ADSORPTION EQUILIBRIUM ISOTHERMS OF Pb^{2+}, Ni^{2+} AND Cd^{2+} ONTO POWDERED EGG SHELLS

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This study reports the adsorption equilibrium of lead (Pb^{2+}), nickel (Ni^{2+}) and cadmium (Cd^{2+}) from aqueous solution by chicken's eggshells. The eggshells were collected from within Obafemi Awolowo University, Ile-Ife, Nigeria. They were washed with distilled water, air dried, pulverized, sieved into different particle sizes and stored for use. The properties of the powdered eggshells (PES) were determined. The PES was used as an adsorbent to remove Pb^{2+}, Ni^{2+} and Cd^{2+} from aqueous solution on a single and multi-component systems basis and from raw water as well as wastewaters in a batch process. Effects of initial concentration of the metals, pH of the solution and particle size of PES on the adsorption capacities of the selected metals onto the PES were monitored. The study revealed that the PES contains calcium, aluminum, and iron as part of its major components. Adsorption capacities for Pb^{2+}, Ni^{2+} and Cd^{2+} onto the PES were 89.4 % ,70.6 % and 89.4 % respectively for mono-components synthetic wastewaters, but dropped to 80 %, 62.3 % and 36.8 % for Pb^{2+}, Ni^{2+} and Cd^{2+} respectively when used for multi-component systems (raw water). There were slight reductions in the adsorption of Pb^{2+}, Ni^{2+} and Cd^{2+} onto larger particle size of the PES. Adsorption capacities were higher when initial concentrations were higher. Adsorption equilibrium isotherms and their parameters were not affected significantly by changes in pH of the solution and particle size of the PES and fitted adequately into different adsorption equilibrium isotherms. Estimated cost of the PES production was found to be lower (0.43USD) than the cost of producing other adsorbents. It was concluded that the PES could be a suitable adsorbent to remove Pb^{2+}, Ni^{2+} and Cd^{2+} from aqueous solutions.

Keywords: Adsorption, Powdered eggshells, Heavy Metal Removal, Synthetic Wastewaters, Raw Water, Isotherms, Adsorption Parameters.

INTRODUCTION

The presence of heavy metals in water and their effects on environment as well as on man have been documented so well in literature. The sources of these heavy metals in water are known to include wastewater to a large extent. Wastewater treatment processes are classified into the following groups: physical, chemical, biological, electrical, membrane and irradiation. The methods applied for the removal of heavy metals from wastewater are chemical precipitation (Krishnan and Anirudhan, 2003; Otun *et al.,* 2006 a and b and Oke *et al.,* 2014), solvent extraction, ultrafiltration, biochemical treatment, ion exchange and adsorption. Out of these methods of removing heavy metals from water and wastewaters, adsorption (which is considered as a third stage of wastewater treatment) has been preferred over other processes because of its cheapness and the high-quality of the treated effluents it produces. Adsorption is a process by which a solid adsorbent can attract a component (adsorbate) 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.

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 (Srinivasan *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 (Chand *et al.,* 1994), coconut tree sawdust carbon (Selvi *et al.,* 2001), sawdust and used tyres carbon (Hamadi *et al.,* 2001), activated carbon (Selvi *et al.,* 2001) , chitosan (Schmub *et al.,* 2001), hazelnut shell carbon (Kobya, 2004), aragonite shell (Kohler *et al.,* 2007) and carbon slurry (Singh and Tiwari , 1997) have been reported in the literature. Ho (2007) reported that about 9058 articles have been published on adsorption of materials. Erhan *et al.* (2004) and Oke (2007) listed 37 carbon materials as low cost adsorbents that have been studied. More on adsorption can be found in literature such as Ismail *et al.* (2009); Adie *et al.* (2010); Olarinoye *et al.* (2012); Oke *et al.* (2014) and Umukoro *et al.* (2014). It can then be summarised that common adsorbent materials are activated carbon, synthetic resins, activated alumina 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 from single or multi-component systems) and from raw water with a particular attention to its equilibrium isotherms. This came as a follow up to the previous studies on PES conducted by Otun *et al.* (2006 a and b) and Oke *et al.* (2008).

MATERIALS AND METHODS

Chicken eggshells were collected from old commercial centre (known as old Buka) in the Obafemi Awolowo University, Ile-Ife, Nigeria. These eggshells were washed with distilled water, air-dried, ground into powder and classified into 75 m (PES_1), 150 m (PES_2), 212 m (PES_3) and 300 m (PES_4) using British Standard (BS) sieve. The classified powdered eggshells were stored in desiccators. Physical and chemical properties 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 by Oke *et al.*(2014) as:

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

where, M_c is moisture contents; W_1 and W_2 are initial and final weights of PES after oven drying 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 and ash content of PES were calculated as follows (APHA, 1998; Oke *et al.,* 2014):

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

where, W_3 is the final weight of the PES after 2 hours burnt in the furnace at 550°C and VS is the volatile solid of the PES

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

where, Ash is the ash content of the PES;

Water and Acid Solubilities Determination

Known dried masses (5 gram) of the samples were separately soaked in 300 mL of distilled water and in 300 mL of 0.25 M of HCl for 24 hours. The samples were filtered using pre-dried and weighed filter papers (Whatman number 1). The samples and the filter papers were dried in the oven at 105°C for 24 hours, cooled in desiccators to balance the temperature and the final weights were measured. Water (W_s) and acid solubilities (A_s) of PES were calculated as follows (APHA, 1998; Oke *et al.,* 2014):

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

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

where, W_S is water soluble of the PES; A_S is acid soluble of the PES; W_4 and W_5 are dry weights of the 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 APHA (1998) method. Total metal concentrations (M_{cc}) were determined using spectrometry method. Metal concentrations were computed following Oke *et al.* (2014) expression as:

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

where, B is dilution factor of the solution; A is the concentration of the metals obtained in the solution (mg/L) and M_{cc} is actual metal concentration in the solution of the PES.

Adsorption capacities of powdered eggshells (PES) were examined on synthetic wastewaters prepared by dissolving 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] in distilled water individually (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 have been reached). The supernatants were filtered through a filter paper Whatman Number 40 to remove suspended solids and to prevent interference of turbidity. Concentrations of Pb^{2+}, Ni^{2+} and Cd^{2+}in the filtrates were determined using Atomic Absorption Spectrophotometer method (APHA, 1998). 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 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.

$$q_e = \frac{(C_0 - C_e)}{M} V \qquad (7)$$

$$q_t = \frac{(C_0 - C_t)}{M} V \qquad (8)$$

where, q_e is the equilibrium solid-phase concentration of sorbate (mg/mg); C_0 is the initial concentration of metal in the solution (mg/l); C_e is the experimental concentration in the solution at equilibrium (mg/l); C_t is the experimental concentration in the solution at time t (mg/l); q_t is the adsorption capacity at time t (mg/g); V is the volume of solution (0.3L) and M is the mass of the adsorbent added (g)

The laboratory analyses of heavy metal concentrations in both synthetic wastewaters and raw water were carried out as specified in APHA (1998) method using the Alpha 4 Atomic Absorption Spectrophotometer (AAS) (Chem Techn Analytical) at the Central Science Laboratory, Obafemi Awolowo University, Ile-Ife, Nigeria. The adsorption capacities of the adsorbent were analyzed through the use of graphical methods for Langmuir, Freundlich, Temkin and Redlich- Peterson isotherm models. These equilibrium models were evaluated statistically using total errors, coefficient of determination (CD) and model of selection criterion (MSC). Estimated costs of production (environmental economics analysis) were conducted on the PES.

RESULTS AND DISCUSSION

Results from this study are discussed in six categories as follows: properties of the PES, ion exchange model, mechanism of the adsorptions, adsorption capacities of Pb^{2+} , Ni^{2+} and Cd^{2+} onto the PES, statistical evaluation of the models and estimated cost of production of the PES from chicken eggshells

Properties of the Powdered Eggshells

Result of the digestion indicated that 1 g of PES contained iron, aluminium and calcium (Table 1). It is well known that eggshell contains calcium in form of $CaCO_3$ as the major components (up to 95% $CaCO_3$) (Kin *et al.,* 1995; Schaafsma and Pakan, 1999; Schaafsma *et al.* 2000; 2002; Masuda, 2002; Rovensky et al., 2003; Shuhadah *et al.,* 2008; Siti and Supri, 2009; Hassan and Aigbodion, 2015). It has been postulated that in the presence of water, inorganic salts undergo displacement reactions as indicated in equations 7- 10. This shows that the PES underwent reactions in equations 10-15 with selected heavy metal ions, which can reduce the pH and the end product reacted with metallic ions to precipitate the pollutant (Kingori, 2011; Than *et al., 2012;* Najwa, *2012*; Nyankson *et al.,* 2013; Oke *et al.,* 2014).

$$CaCO_3 + 2H_2O \xrightarrow{H^+} H_2O + CO_2 + Ca(OH)_2 \quad (9)$$

$$\begin{aligned} &H_2O + CO_2 + Ca(OH)_2 + X^{2+} \rightarrow \\ &H_2O + CO_2 + Ca^{2+} + X(OH)_2 \end{aligned} \qquad (10)$$

$$\begin{aligned} &Al^{3+} + 3H_2O + \frac{3}{2}X[NO_3]_2 \rightarrow \\ &Al[NO_3]_3 + \frac{3}{2}X(OH)_2 + 3H^+ \end{aligned} \qquad (11)$$

$$\begin{aligned} &Fe^{2+} + 2H_2O + X[NO_3]_2 \rightarrow \\ &Fe[NO_3]_2 + X(OH)_2 + 2H^+ \end{aligned} \qquad (12)$$

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 the PES. Figure 1 presents micrograph of the PES. Literature such as Kin et al. (1995); Shuhadah *et al.* (2008); Siti and Supri (2009) and Hassan and Aigbodion (2015) provided more on Scanning Electron Microscopy (SEM) microstructure of PES. The microstructure of the PES particle revealed that the size and shape of the particles vary and PES consists of porous irregular shaped particles. The Energy Dispersive Spectroscopy (EDS) of the PES particles revealed that the particles contain Ca, Si, O, C, Mg and P with the presence of carbon in the carbonized eggshell particles. The carbon presence is due to the carbonization process (Figures 1a to 1e). These elements confirm that the PES particles consist of calcium carbonate in the form of calcite ($CaCO_3$) while the carbonized PES have carbon in graphite form (Hassan and Aigbodion, 2015).

Ion Exchange Model

The PES contains 2.31% volatile solids (Table 1, Supri *et al.,* 2012), which indicates that powdered eggshells were partially cellulose-based adsorbents, which contain polar functional groups that could be involved in chemical bonding. The organic compounds could be 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; Maskhoof *et al.*, 2013; Oke *et al.,* 2014):

$$2PESc^- + X^{2+} \rightleftharpoons XPESc_2 \qquad (13)$$

$$2HPESc + X^{2+} \rightleftharpoons XPESc_2 + 2H^+ \qquad (14)$$

where, $PESc^-$ and H $PESc^-$ are the polar sites on the PES surface and X is the pollutant Literature (Kohler *et al.,* 2007; Oke *et al.,* 2014) reported that the removal of heavy metals such as lead, nickel and cadmium in the presence of $CaCO_3$ can be represented as:

$$\begin{aligned} &yCa^{2+} + zCd^{2+} + CaCO_3 \rightarrow Cd_xCa_{(1-x)}CO_3 \\ &+ (y+x)Ca^{2+} + (z-x)Cd^{2+} \end{aligned} \qquad (15)$$

$$\begin{aligned} &yCa^{2+} + zPb^{2+} + CaCO_3 \rightarrow Pb_xCa_{(1-x)}CO_3 \\ &+ (y+x)Ca^{2+} + (z-x)Pb^{2+} \end{aligned} \qquad (16)$$

$$\begin{aligned} &yCa^{2+} + zNi^{2+} + CaCO_3 \rightarrow Ni_xCa_{(1-x)}CO_3 \\ &+ (y+x)Ca^{2+} + (z-x)Ni^{2+} \end{aligned} \qquad (17)$$

In addition, Maskhoof *et al.* (2013); Abbas *et al.* (2013) reported that on the basis of theoretical consideration, the adsorption of divalent metal ions (M) onto two free binding sites (B) can be explained by the following expressions:

$$M + B \leftrightarrow B_2M \qquad (18)$$

It means that the adsorption rate would be proportional to the concentration of metal ions and the square of the number of free sites onto PES

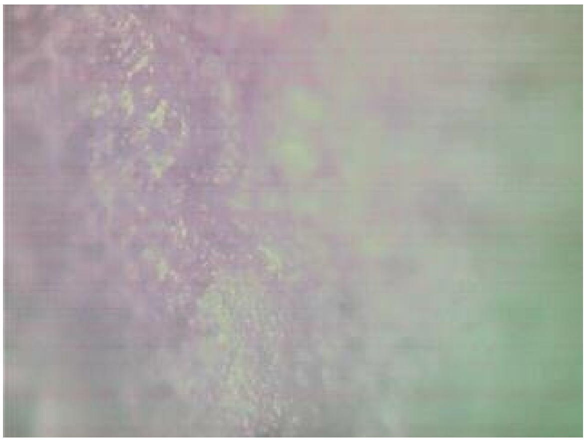


Figure 1: Optimal Microscopy View of the PES (Source: Oke *et al.,* 2014)

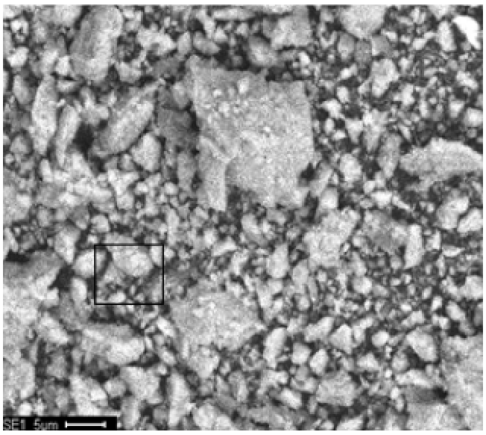


Figure 1ai: SEM Microstructure of the Uncarbonized Eggshell Particles (Source: Hassan and Aigbodion, 2015)

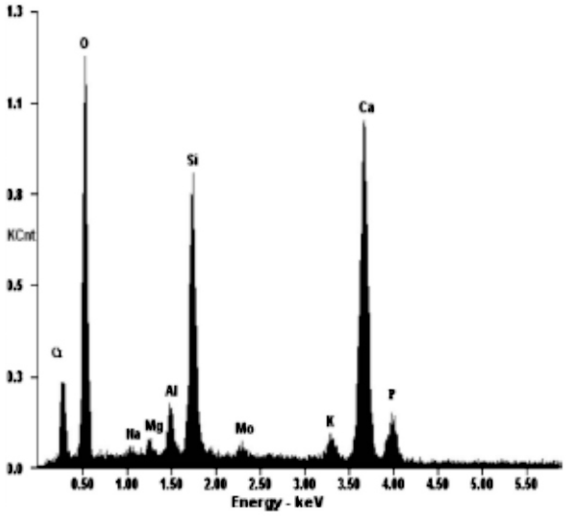


Figure 1aii: EDS Microstructure of the Uncarbonized Eggshell Particles (Source: Hassan and Aigbodion, 2015)

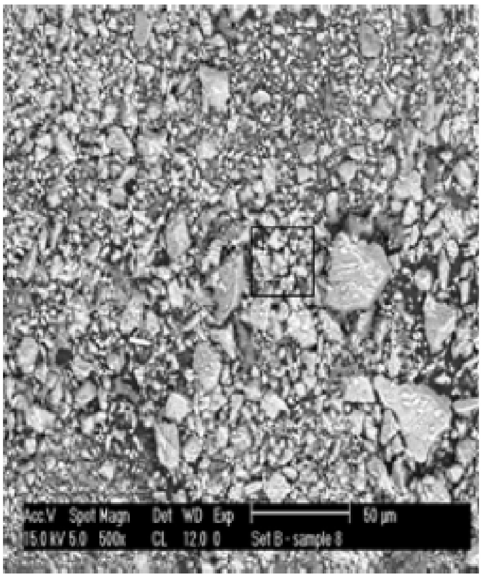


Figure 1bi: SEM/EDS Microstructure of the Carbonized Eggshell Particles (Source: Hassan and Aigbodion, 2015)

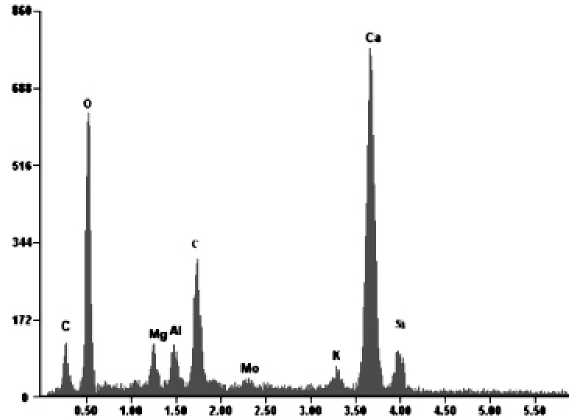
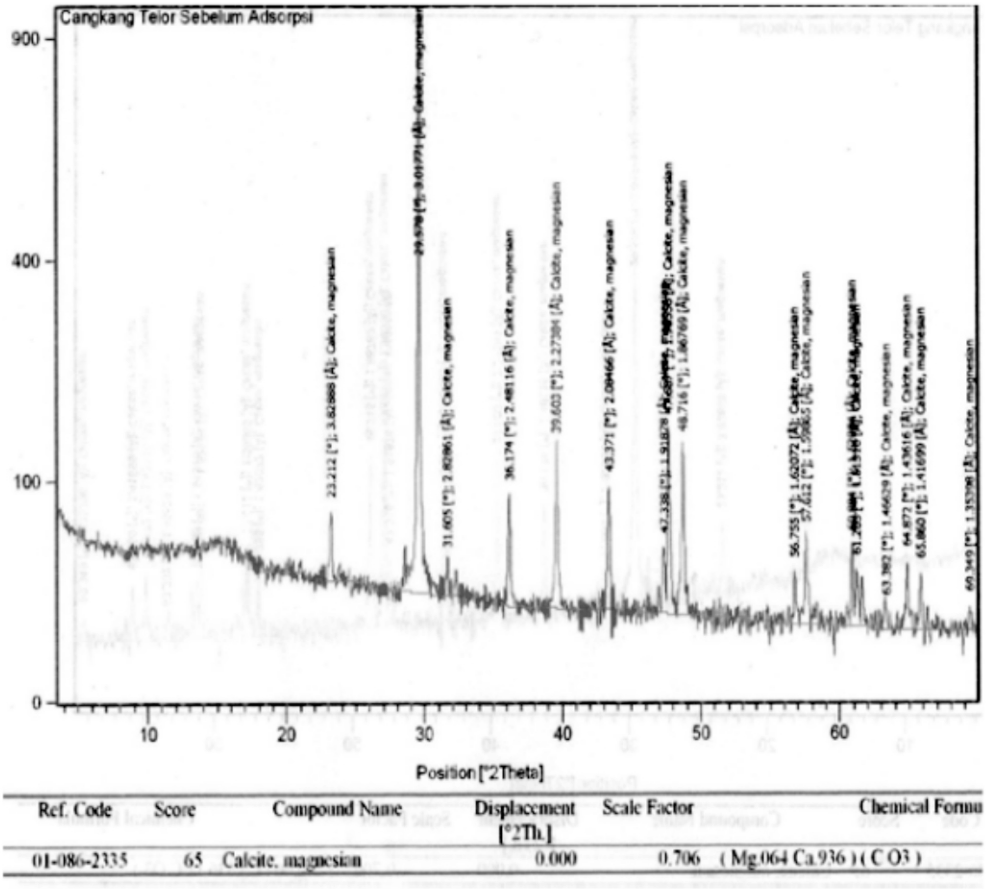


Figure 1bii: EDS Microstructure of the Carbonized Eggshell Particles (Source: Hassan and Aigbodion, 2015)

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



Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formu
01-086-2335	65	Calcite, magnesian	0.000	0.706	(Mg.064 Ca.936) (C O3)

Figure 1c: Diffractogram of Powdered Eggshell(Source: Muhammd *et al.*, 2012)

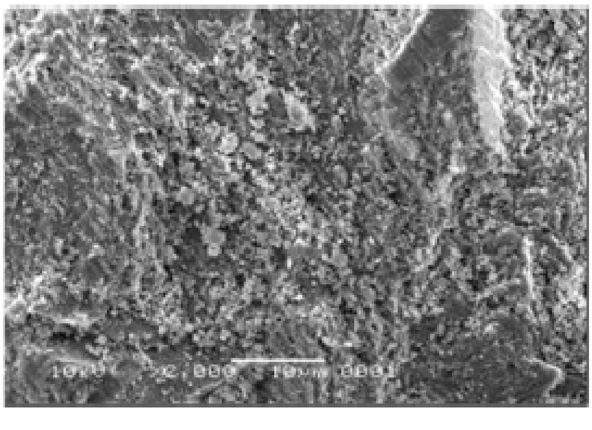


Figure 1d: SEM of Powdered Eggshell (Source: Muhammd *et al.*, 2012)

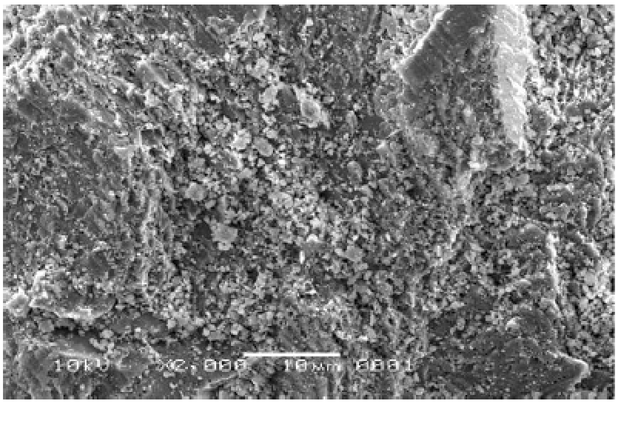


Figure 1e: SEM of Powdered Eggshell (Source: Zulfikar *et al.*, 2013)

Also, Nakano *et al.* (2003); Zou *et al.* (2008) and Hassan and Aigbodion (2015) reported that egg shell membrane is a unique cell surface with various functional groups, providing the potential for adsorption of metal species. Detailed information on functional groups in egg shell membrane can be found in Zou *et al.* (2008). Reactions between the functional groups and the pollutants can be expressed as follows (Oke *et al.*, 2014):

$$-----CONH--- +Cd^{2+} \rightarrow Cd-----CONH---Cd \quad (19)$$

$$-----CONH--- +Pb^{2+} \rightarrow Pb-----CONH---Pb \quad (20)$$

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

From the 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 egg shell membrane, quality and ultra structure of egg shell studied and documented by Krystianik *et al.* (2005) and morphology properties (Lui *et al.,* 2004; Oke *et al.,* 2014).

Mechanism of Adsorption

Figures 2 and 3 show the amount of lead, nickel and cadmium adsorbed onto the PES. From the figure it can be seen that 89.4%, 89.4% and 70.6% of initial pollutant's concentrations were removed in mono-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 the 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 (exponential) parts of the curves are attributed to mass transfer effects, which took place with boundary layer diffusion, while the final (linear) parts 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 figure 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; Oke *et al.,* 2014).

Adsorption Equilibrium Isotherm of Pb^{2+}, Ni^{2+} and Cd^{2+} onto the PES

The nature of adsorption reaction could be described by relating the adsorption capacity (mass of solute adsorbed per unit mass of adsorbent) to the equilibrium concentration of the solute remaining in the solution. Such a relation is known as an adsorption isotherm. There are many basic isotherm models, which include: Langmuir, Freundlich, Brunauer, Emmett and Teller (BET), Temkin, Redlich-Peterson, Nerst and Activated Sludge isotherms. Due to inconvenience of evaluating three isotherm parameters, two-isotherm-parameter equations (Langmuir, Freundlich and Temkin equations) are more widely used than the three-isotherm-parameter equation (Redlich-Peterson equation). Langmuir isotherm is a physically plausible isotherm, which was developed from a theoretical consideration and is based on three assumptions, namely: adsorption cannot proceed beyond monolayer coverage, all surface sites are equivalent and can accommodate at most one adsorbed atom; and the ability of a molecule to adsorb at a given site is independent of the occupation of neighbouring sites. At equilibrium there is no net change of surface coverage; the rate of change of concentration due to adsorption should be equal to the rate of change of concentration due to desorption. As a result, the Langmuir isotherm is expressed as (Alam *et al.*, 2007; Oke *et al.,* 2008):

$$q_e = \frac{abC_e}{1 + aC_e} \quad (22)$$

where, 'a and b' are the Langmuir isotherm parameters.

Rearranging equation (22) gives a linearised equation (23) from which the values of "a and b" can be determined from slope and intercept.

$$\frac{1}{q_e} = \frac{1}{b} + \frac{1}{ab}\frac{1}{C_e} \quad (23)$$

Figure 4 shows graphical method for the parameters estimated. Estimated adsorption parameters by the Langmuir model are shown in Table 2. The Langmuir constants a and b (0.962 l/mg and 0.0169 mg/mg; 0.260 l/mg and 0.0043 mg/mg; 0.255 l/mg and 0.0083 mg/mg for Pb^{2+}, Ni^{2+} and Cd^{2+} respectively) and the square of regression coefficient (R^2 were 0.982, 0.963 and 0.960 for Pb^{2+}, Ni^{2+} and Cd^{2+} respectively) suggested that the adsorption of Pb^{2+} can be adequately modelled by Langmuir equation while adsorption of Ni^{2+} and Cd^{2+} could not be adequately modelled by the Langmuir isotherm ($R^2 < 0.98$; Loveday, 1980). For multi- component synthetic wastewater, the estimated adsorption parameters by the Langmuir model were "a and b" (0.461 l/mg and 0.007 mg/mg; 0.134 l/mg and 0.0038 mg/mg; 0.122 l/mg and 0.0037 mg/mg Pb^{2+}; Ni^{2+} and Cd^{2+} respectively) and the square of regression coefficient were 0.971; 0.981 and 0.981 for Pb^{2+}; Ni^{2+} and Cd^{2+} respectively. The values of "a and b" were lower than the values obtained for mono-component synthetic wastewater, which indicated that there were competitive adsorption between the ions (Igwe *et al.,* 2005). For raw water estimated adsorption parameters by the Langmuir model "a and b" were 0.749 l/mg and 0.0197 mg/mg; 0.264 l/mg and 0.0018 mg/mg; 0.721 l/mg and 0.0016 mg/mg for Pb^{2+}, Ni^{2+} and Cd^{2+} respectively and regression coefficient were 0.981; 0.981 and 0.991 respectively. The values of b for Pb^{2+}, Ni^{2+} and Cd^{2+} indicated that PES as an adsorbent might remove these metals effectively when initial concentrations of Pb^{2+}, Ni^{2+} and Cd^{2+} are higher. Although, these values of "a and b" are lower than the values obtained in literature, but similar to values for hazenut shell activated carbon (HSAC), which indicated that PES is a valuable adsorbent as HSAC. Some studies using biological material to remove Pb^{2+} show that the results obtained in this work are in according to literature. Keskinkan *et al.* (2007) obtained 0.224 and 0.216 mmol.g^{-1} for removal of Pb^{2+} using Myriophyllum spicatum and Ceratophyllum demersum as biosorbents, respectively. Hamza *et al.* (2013) used sugarcane bagasse to Pb^{2+} removal and achieved a maximum uptake of 0.273 mmol.g^{-1}.

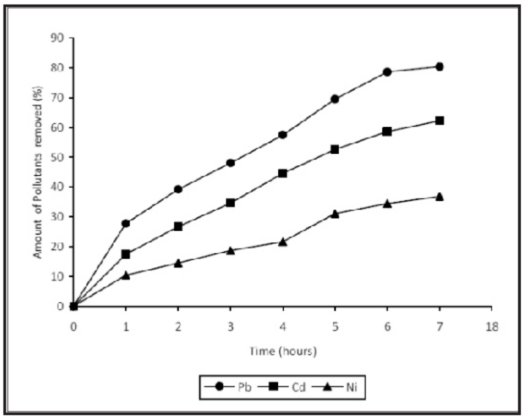


Figure 2: Amount of Pollutants Adsorbed onto the PES Multi-Component Synthetic Wastewater

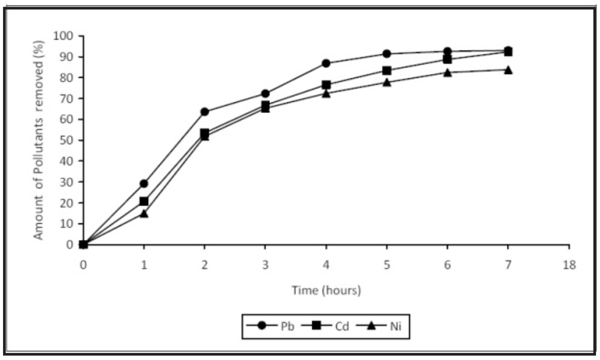
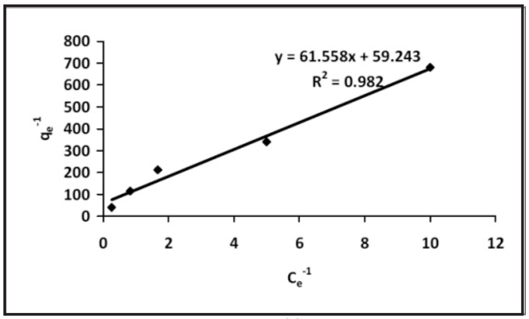
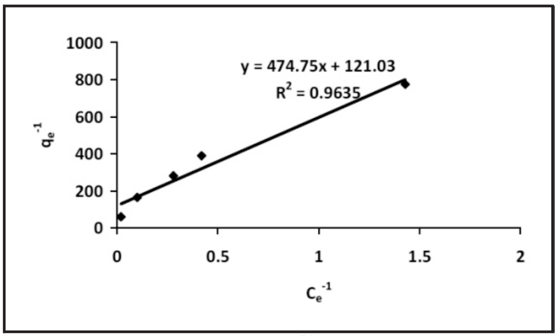


Figure 3: Amount of Pollutants Adsorbed onto the PES Mono Component Synthetic Wastewater



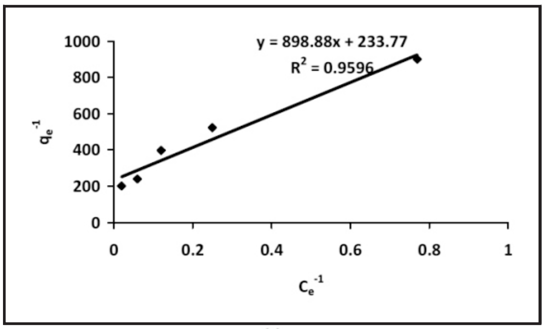
(a)

Figure 4a: Langmuir Model of Pb^{2+} Adsorption onto the PES



(b)

Figure 4b: Langmuir Model of Cd^{2+} Adsorption onto the PES



(c)

Figure 4c: Langmuir Model of Ni^{2+} Adsorption onto the PES

Sekhar *et al.* (2004) used the bark of Hemidesmus indicus plant to remove Pb^{2+} and attained 0.452 $mmol.g^{-1}$ of removal in a continuous system. Lívia *et al.* (2014) studied Pb^{2+} biosorption by salvinia natans biomass and the values were higher than the values obtained in this study. From Table 2, it can be seen that pH, particle size of PES and initial concentration of the pollutant had effects on the adsorption capacities, but the influence or effects are not significant statistically at 95% confidence level. This indicated that adsorption capacities of any material are definite properties that cannot be influenced by any external factors.

It is well documented that the essential characteristic of the Langmuir isotherm may be expressed in terms of the dimensionless parameter (R_L), which has been defined as the isotherm shape that predicts if an adsorption system is favourable or unfavourable (Saswati and Ghosh, 2005). Mamdouth *et al* (2004) states that R_L indicates the isotherm shape according to the following adsorption characteristics, $R_L > 1$ (is unfavourable), $R_L = 1$ (linear adsorption), $R_L = 0$ (is irreversible) and $0 < R_L < 1$ (is favourable) It has been expressed as:

$$R_l = \frac{1}{1+bC_o} \tag{24}$$

where, R_L is the Langmuir equilibrium parameter For mono component systems (R_l = 0.855, 0.959 and 0.923 for Pb^{2+}, Cd^{2+} and Ni^{2+}, respectively) and multi component synthetic wastewaters (R_l = 0.935, 0.963 and 0.964 for Pb^{2+}, Cd^{2+} and Ni^{2+} respectively) and raw wastewater (R_l = 0.9996; 0.9999 and 0.9999 for Pb^{2+}, Cd^{2+} and Ni^{2+} respectively), the values of R_L were found to be $0.0 < R_l < 1.0$ indicating that adsorption of Pb^{2+}, Ni^{2+} and Cd^{2+} on PES is favourable. The values of R_L are similar to the values of R_L for adsorption of iron and manganese onto maize cob and palm fruit bunch (0.87 and 0.86, respectively), indicating that adsorption Pb^{2+}, Ni^{2+} and Cd^{2+} onto PES agrees with adsorption studied by Mamdouth *et al.* (2004). Langmuir adsorption capacity was also used to calculate the specific surface area (S_l, cm^2/g) of the monolayer adsorption of the metals by PES as follows:

$$S_l = \frac{bNA}{M} \tag{25}$$

where, N is the Avogadro's number (6.022×10^{23}), A is the cross-sectional area of metal ion (A^{o2}) and M the atomic mass of the metal ion. The cross-sectional area for Pb^{2+}, Cd^{2+} and Ni^{2+} are 5.56, 4.89 and 5.244 A^{o2} respectively (Ho *et al.* 2002; Kinhikar, 2012; Abbas *et al.,* 2013 and Makshoof *et al.,* 2013). The surface area thus calculated were 27.33 ; 21.83 and 23.10 cm^2/g for for Pb^{2+}, Cd^{2+} and Ni^{2+} respectively. This indicates that surface area for adsorption of Pb^{2+}, Cd^{2+} and Ni^{2+} onto PES are practicable.

It has been reported that Freundlich isotherm is an empirical relationship, which often gives a more satisfactory model of experimental data (Oke *et al.,* 2008). It can be expressed as shown in equation (26):

$$q_e = K_f C_e^{1/N_f} \tag{26}$$

where, N_f is the Freundlich isotherm exponent and K_f is the Freundlich isotherm parameter .

The values of K_f and N_f were obtained by plotting adsorption capacities against equilibrium concentrations (Ho, 2006). Figure 5 shows graphical method for the parameter estimate. For mono- component synthetic wastewater K_f and N_f were 0.0070 mg/mg and 1.645 mg/L; 0.0010 mg/mg and 3.226 mg/L, and 0.0034 mg/mg and 2.381 mg/L and (R^2) for Freundlich isotherm were 0.965, 0.904 and 0.935 for Pb^{2+}, Ni^{2+} and Cd^{2+}, respectively For multi- component synthetic wastewater K_f and N_f were 0.0069 mg/mg and 1.678 mg/L; 0.0010 mg/mg and 3.292 mg/L, and 0.0033 mg/mg and 2.430 mg/L and R^2 for Freundlich isotherm were 0.979, 0.743 and 0.891 for Pb^{2+}, Ni^{2+} and Cd^{2+}, respectively. For raw water K_f and N_f were 0.0067 mg/mg and 1.713 mg/L , 0.0010 mg/mg and 3.359 mg/L , and 0.0033 mg/mg and 3.359 mg/L with R^2 of 0.915; 0.842 and 0.923 for Pb^{2+}, Ni^{2+} and Cd^{2+} , respectively. High values of K_f and N_f (greater than 1) from the Freundlich isotherm suggested that the adsorption capacity of PES was high and that any large change in the equilibrium concentration of Pb^{2+}, Ni^{2+} and Cd^{2+} would not result in a marked change in the amount of Pb^{2+}, Ni^{2+} and Cd^{2+} adsorbed by PES. The values of R^2 also indicated that Freundlich isotherm could not describe the adsorption of Pb^{2+}, Ni^{2+} and Cd^{2+} onto PES adequately. It also indicated that the adsorption capacities were in the order of $Pb^{2+} < Cd^{2+} < Ni^{2+}$. These correlation coefficients disagree with Tebbutt (1991) statement on Freundlich isotherm (Oke *et al.,* 2008). Davis *et al.* (2014) reported that N_f describes the heterogeneity of the adsorbent surface and its affinity for the adsorbate. $1/N_f$ is the heterogeneity factor and N_f is a measure of deviation from linearity of adsorption, higher value of N_f (or a smaller $1/N_f$ value of indicates a stronger bond between the adsorbate and the adsorbent thus values of N_f larger than unity indicate a strong bond which implies favourable adsorption. If N_f is less than 1 , adsorption is a chemical process; if N_f is greater than 1 then adsorption is a physical process. This indicates that adsorption of Pb^{2+}, Ni^{2+} and Cd^{2+} onto PES is a physical process (Davis *et al.*, 2014). The Freundlich isotherm describes reversible adsorption and is not restricted to the formation of monolayer. This means that the assumption of multilayer adsorption is not in agreement with the experiment in the studied concentration range (Hasan and Marzieh, 2013). The values of K_f and N_f are different from the values documented in Mamdouth *et al.* (2004) and in Kobya (2004), which indicated that adsorption onto carbon is different from adsorption onto PES. Disagreement of these values with Tebbutt (1991) statement and deviation of these values from literature can be attributed to composition of PES of mainly inorganic compounds compared to activated carbon and other adsorbents of mainly organic compounds.

The third isotherm was developed by Crombie-Quilty and McLoughin (1983), it describes floc formation at an equilibrium concentration. Oke *et al.* (2008); Adie *et al.* (2008) and Ismail *et al.* (2009) stated that Crombie-Quilty and McLoughin (1983) describes the model which is known as activated sludge model. The activated adsorption equation is as shown in equation (27).

$$q_e = K_m\left(\frac{C_e}{M}\right)^{1/N_m} \tag{27}$$

where, N_m is the exponential constant for activated sludge model (mg/g) and K_m is the constant for activated sludge model. The values of K_m and N_m can be obtained by plotting of adsorption capacity against equilibrium concentration (Ho, 2006). The estimated adsorption parameters by the activated adsorption model are shown in Table 2. A low level of K_m (0.007 – 0048 per unit mass of adsorbent) from the activated sludge isotherm suggests that the tendency of floc formation is possible but low. A lower $1/N_m$ value (less than 1) from the activated sludge isotherm suggests that any large change in the equilibrium concentration of the metals would not result in a remarkable change in the amount of metallic floc formation by PES. The correlation coefficient (R^2) for activated sludge isotherms (0.917 – 0.978) also represents an average fitness of the observed data.

Table 2: Isotherm Parameters for Langmuir, Freundlich and Activated Sludge Models

Description	Metals		Langmuir Model			Freundlich model				Activated sludge model			
			a (L/mg)	b (mg/mg)	R^2	K_f (mg/mg)	$1/N_f$ (L/mg)	N_f (mg/L)	R^2	K_m (mg/mg^2)	$1/N_m$ (L/mg^2)	N_m (mg^2/L)	R^2
Mono component (individual)	Pb^{2+}		0.962	0.0169	0.982	0.0070	0.608	1.645	0.965	0.0048	0.434	2.304	0.978
	Cd^{2+}		0.255	0.0083	0.960	0.0034	0.420	2.381	0.935	0.0023	0.300	3.335	0.948
	Ni^{2+}		0.260	0.0043	0.963	0.0010	0.310	3.226	0.904	0.0007	0.221	4.518	0.917
Multi component	Pb^{2+}		0.461	0.0070	0.971	0.0069	0.596	1.678	0.979	0.0047	0.425	2.351	0.990
	Cd^{2+}		0.122	0.0037	0.981	0.0033	0.412	2.430	0.743	0.0023	0.294	3.403	0.960
	Ni^{2+}		0.138	0.0038	0.991	0.0010	0.304	3.292	0.891	0.0007	0.217	4.610	0.930
Raw water	Pb^{2+}		0.749	0.0197	0.981	0.0067	0.584	1.713	0.915	0.0046	0.417	2.399	0.987
	Cd^{2+}		0.721	0.0016	0.991	0.0033	0.403	2.479	0.923	0.0022	0.288	3.472	0.974
	Ni^{2+}		0.264	0.0018	0.981	0.0010	0.298	3.359	0.842	0.0007	0.213	4.704	0.949
Effect pH on mono component	Pb^{2+}	3.0	0.962	0.0169	0.982	0.0070	0.6080	1.645	0.965	0.0048	0.434	2.304	0.978
		7.6	0.959	0.0173	0.973	0.0070	0.6220	1.608	0.956	0.0047	0.444	2.252	0.969
		11.7	0.956	0.0177	0.964	0.0070	0.6363	1.572	0.948	0.0047	0.454	2.201	0.961
	Cd^{2+}	3.0	0.255	0.0083	0.960	0.0034	0.4200	2.381	0.935	0.0023	0.300	3.335	0.948
		7.6	0.254	0.0085	0.951	0.0034	0.4297	2.327	0.927	0.0023	0.307	3.260	0.940
		11.7	0.253	0.0087	0.943	0.0034	0.4395	2.275	0.918	0.0023	0.314	3.186	0.931
	Ni^{2+}	3.0	0.260	0.0040	0.963	0.0010	0.3100	3.226	0.904	0.0007	0.221	4.518	0.917
		7.6	0.259	0.0044	0.954	0.0010	0.3171	3.153	0.914	0.0007	0.226	4.416	0.994
		11.7	0.258	0.0045	0.946	0.0010	0.3244	3.082	0.915	0.0007	0.232	4.317	0.998
Particle size on mono —	Pb^{2+}	300	0.962	0.0169	0.982	0.0070	0.6080	1.645	0.965	0.0048	0.434	2.304	0.978
		150	0.940	0.0169	0.971	0.0068	0.6095	1.641	0.954	0.0047	0.435	2.298	0.967
		75	0.947	0.0175	0.964	0.0069	0.6299	1.587	0.948	0.0047	0.450	2.223	0.961
	Cd^{2+}	300	0.255	0.0083	0.960	0.0034	0.4200	2.381	0.935	0.0023	0.300	3.335	0.948
		150	0.249	0.0083	0.951	0.0033	0.4211	2.375	0.927	0.0023	0.301	3.326	0.940
		75	0.251	0.0086	0.952	0.0033	0.4351	2.298	0.927	0.0023	0.311	3.219	0.940
	Ni^{2+}	300	0.260	0.0043	0.963	0.0010	0.3100	3.226	0.904	0.0007	0.221	4.518	0.917
		150	0.254	0.0043	0.954	0.0010	0.3108	3.218	0.905	0.0007	0.222	4.506	0.995
		75	0.256	0.0045	0.955	0.0010	0.3212	3.114	0.904	0.0007	0.229	4.361	0.994
Initial concentration on mono component (mg/L)	Pb^{2+}	20.45	0.962	0.0169	0.982	0.0070	0.6080	1.645	0.965	0.0048	0.434	2.304	0.978
		15.02	0.921	0.0166	0.969	0.0067	0.5974	1.674	0.953	0.0046	0.427	2.345	0.966
		0.13	0.937	0.0173	0.964	0.0068	0.6236	1.604	0.948	0.0046	0.445	2.246	0.961
	Cd^{2+}	20.45	0.255	0.0083	0.960	0.0034	0.4200	2.381	0.935	0.0023	0.300	3.335	0.948
		15.02	0.244	0.0082	0.951	0.0033	0.4126	2.423	0.927	0.0022	0.295	3.394	0.940
		0.13	0.248	0.0085	0.962	0.0033	0.4308	2.321	0.937	0.0023	0.308	3.251	0.950
	Ni^{2+}	20.45	0.260	0.0043	0.963	0.0010	0.3100	3.226	0.904	0.0007	0.221	4.518	0.917
		15.02	0.249	0.0042	0.954	0.0010	0.3046	3.283	0.905	0.0007	0.217	4.598	0.995

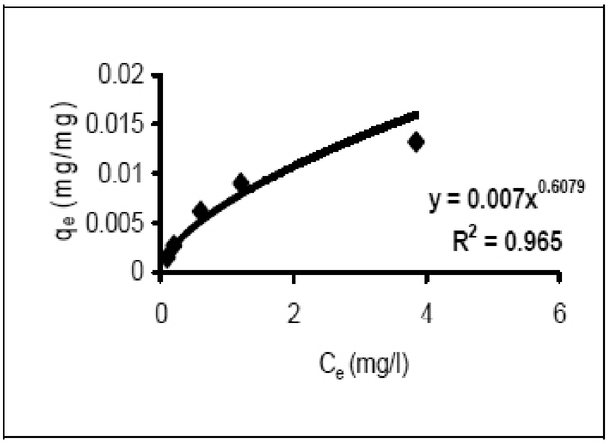


Figure 5a Freundlich Model of Pb^{2+} Adsorption onto the PES

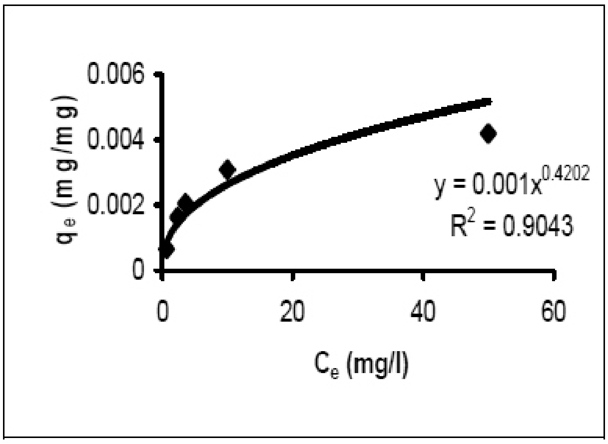


Figure 5b: Freundlich Model of Cd^{2+} Adsorption onto the PES

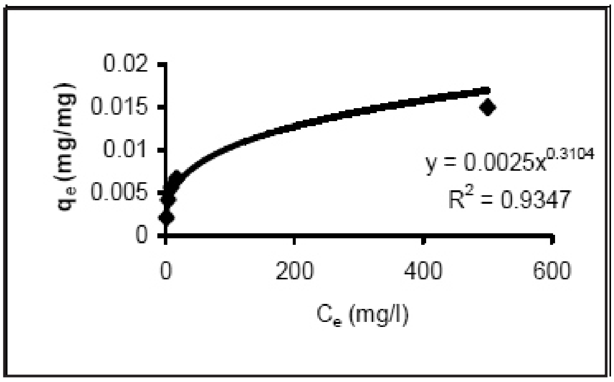


Figure 5c: Freundlich Model of Ni^{2+} Adsorption onto the PES

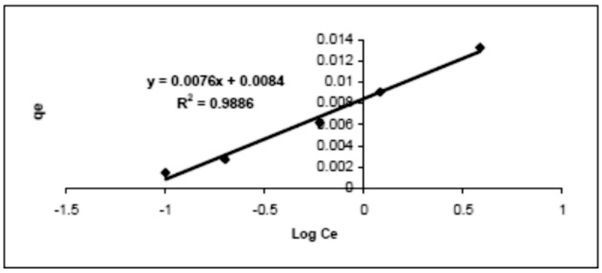


Figure 6a:Temkin Model of Pb^{2+} onto the PES

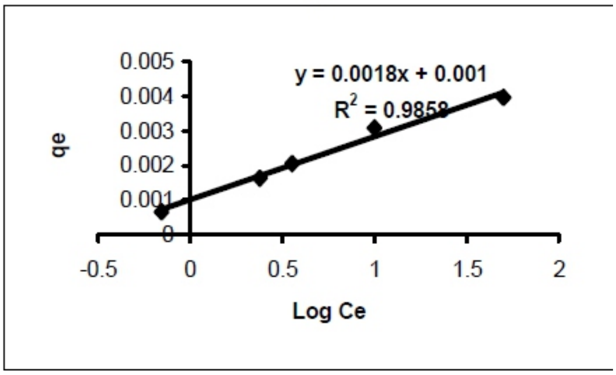


Figure 6b:Temkin Model of Cd^{2+} onto the PES

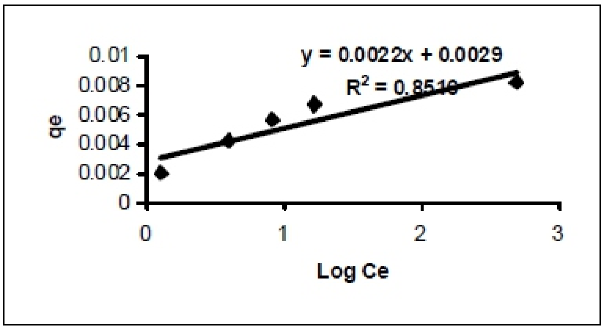


Figure 6c:Temkin Model of Ni^{2+} onto the PES

The Temkin isotherm is an empirical relationship, which often gives a more satisfactory model of experimental data (Otun *et al.,* 2006b). Hasan and Marzieh (2013) stated that because of the existence of adsorbent- adsorbate interactions, the heat of adsorption should decrease linearly with the surface coverage and that the Tempkin isotherm equation assumes that the adsorption is characterized by a uniform distribution of the binding energies, up to some maximum binding energy. Temkin isotherm can be expressed as shown in equation (28).

$$q_e = a_t + 2.3b_t \log C_e \qquad (28)$$

where, b_t is the constants related to adsorbent only by Temkin model and a_t is the constant related to adsorbent and adsorbate by Temkin model.

The values of a_t and b_t were obtained by plotting of adsorption capacity against logarithms of equilibrium concentration. Figure 6 shows graphical method for the parameter estimate. Estimated adsorption parameters by the Temkin model were shown in Table 3. The values of a_t and b_t from the Temkin isotherm model (mono synthetic wastewater: 0.0084l/mg and 0.0033 mg/mg; 0.0029 l/mg and 0.0010 mg/mg; and 0.0010 l/mg and 0.0008 mg/mg; multi component 0.0066 l/mg and 0.0026 mg/mg; 0.0023 l/mg and 0.0008 mg/mg;and 0.0008 l/mg and 0.0006 mg/mg; raw water: 0.0051 l/mg and 0.0020 mg/mg; 0.0018 l/mg and 0.0006 mg/mg;and 0.0006 l/mg and 0.0005 mg/mg; for Pb^{2+}, Ni^{2+} and Cd^{2+} respectively) and R^2 suggested that the adsorption capacity of PES was high and that any large change in the equilibrium concentration of Pb^{2+}, $Ni^{2+}$and Cd^{2+} would result in a marked change in the amount of Pb^{2+}, Ni^{2+} and Cd^{2+} adsorbed by PES. This low correlation coefficient for Ni^{2+} and Cd^{2+} confirms Sawasti and Ghosh (2005) statement on Temkin isotherm (the three-isotherm- parameters equations mostly provide a better fit of the isotherm data than a two-isotherm-parameters).

The disadvantage of the Freundlich model is that it does not reduce to Henry's law as the concentration approaches zero. Redlich–Peterson model fulfils this condition. The model has a linear dependence on concentration in the numerator and an exponential function in the denominator as presented by equation (29). The Redlich- Peterson isotherm is an empirical relationship, which often gives a more satisfactory model of experimental data.

$$q_e = \frac{\alpha_t C_e}{1+\beta_t C_e^{\gamma}} \qquad (29)$$

Where; γ is the Redlich–Peterson isotherm exponent; α_t is the Redlich–Peterson isotherm parameter and β_t is the Redlich–Peterson isotherm parameter

For $\beta_t = 1$, the equation converts to the Langmuir isotherm; for $1 >> \beta_t C_e^{\gamma}$ it simplifies to Henry's law; and for $1 << \beta_t C_e^{\gamma}$ it is identical with the Freundlich isotherm. The linear form is given in equation (30) from which the constants α_t, γ and β_t which characterized the isotherm can be determined. Since there are three unknowns in the equation, α_t is assumed to be equal to *a* of the Langmuir model:

$$\frac{C_e}{q_e} = \frac{1}{\alpha_t} + \frac{\beta_t}{\alpha_t} C_e^{\gamma} \qquad (30)$$

Table 3: Isotherm parameters for Temkin and Redlich- Peterson models

Description	Metals		Temkin			Redlich- Peterson			
			a_t (L/mg)	b_t (mg/g)	R^2	α(L/mg)	β (mg/g)	γ(mg/g)	R^2
Mono component (individual)	Pb^{2+}		0.0084	0.0033	0.989	0.962	0.262	0.204	0.941
	Cd^{2+}		0.0010	0.0008	0.966	0.255	0.676	0.361	0.976
	Ni^{2+}		0.0029	0.0010	0.852	0.260	0.704	0.397	0.890
Multi component	Pb^{2+}		0.0066	0.0026	0.799	0.461	0.257	0.200	0.953
	Cd^{2+}		0.0008	0.0006	0.710	0.122	0.662	0.354	0.968
	Ni^{2+}		0.0023	0.0008	0.970	0.138	0.690	0.389	0.903
Raw water	Pb^{2+}		0.0051	0.0020	0.771	0.249	0.252	0.196	0.964
	Cd^{2+}		0.0006	0.0005	0.817	0.721	0.649	0.347	0.989
	Ni^{2+}		0.0018	0.0006	0.589	0.264	0.676	0.381	0.961
Effect pH on mono component	Pb^{2+}	3.0	0.0084	0.0033	0.989	0.962	0.262	0.204	0.941
		7.6	0.0084	0.0033	0.980	0.959	0.268	0.209	0.933
		11.7	0.0083	0.0033	0.971	0.956	0.274	0.213	0.924
	Cd^{2+}	3.0	0.0010	0.0008	0.966	0.255	0.676	0.361	0.976
		7.6	0.0010	0.0008	0.947	0.254	0.692	0.369	0.967
		11.7	0.0010	0.0008	0.968	0.253	0.707	0.378	0.959
	Ni^{2+}	3.0	0.0029	0.0010	0.951	0.260	0.704	0.397	0.890
		7.6	0.0029	0.0010	0.942	0.259	0.720	0.406	0.978
		11.7	0.0029	0.0010	0.934	0.258	0.737	0.415	0.969
Particle size on mono component (µm)	Pb^{2+}	300	0.0084	0.0033	0.989	0.962	0.262	0.204	0.941
		150	0.0082	0.0032	0.978	0.940	0.263	0.205	0.931
		75	0.0083	0.0032	0.971	0.947	0.271	0.211	0.924
	Cd^{2+}	300	0.0010	0.0008	0.966	0.255	0.676	0.361	0.976
		150	0.0010	0.0008	0.957	0.249	0.678	0.362	0.967
		75	0.0010	0.0008	0.958	0.251	0.700	0.374	0.968
	Ni^{2+}	300	0.0029	0.0010	0.951	0.260	0.704	0.397	0.890
		150	0.0028	0.0010	0.942	0.254	0.706	0.398	0.979
		75	0.0029	0.0010	0.943	0.256	0.729	0.411	0.979
Initial concentration on mono component (mg/l)	Pb^{2+}	20.45	0.0084	0.0033	0.989	0.962	0.262	0.204	0.941
		15.02	0.0080	0.0032	0.976	0.921	0.257	0.200	0.929
		0.13	0.0082	0.0032	0.971	0.937	0.269	0.209	0.924
	Cd^{2+}	20.45	0.0010	0.0008	0.966	0.255	0.676	0.361	0.976
		15.02	0.0010	0.0008	0.957	0.244	0.664	0.355	0.967
		0.13	0.0010	0.0008	0.958	0.248	0.693	0.370	0.978
	Ni^{2+}	20.45	0.0029	0.0010	0.951	0.260	0.704	0.397	0.890
		15.02	0.0028	0.0010	0.942	0.249	0.692	0.390	0.979
		0.13	0.0028	0.0010	0.953	0.253	0.722	0.407	0.980

Equation (30) can be transformed to equation (31), which can be expressed as follows (equation 32):

$$\frac{\alpha_t C_e}{q_e} - 1 = \beta_t C_e^{\gamma} \qquad (31)$$

$$\log\left(\frac{\alpha_t C_e}{q_e} - 1\right) = \log \beta_t + \gamma \log C_e \qquad (32)$$

Plotting of logarithms of left hand side values against logarithms of equilibrium concentrations the unknown parameters will be found (the values of $_t$ and $_t$ can be obtained). Estimated adsorption parameters by the Redlich- Peterson model were shown in Table 3. The values of $_t$ and $_t$ (greater than 1 for mono, multi synthetic wastewaters and raw water) from the Redlich- Peterson isotherm suggested that the adsorption capacity of PES was high and that any large change in the equilibrium concentration of Pb^{2+}, Ni^{2+} and Cd^{2+} would result in a marked change in the amount of Pb^{2+}, $Ni^{2+}$and Cd^{2+} adsorbed by the PES. The correlation coefficient (R^2) for Redlich- Peterson isotherm were 0.941, 0.976 and 0.890 representing an average fit of the observed data for adsorption $Pb^{2+}$and Cd^{2+} and a good fit of observed data for Ni^{2+} adsorption onto the PES. The values of $_t$ and $_t$ are different from the values documented in Mamdouth *et al* (2004) and in Kobya (2004), which indicate that adsorptions onto carbon are different from adsorption onto the PES.

Effect of pH on Adsorption Capacities

The pH of an aqueous solution is probably the most important parameter for effective adsorption of metal ions on to the biomass. It is directly related to the competitive ability of hydrogen ions and metal ions to bind to active sites present on the biomass. Generally, metal adsorption involves complex mechanisms of ion exchange, chelation, adsorption by physical forces and ion entrapment in inter and intrafibrillar capillaries and spaces of the cell structural network of a adsorbent (Farooq *et al.*, 2010; Munagapati *et al.* 2010; Maskhoof *et al.*, 2013). SEM, acid digestion and EDS analyses showed that PES had a variety of pore and functional groups, such as carboxyl, hydroxyl and amine, involved in almost all potential binding mechanisms. Moreover, depending on the pH values of the aqueous solutions, these functional groups participate in metal ion bindings. The effect of pH on the adsorption of Pb^{2+}, Cd^{2+} and Ni^{2+} onto PES was studied at pH 3– 11.7 and the results were given in Figure 7. The maximum adsorption was observed at pH 3.0 which indicates very low pH, the concentration of H^+ ions was high. This led to the development of positive charge on the active sites of biomass and also a competition between Pb^{2+}, Cd^{2+} and Ni^{2+} and H^+ in the bulk of solution to attach with the active binding sites of PES. So, there was a minimum binding of Pb^{2+}, Cd^{2+} and Ni^{2+} at low pH. As the pH of a solution increases, PES becomes less positive and the concentration of H^+ also decreases. Thus, there is less competition of Pb^{2+}, Cd^{2+} and Ni^{2+} with H^+ and this resulted in more adsorption. In summary, the adsorption of Pb^{2+}, Cd^{2+} and Ni^{2+} at low pH follows various other mechanisms in addition to the simple ion exchange.

Effect of Initial Concentration on Adsorption Capacities

Das *et al.* (2014) reported that the rate of adsorption is a function of the initial concentration of the adsorbate, which makes it an important factor to be considered for effective adsorption. The effect of different initial Pb^{2+}, $Ni^{2+}$and Cd^{2+} concentrations on adsorption of Pb^{2+}, $Ni^{2+}$and Cd^{2+} onto PES is presented in Figure 8. The percentage removal of Pb^{2+}, $Ni^{2+}$and Cd^{2+} decreased with increasing of the initial Pb^{2+}, $Ni^{2+}$and Cd^{2+} concentration. This can be explained by the fact that all adsorbents have a limited number of active sites and at a certain concentration, the active sites become saturated (Tsai and Chen 2010; Das *et al.,* 2014). However, the adsorption capacity at equilibrium increased with increase in initial Pb^{2+}, $Ni^{2+}$and Cd^{2+} concentration. It is possible that the initial concentration of the metal ions provides the necessary driving force to overcome the mass transfer resistance of Pb^{2+}, Ni^{2+} and Cd^{2+} between the aqueous and the solid phase (Chowdhury and Saha 2010). The increase in the initial Pb^{2+}, $Ni^{2+}$and Cd^{2+} concentration also enhances the interaction between the Pb^{2+}, $Ni^{2+}$and Cd^{2+} in the aqueous phase and the PES surface. Therefore, a higher initial concentration of Pb^{2+}, $Ni^{2+}$and Cd^{2+} enhances the rate of adsorption. Similar results were obtained in the adsorption of copper and lead ions by manganese oxide-coated sand (Han *et al.* 2006a, b). This observation disagrees with literature for it is well known that increasing adsorbate concentration generally caused a decrease in adsorption capacity (Izanloo and Nasseri, 2005).

Effect of Particle Size on Adsorption Capacities

The effect of particle size of PES on Pb^{2+}, Ni^{2+} and Cd^{2+} adsorption is shown in Figure 9 and it appears that particle size of PES has pronounced an effect on the amount of Pb^{2+}, Ni^{2+} and Cd^{2+} adsorbed. As the particle size of PES increased from 75 to 300 μm, the adsorption capacity decreased from 0.0175 to 0.0169; 0.0045 to 0.0043 and 0.0086 to 0.0083 mg mg-1 for Pb^{2+}, Ni^{2+} and Cd^{2+} respectively. However, beyond 150 μm, the adsorption capacity remained constant and the particle size of PES of 150 μm was selected in subsequent analysis. The increase in adsorption capacity at a lower particle size of PES could be explained in terms of the reduction of boundary layer thickness around the adsorbent particles (Hanafiah *et al.,* 2009) and increase in surface area of the adsorbent (PES). Therefore, with decreasing particle size of PES, the concentrations of Pb^{2+}, Ni^{2+} and Cd^{2+} near the adsorbent surface would be increased. A lower particle size of PES also encouraged a better mass transfer of Pb^{2+}, Ni^{2+} and Cd^{2+} from bulk solution to the surface of the adsorbent and shortened the adsorption equilibrium time.

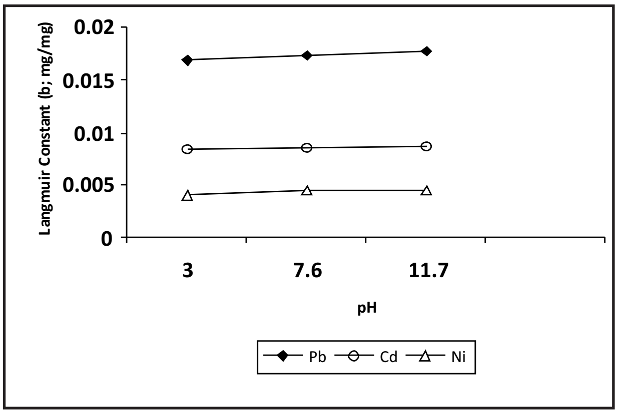


Figure 7: Effect of pH of Adsorption Capacity of PES

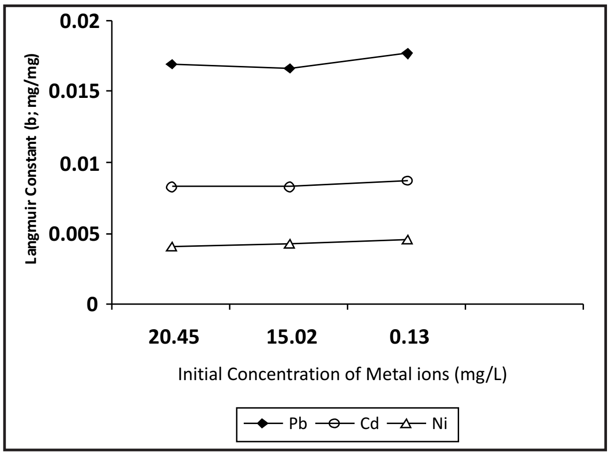


Figure 8: Effect of Initial Concentration of metal ion on Adsorption Capacity of PES

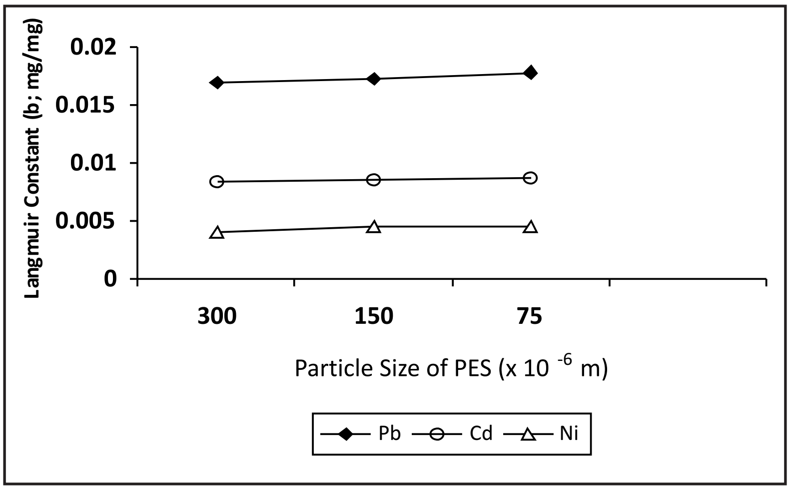


Figure 9: Effect of Particle of PES on Adsorption Capacity of PES

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 estimate values with the observed values. These statistical expressions are total error, coefficient of determination (CD) and model of selection criterion (MSC). Total error (Err^2) can be computed using equation (33) as follows [Oke, 2007; Babatola *et al.,* 2008]:

$$Err^2 = \sum_{i=1}^{n}\left(Y_{obsi} - Y_{cali}\right)^2 \qquad (33)$$

Where; Y_{obsi} is observed concentration and Y_{cali} is calculated concentration

Table 4 shows the values of total error 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. CD can be expressed as follows:

$$CD = \frac{\sum_{i=1}^{n}\left(Y_{obsi} - \bar{Y}_{cali}\right)^2 - \sum_{i=1}^{n}\left(Y_{obsi} - Y_{cali}\right)^2}{\sum_{i=1}^{n}\left(Y_{obsi} - \bar{Y}_{cali}\right)^2} \qquad (34)$$

where, $\bar{Y}_{obsi}$ is the average of observed flow and $\bar{Y}_{cali}$ is the average of calculated flow.

The CD values ranged from 0.589 to 0.998 (Table 4). The least CD value (0.589) came from Temkin model and the highest value (0.998) came from activated sludge model. MSC can be computed using equation (35) as follows:

$$MSC = \ln \frac{\sum_{i=1}^{n}\left(Y_{obsi} - \bar{Y}_{obsi}\right)^2}{\sum_{i=1}^{n}\left(Y_{obsi} - Y_{cali}\right)^2} - \frac{2p}{n} \qquad (35)$$

where; p is number of parameters and n is number of samples

Values of MSC were in the range of 4.906 to 6.687 (Table 4). The lowest value of MSC (4.906) was from Temkin model and the highest value (6.687) was from activated sludge model. The table revealed that Temkin model, Redlich-Peterson model and Langmuir model described the adsorption of lead, cadmium and nickel unto PES in monocomponent aqueous solution than other models because highest CD and MSC and lowest total error values were recorded for them.

Estimated Cost of Producing the PES

Cost of producing the PES were based on 95% yield from every used egg shell collected, assuming availability of eggshell in 320 days per year, 300 kilograms of powdered egg shell would be produced per day by 3 men per a shift of 8 hours. Table 5 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 US$ /kg of powdered egg shell (PES) at two different electricity sources. The estimated cost is cheaper compared to the cost of producing empty fruit bunches (0.50 US$ /kg, Alam *et al.,* 2008), pencon shell based activated carbon (2.72 US$/kg) and sugar cane based granular activated carbon by steam (3.12 US$/kg).

Table 4: Results of Statistical Evaluation of these Equilibrium Models

Description	Metal		Langmiur model			Freundlich model			Activated Sludge			Temkin Model			Redlich-Peterson Model		
			MSC	Error	CD	MSC	Error	CD	MSC	Error	CD	MSC	Error	CD	MSC	Error	CD
Mono component (individual)	Pb^{2+}		6.618	26.486	0.982	6.544	26.832	0.965	6.600	26.567	0.978	6.648	26.344	0.989	6.439	27.319	0.941
	Cd^{2+}		6.522	26.933	0.960	6.413	27.441	0.935	6.469	27.177	0.948	6.548	26.811	0.966	6.591	26.608	0.976
	Ni^{2+}		6.535	26.872	0.963	6.278	28.072	0.904	6.334	27.807	0.917	6.051	29.129	0.852	6.217	28.356	0.890
Multi component	Pb^{2+}		6.570	26.710	0.971	6.605	26.547	0.979	6.652	26.323	0.990	5.820	30.206	0.799	6.491	27.076	0.953
	Cd^{2+}		6.613	26.506	0.981	5.577	31.345	0.743	6.522	26.933	0.960	5.433	32.016	0.710	6.557	26.771	0.968
	Ni^{2+}		6.657	26.303	0.991	6.221	28.336	0.891	6.391	27.543	0.930	6.565	26.730	0.970	6.273	28.092	0.903
Raw water	Pb^{2+}		6.613	26.506	0.981	6.326	27.848	0.915	6.639	26.384	0.987	5.698	30.776	0.771	6.539	26.852	0.964
	Cd^{2+}		6.657	26.303	0.991	6.361	27.685	0.923	6.583	26.649	0.974	5.899	29.840	0.817	6.648	26.344	0.989
	Ni^{2+}		6.613	26.506	0.981	6.008	29.332	0.842	6.474	27.157	0.949	4.906	34.476	0.589	6.526	26.913	0.961
Effect pH on mono component	Pb^{2+}	3.0	6.618	26.486	0.982	6.544	26.832	0.965	6.600	26.567	0.978	6.648	26.344	0.989	6.439	27.319	0.941
		7.6	6.578	26.669	0.973	6.504	27.015	0.956	6.561	26.750	0.969	6.609	26.527	0.980	6.404	27.482	0.933
		11.7	6.539	26.852	0.964	6.469	27.177	0.948	6.526	26.913	0.961	6.570	26.710	0.971	6.365	27.665	0.924
	Cd^{2+}	3.0	6.522	26.933	0.960	6.413	27.441	0.935	6.469	27.177	0.948	6.548	26.811	0.966	6.591	26.608	0.976
		7.6	6.483	27.116	0.951	6.378	27.604	0.927	6.435	27.340	0.940	6.465	27.197	0.947	6.552	26.791	0.967
		11.7	6.448	27.279	0.943	6.339	27.787	0.918	6.395	27.523	0.931	6.557	26.771	0.968	6.517	26.954	0.959
	Ni^{2+}	3.0	6.535	26.872	0.963	6.278	28.072	0.904	6.334	27.807	0.917	6.483	27.116	0.951	6.217	28.356	0.890
		7.6	6.496	27.055	0.954	6.321	27.868	0.914	6.670	26.242	0.994	6.443	27.299	0.942	6.600	26.567	0.978
		11.7	6.461	27.218	0.946	6.326	27.848	0.915	6.687	26.161	0.998	6.409	27.462	0.934	6.561	26.750	0.969
Particle size on mono component (μm)	Pb^{2+}	300	6.618	26.486	0.982	6.544	26.832	0.965	6.600	26.567	0.978	6.648	26.344	0.989	6.439	27.319	0.941
		150	6.570	26.710	0.971	6.496	27.055	0.954	6.552	26.791	0.967	6.600	26.567	0.978	6.395	27.523	0.931
		75	6.539	26.852	0.964	6.469	27.177	0.948	6.526	26.913	0.961	6.570	26.710	0.971	6.365	27.665	0.924
	Cd^{2+}	300	6.522	26.933	0.960	6.413	27.441	0.935	6.469	27.177	0.948	6.548	26.811	0.966	6.591	26.608	0.976
		150	6.483	27.116	0.951	6.378	27.604	0.927	6.435	27.340	0.940	6.509	26.994	0.957	6.552	26.791	0.967
		75	6.487	27.096	0.952	6.378	27.604	0.927	6.435	27.340	0.940	6.513	26.974	0.958	6.557	26.771	0.968
	Ni^{2+}	300	6.535	26.872	0.963	6.278	28.072	0.904	6.334	27.807	0.917	6.483	27.116	0.951	6.217	28.356	0.890
		150	6.496	27.055	0.954	6.282	28.051	0.905	6.674	26.222	0.995	6.443	27.299	0.942	6.605	26.547	0.979
		75	6.500	27.035	0.955	6.278	28.072	0.904	6.670	26.242	0.994	6.448	27.279	0.943	6.605	26.547	0.979
Initial concentration on mono component (mg/l)	Pb^{2+}	20.45	6.618	26.486	0.982	6.544	26.832	0.965	6.600	26.567	0.978	6.648	26.344	0.989	6.439	27.319	0.941
		15.02	6.561	26.750	0.969	6.491	27.076	0.953	6.548	26.811	0.966	6.591	26.608	0.976	6.387	27.563	0.929
		0.13	6.539	26.852	0.964	6.469	27.177	0.948	6.526	26.913	0.961	6.570	26.710	0.971	6.365	27.665	0.924
	Cd^{2+}	20.45	6.522	26.933	0.960	6.413	27.441	0.935	6.469	27.177	0.948	6.548	26.811	0.966	6.591	26.608	0.976
		15.02	6.483	27.116	0.951	6.378	27.604	0.927	6.435	27.340	0.940	6.509	26.994	0.957	6.552	26.791	0.967
		0.13	6.530	26.893	0.962	6.422	27.401	0.937	6.478	27.137	0.950	6.513	26.974	0.958	6.600	26.567	0.978
	Ni^{2+}	20.45	6.535	26.872	0.963	6.278	28.072	0.904	6.334	27.807	0.917	6.483	27.116	0.951	6.217	28.356	0.890
		15.02	6.496	27.055	0.954	6.282	28.051	0.905	6.674	26.222	0.995	6.443	27.299	0.942	6.605	26.547	0.979
		0.13	6.544	26.832	0.965	6.282	28.051	0.905	6.674	26.222	0.995	6.491	27.076	0.953	6.609	26.527	0.980

Table 5: Estimated Cost Analysis of the PES

Items	Public Electricity		Non- Public Electricity		Items	Public Electricity		Non-Public Electricity	
	Naira(₦) per day	US$ (USD) per day	Naira(₦) per day	US$ (USD) per day		Naira(₦) per day	US$ (USD) per day	Naira(₦) per day	US$ (USD) per day
Plant and Machinery	80000	484.85	280000	1696.97	Raw materials	0.00	0.00	0.00	0.00
Building	310000	1878.79	460000	2787.88	Utilities (water, fuel and electricity)	10500.00	63.64	17500.00	106.06
Contingencies	80000	484.85	80000	484.85	Labour	7500.00	45.45	7500.00	45.45
Total(for 20 years)	470000	2848.48	820000	4969.70	Supplies	2500.00	15.15	2500.00	15.15
Average per year of 20[∇]	23500	142.42	41000	248.48	Depreciation	750.00	4.55	750.00	4.55
average per day	73.4375	0.45	128.125	0.78	sub total	21250.00	128.79	28250.00	171.21
					Cost per day	21323.44	129.23	28378.13	171.99
Cost per day (300 kg of day)	21396.88	129.68	28506.25	172.77					
Cost per kilogram	71.32292	0.43	95.02083	0.58					

[∇] capital costs divided by an economic life of 20 years

CONCLUSION

This study investigated adsorption capacities 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 can be used to remove Pb^{2+}, $Ni^{2+}$and Cd^{2+} from aqueous solution, the PES is an inexpensive adsorbent from household waste product – the powdered eggshell (0.43 or 0.58 USD /kg), and there is the need to optimise the adsorbent dose and determine factors and interactions that can influence efficacy of the adsorbent.

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