount of pollutant adsorbed decreases with increasing adsorbent mass, which indicates that optimum adsorbent masses are required in application of PES to pollutant's adsorption. It is an evident from Tables 2 to 5 that the removal of Pb^{2+}, Ni^{2+} and Cd^{2+} from

aqueous solution depends on the initial concentrations of Pb^{2+}, Ni^{2+} and Cd^{2+}, the pH and the particle size of PES. The adsorption dynamic kinetics changes with an increase in the Pb^{2+}, Ni^{2+} and Cd^{2+} concentration. The results also show that the adsorption reaction can be approximated with the Elovich kinetic model. This observation is similar to Lazaridis and Asouhidou (2003) observation on kinetic equations. Lazaridis and Asouhidou (2003) used three kinetic equations (pseudo 1st , 2nd and Elovich model equations) to describe chromium VI sorption onto hydrotalcite and their result showed that adsorption of chromium onto hyrotalcite fitted into the first pseudo model best.
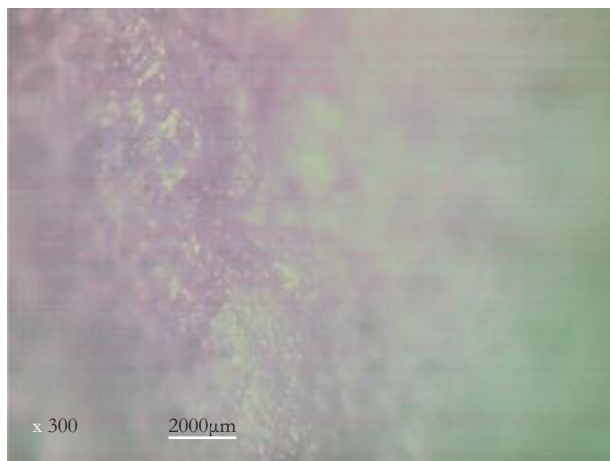

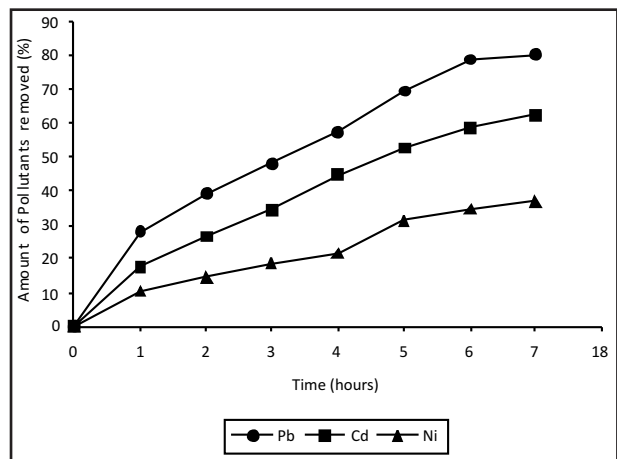**Figure 1:** Optimal Microscopy View of the PES

Figure 2: Mechanism of Adsorption of Pollutants onto PES Multi-Component Synthetic Wastewater
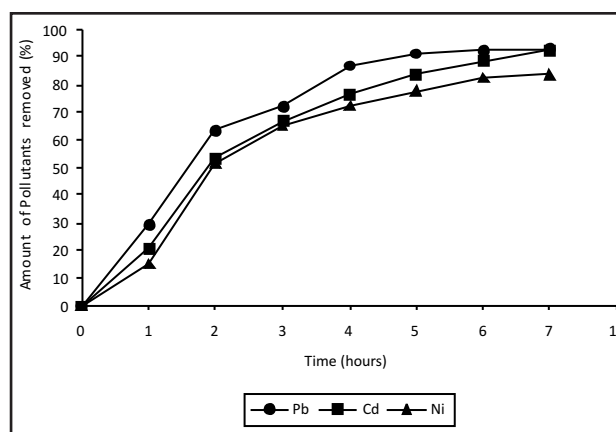

Figure 3: Mechanism of Adsorption of Pollutants onto PES Mono Component Synthetic Wastewater

Table 2: The Adsorption Kinetic Model Rate Constants for the Synthetic Wastewater at Different pH.

Initial pH		Pseudo first-order			Pseudo second-order				Elovich model			Intraparticle diffusion		
		k_1 (l/h)	q_e (mg/mg)	R^2	k_2 (mg/mg.h)	h^{-1} (mg/mg.h)$^{-1}$	q_e^{-1} (mg/mg)$^{-1}$	R^2	β (mg/mg)	α (mg/mg.h)	R^2	k_{id} (l/h)	a (%/h)	R^2
Pb^{2+}	3.0	0.696	5.540	0.991	0.042	0.712	0.173	0.965	0.519	6.330	0.979	20.227	0.650	0.994
	4.5	0.705	8.460	0.926	0.012	0.496	0.077	0.974	0.466	2.029	0.984	33.649	0.635	0.917
	7.6	0.646	4.580	0.980	0.065	0.767	0.224	0.959	0.433	2.012	0.975	17.299	0.707	0.963
	11.7	0.641	4.450	0.975	0.011	1.049	0.106	0.973	0.503	2.335	0.976	16.857	0.704	0.956
Ni^{2+}	3.0	0.692	5.439	0.981	0.051	0.708	0.180	0.956	0.519	6.213	0.969	19.832	0.647	0.984
	4.5	0.701	8.301	0.917	0.022	0.496	0.085	0.965	0.467	1.998	0.974	32.986	0.632	0.909
	7.6	0.643	4.498	0.970	0.074	0.762	0.230	0.950	0.434	1.982	0.966	16.963	0.703	0.954
	11.7	0.638	4.371	0.966	0.021	1.038	0.114	0.964	0.503	2.298	0.966	16.530	0.700	0.947
Cd^{2+}	3.0	0.688	5.340	0.972	0.060	0.704	0.186	0.947	0.518	6.099	0.960	19.446	0.644	0.974
	4.5	0.697	8.145	0.909	0.031	0.496	0.094	0.955	0.467	1.968	0.965	32.336	0.630	0.900
	7.6	0.640	4.418	0.961	0.082	0.756	0.235	0.941	0.436	1.952	0.956	16.634	0.699	0.945
	11.7	0.635	4.294	0.956	0.030	1.027	0.122	0.954	0.503	2.262	0.957	16.209	0.696	0.938

Table 3: The Adsorption Kinetic Model Rate Constants for the Synthetic Wastewater at Different Particle Sizes
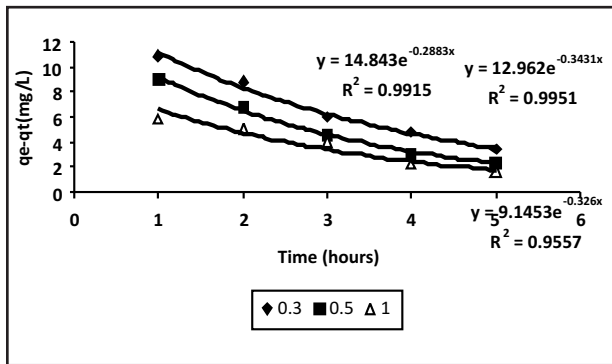
Particle sizes (μm)		Pseudo first-order			Pseudo second-order				Elovich model			Intraparticle diffusion		
		q_e (mg/mg)	k_1 (l/h)	R^2	k_2 (mg/mg.h)	h^{-1} (mg/mg.h)$^{-1}$	q_e^{-1} (mg/mg)$^{-1}$	R^2	β (mg/mg)	α (mg/mg.h)	R^2	k_{id} (l/h)	a (%/h)	R^2
Pb^{2+}	300	5.740	1.020	0.988	0.008	0.525	0.063	0.962	0.527	6.472	0.988	20.137	1.067	0.869
	212	6.050	0.897	0.984	0.000	0.810	0.016	0.971	0.462	4.301	0.990	23.111	0.874	0.950
	150	7.800	1.232	0.990	0.020	0.480	0.098	0.994	0.445	4.385	0.995	18.150	1.085	0.921
	75	6.250	1.282	0.990	0.026	0.423	0.104	0.983	0.470	5.057	0.984	18.239	1.115	0.900
Ni^{2+}	300	5.635	1.010	0.978	0.018	0.525	0.072	0.953	0.526	6.353	0.978	19.744	1.056	0.862
	212	5.939	0.889	0.974	0.010	0.804	0.026	0.962	0.463	4.225	0.980	22.659	0.867	0.941
	150	7.654	1.217	0.980	0.030	0.480	0.106	0.984	0.446	4.307	0.985	17.797	1.073	0.913
	75	6.135	1.266	0.980	0.035	0.425	0.112	0.973	0.471	4.966	0.974	17.884	1.103	0.892
Cd^{2+}	300	5.532	0.999	0.969	0.027	0.524	0.080	0.944	0.526	6.236	0.969	19.359	1.045	0.854
	212	5.830	0.881	0.965	0.020	0.798	0.035	0.952	0.464	4.150	0.971	22.216	0.859	0.932
	150	7.511	1.203	0.971	0.039	0.481	0.114	0.974	0.447	4.231	0.975	17.451	1.062	0.904
	75	6.022	1.251	0.971	0.045	0.426	0.120	0.964	0.471	4.877	0.965	17.537	1.091	0.884

Table 4: The Adsorption Kinetic Model Rate Constants for the Synthetic Wastewater at Different Initial Concentrations
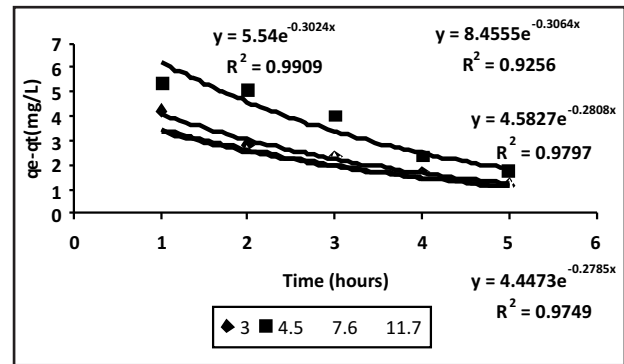
Initial Concentration (mg/L)		Pseudo first-order			Pseudo second-order				Elovich model			Intraparticle diffusion		
		q_e (mg/mg)	k_1 (l/h)	R^2	k_2 (mg/mg.h)	h^{-1} (mg/mg.h)$^{-1}$	q_e^{-1} (mg/mg)$^{-1}$	R^2	β (mg/mg)	α (mg/mg.h)	R^2	k_{id} (l/h)	a (%/h)	R^2
Pb^{2+}	15.02	7.792	1.297	0.953	0.006	1.361	0.091	0.982	0.563	13.623	0.805	21.702	1.112	0.884
	0.13	0.031	1.357	0.997	22.285	23.031	22.655	0.996	63.694	0.188	0.974	56.242	0.356	0.961
	20.45	14.441	3.448	0.973	0.035	0.369	0.113	0.961	0.591	7.650	0.907	32.558	0.691	0.929
	0.25	0.059	0.924	0.982	6.324	18.650	10.860	0.996	58.140	0.033	0.986	46.894	0.426	0.945
Ni^{2+}	15.02	7.646	1.281	0.944	0.016	1.344	0.099	0.972	0.562	13.361	0.799	21.278	1.100	0.876
	0.13	0.040	1.340	0.987	21.849	22.580	22.212	0.986	62.430	0.194	0.965	55.127	0.359	0.952
	20.45	14.162	3.389	0.964	0.044	0.372	0.121	0.952	0.589	7.507	0.899	31.917	0.687	0.920
	0.25	0.068	0.916	0.972	6.208	18.287	10.653	0.986	56.987	0.042	0.976	45.966	0.427	0.936
Cd^{2+}	15.02	7.503	1.265	0.935	0.026	1.327	0.107	0.963	0.561	13.103	0.793	20.862	1.088	0.869
	0.13	0.050	1.323	0.977	21.422	22.139	21.778	0.976	61.192	0.200	0.955	54.035	0.362	0.943
	20.45	13.889	3.331	0.954	0.053	0.374	0.128	0.943	0.587	7.367	0.891	31.289	0.683	0.912
	0.25	0.076	0.907	0.963	6.093	17.931	10.450	0.976	55.857	0.051	0.967	45.057	0.429	0.927

Table 5: The Adsorption Kinetic Model Rate Constants for the Synthetic Wastewater at Different Adsorbent Masses
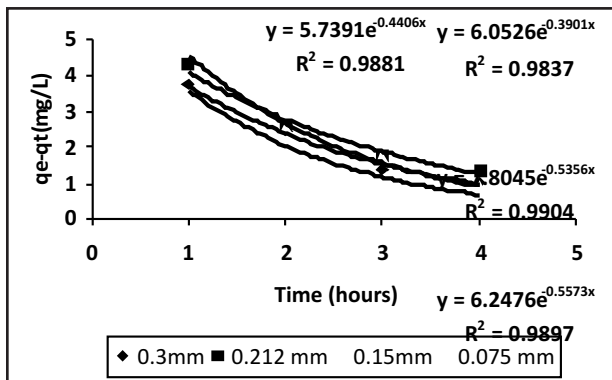
| Mass of the adsorbent (g)		Pseudo first-order			Pseudo second-order				Elovich model			Intraparticle diffusion		
		q_e (mg/mg)	k_1 (l/h)	R^2	k_2 (mg/mg.h)	h^{-1} (mg/mg.h)$^{-1}$	q_c^{-1} (mg/mg)$^{-1}$	R^2	β (mg/mg)	α (mg/mg.h)	R^2	k_{id} (l/h)	a (%/h)	R^2
Pb^{2+}	0.300	14.840	0.663	0.992	0.008	0.252	0.045	0.968	0.469	2.003	0.983	15.783	0.763	0.966
	0.500	12.960	0.785	0.995	0.004	0.372	0.037	0.974	0.314	2.530	0.988	31.939	0.621	0.961
	1.000	9.150	0.750	0.956	0.018	0.471	0.092	0.981	0.520	6.352	0.980	18.371	0.812	0.945
Ni^{2+}	0.300	14.553	0.660	0.982	0.018	0.257	0.054	0.959	0.470	1.973	0.973	15.477	0.758	0.957
	0.500	12.711	0.779	0.985	0.014	0.375	0.046	0.965	0.318	2.489	0.978	31.310	0.619	0.952
	1.000	8.977	0.745	0.947	0.028	0.472	0.100	0.971	0.520	6.235	0.970	18.014	0.806	0.936
Cd^{2+}	0.300	14.272	0.657	0.973	0.027	0.262	0.063	0.949	0.470	1.943	0.964	15.178	0.753	0.948
	0.500	12.467	0.774	0.975	0.024	0.377	0.055	0.955	0.321	2.450	0.969	30.694	0.616	0.943
	1.000	8.807	0.740	0.938	0.037	0.472	0.108	0.962	0.519	6.120	0.961	17.663	0.800	0.927

(a)

(b)

(c)
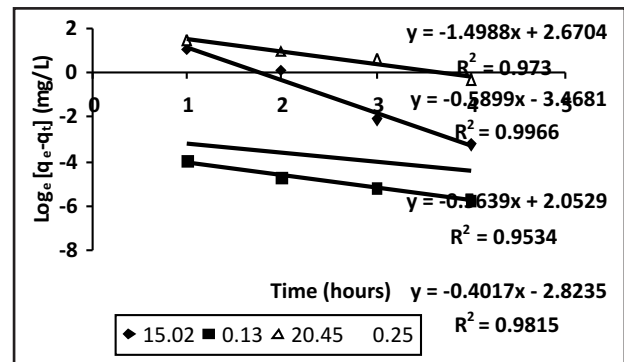
(d)

Figure 4: Pseudo First Order Models of Pb^{2+} Adsorption onto PES in Respect to Time at Different
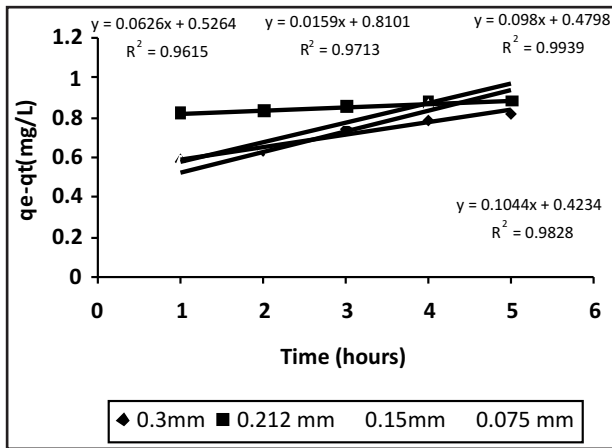(a)   Masses of Adsorbent
(b)   pH
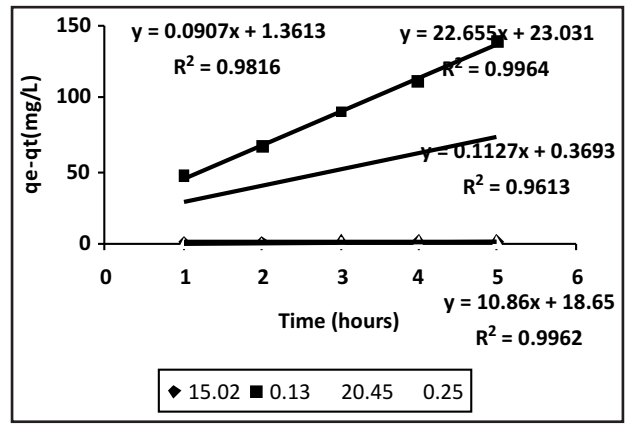(c)   Particle Size of the PES
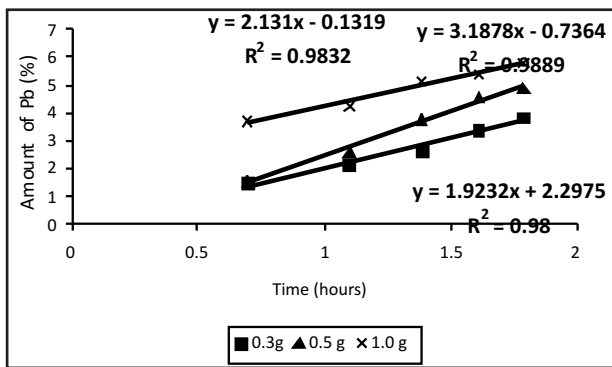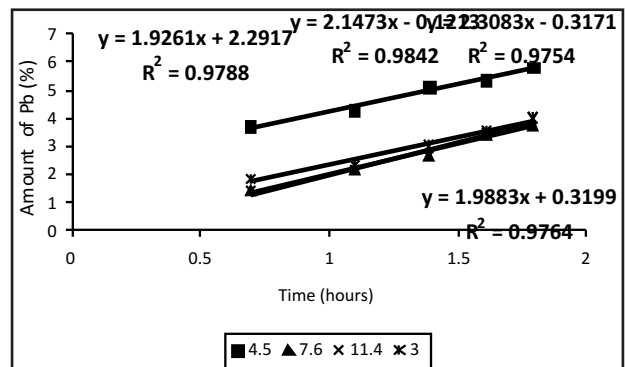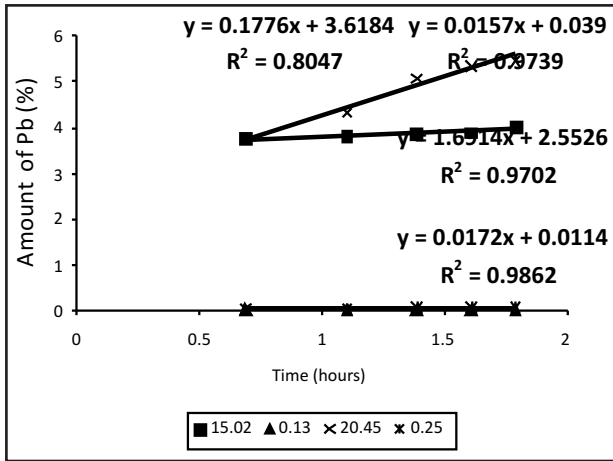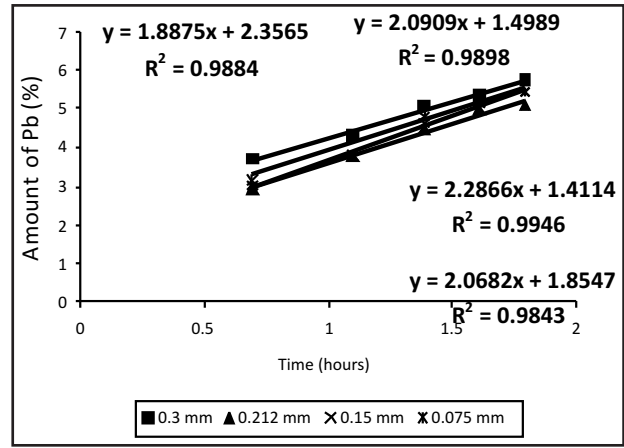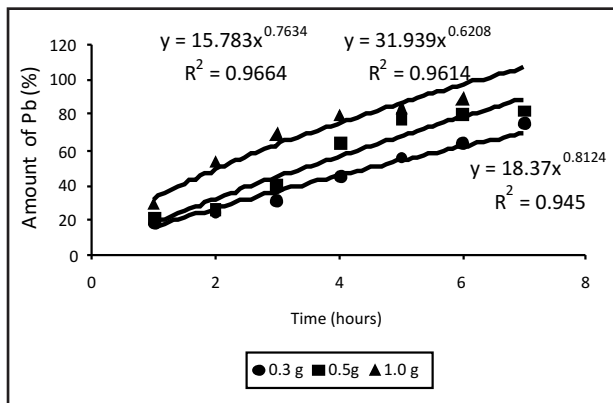(d)   Initial Lead Concentration
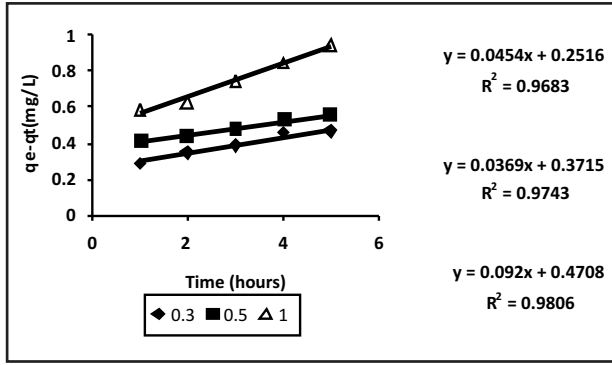
(a)
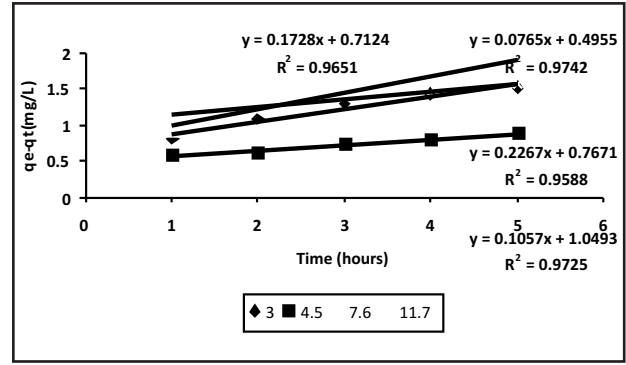
(b)

(c)

(d)

Figure 5: Pseudo Second Order Models of Pb^{2+} Adsorption onto PES in Respect to Time at Different
(a)   Masses of Adsorbent
(b)   pH
(c)   Particle Size of the PES
(d)   Initial Lead Concentration
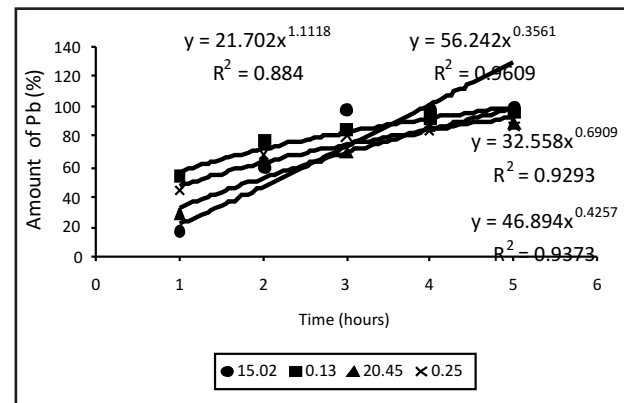

(a)

(b)

(c)

(d)

Figure 6: Elovich Models of Pb^{2+} Adsorption onto PES in Respect to Time at Different
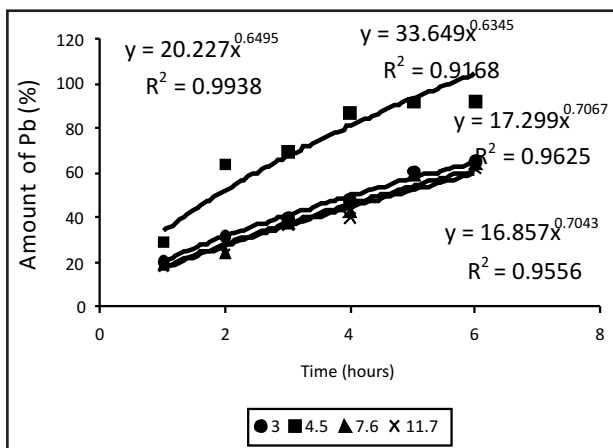
(a)   Adsorbent Masses
(b)   pH
(c)   Initial Lead Concentration
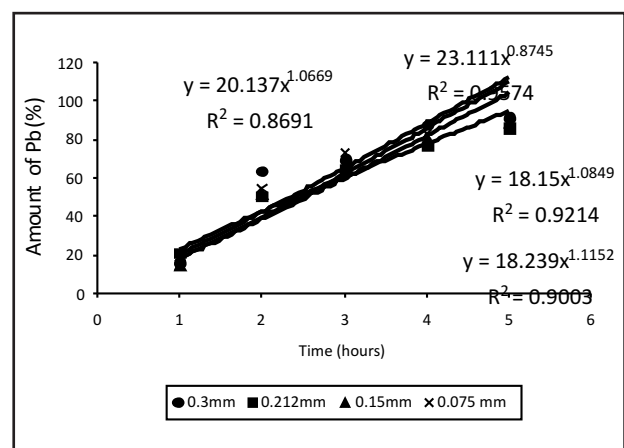(d)   Particle Size of the PES

(a)

(b)

(c)

(d)

Figure 7i: Intraparticle Models of Pb^{2+} Adsorption onto PES in Respect to Time at Different

a.   Adsorbent Masses
b.   Initial lead Concentration
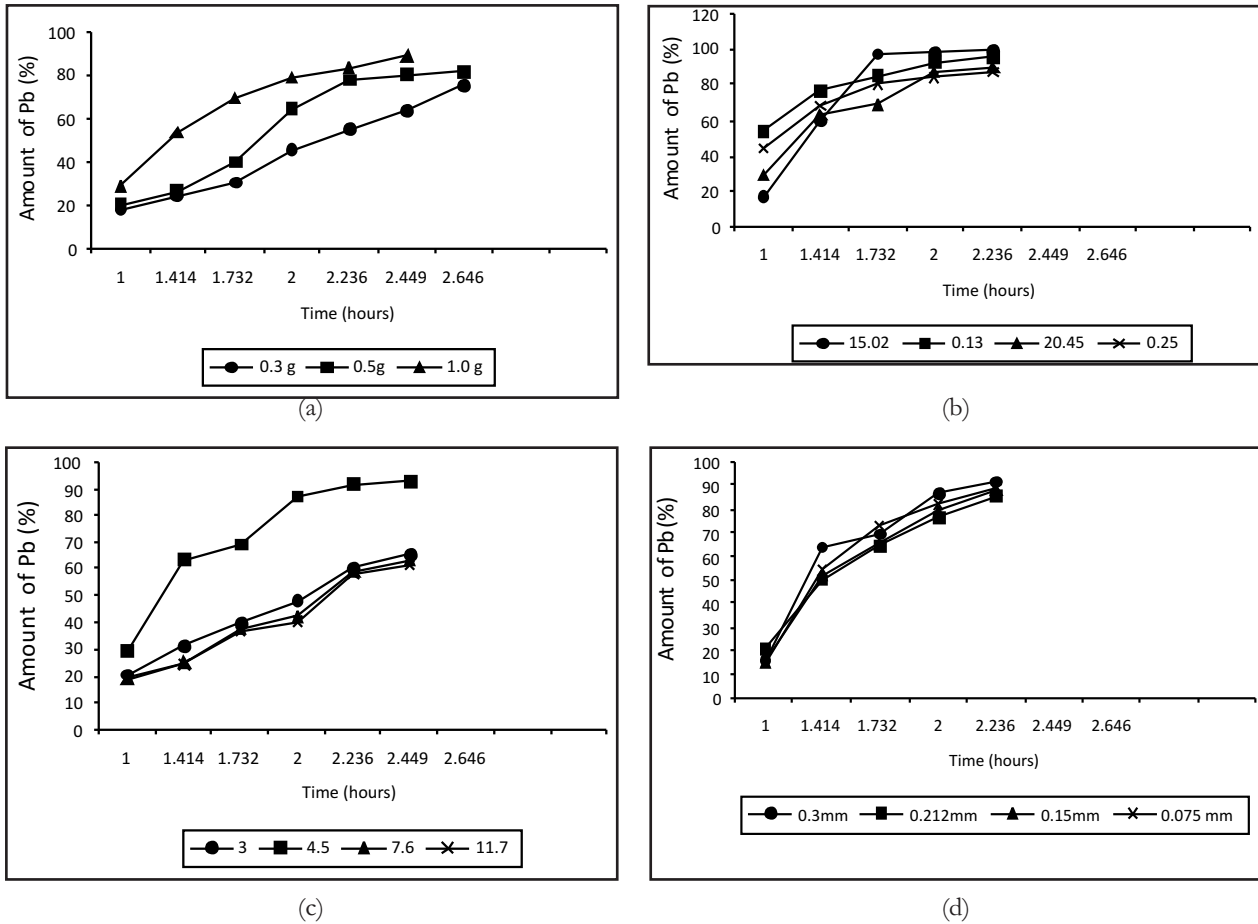c.   pH
d.   Particle Size of the PES

(a)

(b)

(c)

(d)

Figure 7ii: Intraparticle Models of Pb^{2+} Adsorption onto PES in Respect to Time at Different

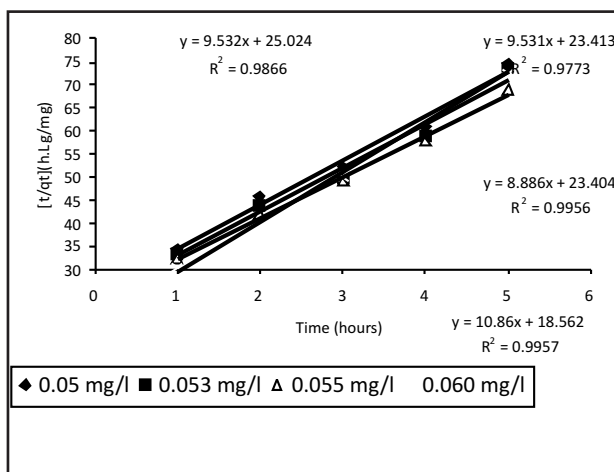|	
a	Adsorbent Masses
b	Initial lead Concentration
c	pH
d	Particle Size of the PES

Figure 8: Pseudo Second Order Models of Pb^{2+} Adsorption onto PES in Respect to Time at Different Concentrations of Raw Water
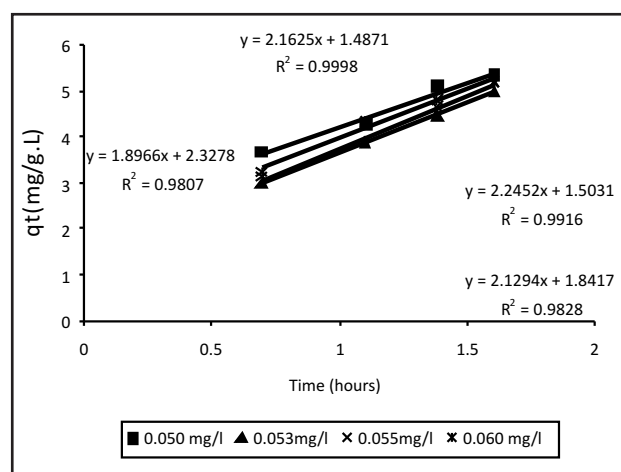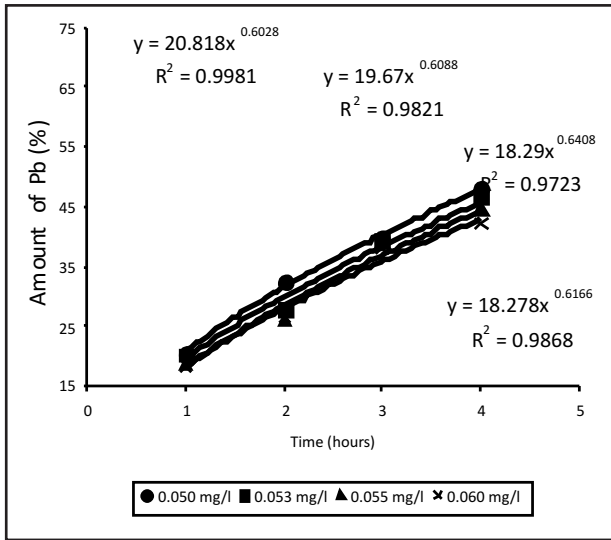
Figure 9: Elovich Models of Pb^{2+} Adsorption onto PES in Respect to Time at Different Concentrations of Raw Water

(a)

Figure 10a: Intraparticle Models of Pb²⁺ Adsorption onto PES in Respect to Time at Different Concentrations of Raw Water

The kinetic data were further analyzed using the kinetic expression given by Boyd *et al.* (1947) to check whether sorption proceeds via external diffusion or intraparticle diffusion mechanism, which is expressed as follows (Yasmin *et al.*, 2009):

$$F = 1 - \frac{6}{\Pi^2}\exp\left(-B_b t\right) \qquad (31)$$

B_b is a constant and F is the fractional attainment of equilibrium at time t given by Yasmin *et al.*, 2009:

$$F = \frac{q_t}{q_e} \qquad (32)$$

q_e and q_t represent the amount of Cd²⁺ sorbed (mg g⁻¹) at equilibrium and any time t, respectively. To compute $B_b t$, equation (30) is substituted into equation (31) and the kinetic expression becomes:

$$B_b t = -0.4977 - \ln\left(1 - \frac{q_t}{q_e}\right) \qquad (33)$$

Thus, the value of $B_b t$ can be computed for each value of F, and then plotted against time (Figures 12a and b) to configure the so-called Boyd plots. Linearity of this plot is employed to distinguish between external-transport- (film diffusion) and intraparticle transport- controlled rates of sorption (Yasmin *et al.*, 2009). A straight line passing through the origin is indicative of sorption processes governed by particle-diffusion mechanisms; otherwise they are governed by film
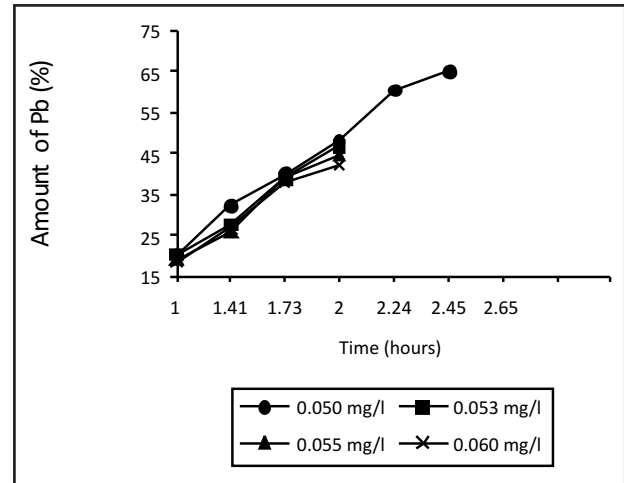
(b)

Figure 10b: Intraparticle Models of Pb²⁺ Adsorption onto PES in Respect to Time at Different Concentrations of Raw Water

diffusion. In the present study, the plots were neither perfectly linear nor passed through the origin (Figures 12a and b). This indicates that, in all the sorbents, film diffusion is the rate-limiting sorption process for Pb²⁺, Ni²⁺ and Cd²⁺.

## Statistical Evaluation of the Equilibrium Isotherm Models

Three different statistical expressions were used to evaluate the performance of the model estimations or to compare the model estimated values with the observed values. These statistical expressions are total error, coefficient of determination (CD) and model of selection criterion (MSC). Table 6 shows the values of total error, CD and MSC for each of the methods. The total errors are in the range of 26.161 to 34.476. The least total error (26.161) was from activated sludge model and the highest (34.476) from Temkin model. Like total error, CD values ranged from 0.589 to 0.998 (Table 6). The least CD value (0.589) came from Temkin model and the highest value (0.998) came from activated sludge model. . Like total errors and CD, MSC values were in the range of 4.906 to 6.687 (Table 6). The lowest value of MSC (4.906) was from Temkin model and the highest value (6.687) was from activated sludge model.

## Estimated Cost of Producing PES

Costs of producing PES were based on 95% yield from every used eggshell collected, assuming that

320 days per year, 300 kilograms of powdered eggshell were produced per day and 3 men per a shift of 8 hours. Tables 7(a and b) shows the breakdown of the estimated cost. It can then be said that the study has identified the estimated cost of 0.43 and 0.58 USD /kg of powdered eggshell (PES) at two different electricity sources. Table 7a presents unit cost using public (subside electricity)

source and Table 7b presents unit cost using generator (commercial electricity) source. The cost in this study is cheaper compared to the cost of producing empty fruit bunches (0.50USD/kg, Alam *et al.,* 2007), pencon shell based activated carbon (2.72 USD/kg) and sugar cane based granular activated carbon by steam (3.12 USD/kg).
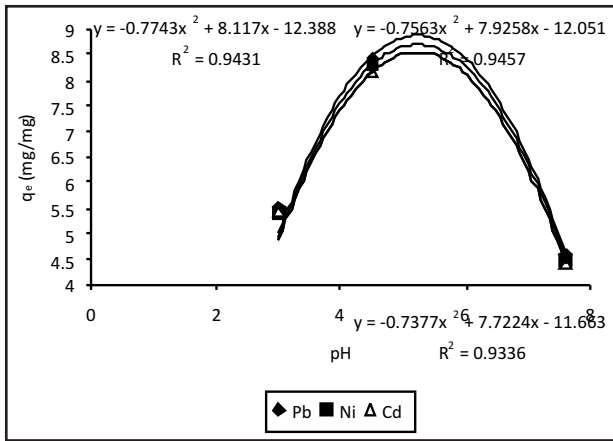
(a)
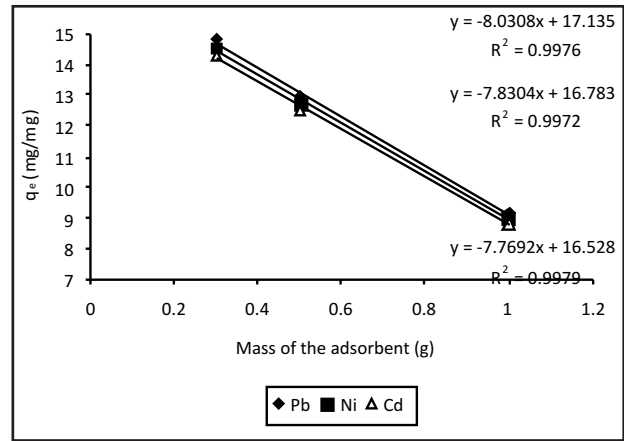
(b)

Figure 11: Relationship between Adsorption onto PES and Selected Factors
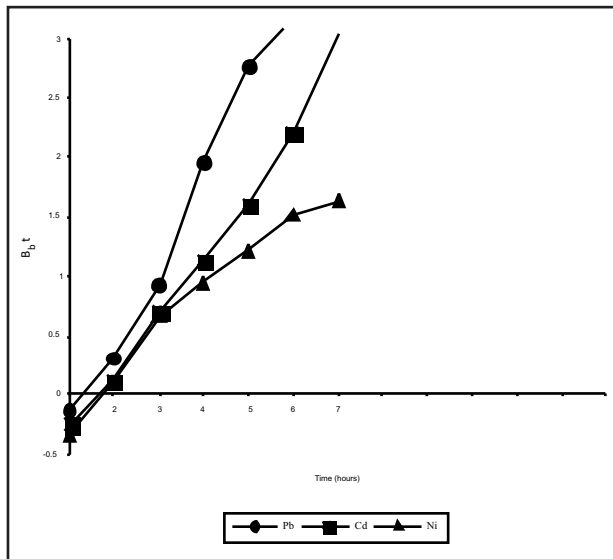(a)   pH ;
(b)   Adsorbent Masses

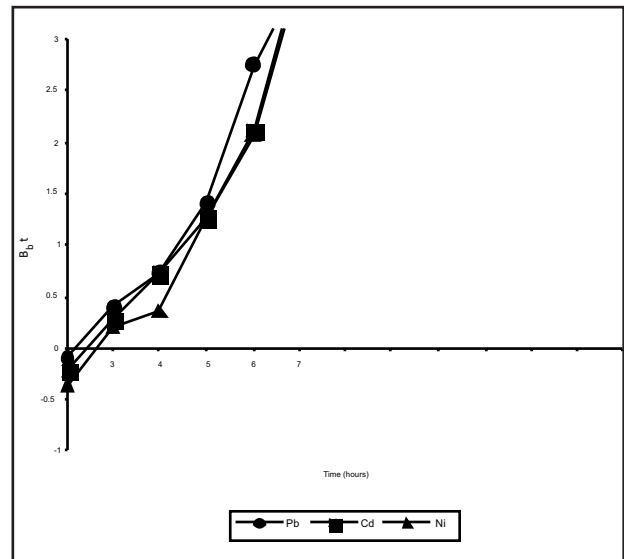Figure 12(a) Boyd plot for the sorption of Pb²⁺ , Cd²⁺ and Ni²⁺ adsorption onto PES (mono component)

Figure 12(b) Boyd plot for the sorption of Pb²⁺ , Cd²⁺ and Ni²⁺ adsorption onto PES (multi component)

Table 6: Result of Statistical Evaluation of the Kinetic Model

Effect of	Element	Factor	Pseudo first-order			Pseudo second-order			Elovich model			Intraparticle diffusion		
			MSC	Error	CD	MSC	Error	CD	MSC	Error	CD	MSC	Error	CD
pH	Pb²⁺	3.0	6.618	16.843	0.991	6.396	18.894	0.965	6.515	17.796	0.979	6.644	16.603	0.994
		4.5	6.075	21.868	0.926	6.472	18.190	0.974	6.558	17.400	0.984	6.003	22.537	0.917
		7.6	6.524	17.717	0.980	6.346	19.359	0.959	6.481	18.111	0.975	6.380	19.049	0.963
		11.7	6.481	18.111	0.975	6.464	18.268	0.973	6.489	18.033	0.976	6.321	19.591	0.956
	Cd²⁺	3.0	6.532	17.638	0.981	6.321	19.591	0.956	6.430	18.582	0.969	6.558	17.400	0.984
		4.5	6.003	22.537	0.917	6.396	18.894	0.965	6.472	18.190	0.974	5.939	23.126	0.909
		7.6	6.439	18.504	0.970	6.271	20.052	0.95	6.405	18.816	0.966	6.304	19.745	0.954
		11.7	6.405	18.816	0.966	6.388	18.971	0.964	6.405	18.816	0.966	6.247	20.282	0.947
	Ni²⁺	3.0	6.455	18.347	0.972	6.247	20.282	0.947	6.354	19.282	0.96	6.472	18.190	0.974
		4.5	5.939	23.126	0.909	6.313	19.668	0.955	6.396	18.894	0.965	5.868	23.783	0.9
		7.6	6.363	19.204	0.961	6.197	20.739	0.941	6.321	19.591	0.956	6.230	20.434	0.945
		11.7	6.321	19.591	0.956	6.304	19.745	0.954	6.329	19.514	0.957	6.173	20.966	0.938
Particle size	Pb²⁺	300	6.592	17.082	0.988	6.371	19.127	0.962	6.592	17.082	0.988	5.629	25.994	0.869
		212	6.558	17.400	0.984	6.447	18.425	0.971	6.609	16.923	0.99	6.271	20.052	0.95
		150	6.609	16.923	0.99	6.644	16.603	0.994	6.653	16.522	0.995	6.035	22.240	0.921
		75	6.609	16.923	0.99	6.549	17.480	0.983	6.558	17.400	0.984	5.868	23.783	0.9
	Cd²⁺	300	6.506	17.875	0.978	6.296	19.822	0.953	6.506	17.875	0.978	5.577	26.483	0.862
		212	6.472	18.190	0.974	6.371	19.127	0.962	6.524	17.717	0.98	6.197	20.739	0.941
		150	6.524	17.717	0.98	6.558	17.400	0.984	6.566	17.321	0.985	5.971	22.832	0.913
		75	6.524	17.717	0.98	6.464	18.268	0.973	6.472	18.190	0.974	5.806	24.361	0.892
	Ni²⁺	300	6.430	18.582	0.969	6.222	20.510	0.944	6.430	18.582	0.969	5.517	27.037	0.854
		212	6.396	18.894	0.965	6.288	19.899	0.952	6.447	18.425	0.971	6.124	21.418	0.932
		150	6.447	18.425	0.971	6.472	18.190	0.974	6.481	18.111	0.975	5.900	23.492	0.904
		75	6.447	18.425	0.971	6.388	18.971	0.964	6.396	18.894	0.965	5.744	24.934	0.884
Table 6: Continued	Pb²⁺	15.02	6.296	19.822	0.953	6.541	17.559	0.982	5.163	30.315	0.805	5.744	24.934	0.884
		0.13	6.670	16.362	0.997	6.661	16.442	0.996	6.472	18.190	0.974	6.363	19.204	0.961
		20.45	6.464	18.268	0.973	6.363	19.204	0.961	5.923	23.273	0.907	6.099	21.644	0.929
		0.25	6.541	17.559	0.982	6.661	16.442	0.996	6.575	17.241	0.986	6.230	20.434	0.945
Initial concentration	Cd²⁺	15.02	6.222	20.510	0.944	6.455	18.347	0.972	5.121	30.703	0.799	5.683	25.502	0.876
		0.13	6.583	17.162	0.987	6.575	17.241	0.986	6.396	18.894	0.965	6.288	19.899	0.952
		20.45	6.388	18.971	0.964	6.288	19.899	0.952	5.861	23.855	0.899	6.027	22.315	0.92
		0.25	6.455	18.347	0.972	6.575	17.241	0.986	6.489	18.033	0.976	6.156	21.117	0.936
	Ni²⁺	15.02	6.148	21.193	0.935	6.380	19.049	0.963	5.079	31.089	0.793	5.629	25.994	0.869
		0.13	6.498	17.954	0.977	6.489	18.033	0.976	6.313	19.668	0.955	6.214	20.587	0.943
		20.45	6.304	19.745	0.954	6.214	20.587	0.943	5.798	24.433	0.891	5.963	22.906	0.912
		0.25	6.380	19.049	0.963	6.489	18.033	0.976	6.413	18.738	0.967	6.083	21.793	0.927
Mass of adsorbent	Pb²⁺	0.300	4.255	38.722	0.663	6.422	18.660	0.968	6.549	17.480	0.983	6.405	18.816	0.966
		0.500	5.024	31.598	0.785	6.472	18.190	0.974	6.592	17.082	0.988	6.363	19.204	0.961

Table 7a: Estimated Cost Producing of PES using Public Electricity.

Items	Naira(₦)	US Dollar	Items	Naira(₦) per day	USD per day
Plant and Machinery	80000	484.85	Raw materials	0.00	0.00
Building	310000	1878.79	Utilities (water, fuel and electricity)	10500.00	63.64
Contingencies	80000	484.85	Labour	7500.00	45.45
Total	470000	2848.48	Supplies	2500.00	15.15
Average per year of 20ᵛ	23500	142.42	Depreciation	750.00	4.55
average per day	73.4375	0.45	sub total	21250.00	128.79
			Cost per day	21323.44	129.23
Cost per day (300 kg of day)	21396.88	129.68			
Cost per kilogram	71.32292	0.43			

ᵛcapital costs divided by an economic life of 20 years

Table 7b: Estimated Cost Producing of PES using non-Public Electricity

Items	Naira(₦)	US Dollar	Items	Naira(₦) per day	USD per day
Plant and Machinery	280000	1696.97	Raw materials	0.00	0.00
Building	460000	2787.88	Utilities (water, fuel and electricity)	17500.00	106.06
Contingencies	80000	484.85	Labour	7500.00	45.45
Total	820000	4969.70	Supplies	2500.00	15.15
Average per year of 20^v	41000	248.48	Depreciation	750.00	4.55
average per day	128.125	0.78	sub total	28250.00	171.21
			Cost per day	28378.13	171.99
Cost per day (300 kg of day)	28506.25	172.77			
Cost per kilogram	95.02083	0.58			

CONCLUSION

This study investigated adsorption capacities and kinetics models of Pb^{2+}, Ni^{2+} and Cd^{2+} onto PES. Chicken eggshells were collected and processed for adsorption of selected heavy metals. Effects of selected factors on adsorption capacities were studied. The study concluded that PES could be used to remove Pb^{2+}, Ni^{2+} and Cd^{2+} from aqueous solution. PES is an effective and inexpensive adsorbent for the removal of Pb^{2+}, Ni^{2+} and Cd^{2+} from wastewaters. Kinetic of Pb^{2+}, Ni^{2+} and Cd^{2+} adsorption from wastewaters is the order of intraparticle diffusion > Pseudo first > Pseudo second > Elovich.

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