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Adsorption Isotherms of Pb (II), Ni (II) and Cd (II) Ions onto PES

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Abstract: This study reports on removal of selected metal ions (lead, nickel and cadmium) from aqueous solution by adsorption. Powdered egg shell of particle size 63 μm was used as an adsorbent to remove each metal ion from individual, multi-component systems and from natural water in a batch process. The study revealed that adsorption capacities for lead ions on Powdered Eggshell (PES) were in the 76.2-99.4% range and for nickel and cadmium ions in the 15.0-68.4 and 24-40% ranges, respectively for mono-components synthetic waste waters and dropped to 62.7-90, 11.1-62.3 and 10.7-36.8% for Pb^{2+}, Ni^{2+} and Cd^{2+}, respectively when used for multi-component systems (natural water and synthetic wastewater). Adsorption capacity analysis shows that adsorption of Pb^{2+} fitted well into Langmuir isotherm for mono-synthetic wastewater, Freundlich isotherm for multi-component synthetic wastewater; Langmuir and Redlich-Peterson isotherms for natural water. Cd^{2+} and Ni^{2+} ions removal fitted well into Freundlich isotherm, Langmuir isotherm and Langmuir and Redlich-Peterson isotherms for mono component synthetic wastewater, multi component synthetic wastewater and natural water, respectively. The study also revealed that adsorption capacity of the metal ions is a function of adsorption dose and PES is a valuable adsorbent that needs to be used.

Key words: Adsorption isotherms, PES, heavy metal ions removal, synthetic wastewaters, natural water, isotherms' parameters

INTRODUCTION

Waste water treatment processes could be classified into the following groups physical, chemical, biological, electrical, membrane and irradiation (Noyes, 1994) and the methods applied for the removal of heavy metals from wastewater include chemical precipitation (Noyes, 1994; Martins and Martins, 1993; Mahvi *et al*., 2005; Oke and Okuofu, 2001), solvent extraction, ultrafiltration, biochemical treatment, ion exchange and adsorption (Metcalf and Eddy, 1991). Out of these methods, 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 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 thereby form an attachment through a physical or chemical bond, thus removing the component from the aqueous phase (Metcalf and Eddy, 1991). 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 (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 (Schmubil *et al*., 2001), hazelnut shell carbon (Kobya, 2004) and carbon slurry (Singh and Tiwari, 1997) have been reported in the literature. It can then be summarised that common adsorbent materials are activated carbon, synthetic resins, activated alumina and natural adsorbents. The objective of the study was to test effectiveness of a solid waste (powdered egg shell) towards adsorption of Pb^{2+}, Ni^{2+} and Cd^{2+} ions from synthetic wastewaters (either in individual or multi-component systems) and from natural water. Cadmium is among the elements in-group IIB of periodic table. It is normally exist in the form of Cd^{+2} in solution. Cadmium in waters originated from batteries, plastics, graphics

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composites and manures, fertilizer and fossil fuel combustion industries. Cadmium causes kidney disease and joint pain in man. It can be accumulated by aquatic animals thus affect ecological system of the environment. It is a common environmental pollutant, which is widely distributed in the aquatic environment. Lead also is among heavy metals in-group IVB and in period VI of periodic table. Lead occurs in nature as galena and as lead sulphide. It is distributed widely in the earth's crust. It is used in manufacturing of water and gas pipes, lead sheet for roofing and as alloys for engineering uses. Lead is also used in manufacturing of electrical accumulators and paints. Literature reports that lead in waters originated from wastes from storage and battery manufacture environment. Lead is cumulative poison, it damages brain of young children and may cause death, it causes severe malfunctioning of the alimentary tracts, general weakness and malaise, impairs functioning of the nervous system and sometimes paralysis of the exteriors muscles of the forearm.

Nickel is an essential element for plant growth. It belongs to group VIIIA and in period VI of periodic table. It is among the major elements used in engineering construction. Waters with nickel originated from metal processing, steel foundries and motor vehicle, aircraft, printing and chemical industries. Removal of lead, nickel and cadmium ions from wastewater can be through the action of chemical treatment processes such as chemical precipitation, ion exchange and by membrane treatment processes such as electrodialysis and reverse osmosis.

MATERIALS AND METHODS

Egg shells, collected within the Obafemi Awolowo University, Ile-Ife, Nigeria campus were washed with distilled water, air-dried, ground into powder and classified using British Standard (BS) sieve. Powdered eggshell with sieve sizes of 63 μm (PES), 75 μm (PES_2) and 150 μm (PES_3) were separated and stored in desiccators. Selected properties of the powdered eggshell were determined.

Adsorption capacities of Powdered Egg Shells (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 $Cd(NO_3)_2$-4 H_2O in 100 mL of distilled water and was made up to 1000 mL mark with distilled water) ions 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 rpm for 3 min and allowed to stand for 18 h (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+} ions concentration in the filtrate was determined. The procedures were repeated for natural water collected and for multi-component synthetic wastewater prepared. The amount of solute removed at equilibrium (adsorbed) was computed using Eq. 1.

$$q_e = \frac{(C_0 - C_e)}{M} V \tag{1}$$

The laboratory analysis of heavy metal concentrations in both synthetic wastewaters and natural water used 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. Isotherm models' parameters were determined for selected heavy metals and effect of adsorbent dose on these parameters were studied further. The adsorption capacities of the adsorbent were analyzed through the use of graphical methods for Langmuir, Freundlich and Temkin, Redlich-Peterson isotherms.

RESULTS AND DISCUSSION

Result of the digestion indicates that one gram of PES contained 22.4 mg Fe, 12.45 mg aluminium as Al^{3+} and 401 mg Ca as Ca^{2+} (Table 1) and 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 present of water calcium salts undergo displacement reaction as indicated in Eq. 1a. This shows that the PES underwent the reaction in Eq. 1b with selected heavy metal ions, which can reduce the pH and the end product reacted with metallic ions to precipitate the pollutant.

$$CaCO_3 + 2H_2O \rightarrow H_2O + CO_2 + Ca(OH)_2 \tag{1a}$$

$$H_2O + CO_2 + Ca(OH)_2 + X^{+2} \rightarrow H_2O + CO_2 + Ca^{+2} + X(OH)_2 \tag{1b}$$

Table 1: Some properties and components of powdered egg shell

Parameters	Mean	Standard deviation
Ash content (%)	97.58	1.84
Moisture content (%)	1.06	0.36
Calcium as Ca^{2+} ($g\ g^{-1}$)	0.401	0.0032
Aluminium as Al^{3+} ($g\ g^{-1}$)	0.01245	0.0001
Iron as Fe^{2+} ($g\ g^{-1}$)	0.0224	0.0020

Table 2: Adsorption parameters for mono component systems (synthetic waste waters)

	Langmuir model			Freundlich model			Temkin model			Redlich-Peterson model			
Pollutants	a (L mg^{-1})	b (mg mg^{-1})	R^2	K_f (mg mg^{-1})	N_f (L mg^{-1})	R^2	a_t (mg mg^{-1})	b_t (L mg^{-1})	R^2	α (mg mg^{-1})	β (L mg^{-1})	γ (L mg^{-1})	R^2
Pb^{2+}	0.982	0.017	0.972	0.009	1.29	0.968	0.0132	0.007	0.760	0.017	2.00	0.225	0.717
Ni^{2+}	0.281	0.007	0.934	0.001	1.56	0.993	0.0001	0.004	0.849	0.007	4.74	0.361	0.976
Cd^{2+}	0.241	0.004	0.845	0.001	1.68	0.950	0.0014	0.003	0.804	0.004	5.06	0.396	0.890

By expressing the mass of PES in terms of Fe^{2+}, Ca^{2+} and Al^{3+} contents 0.010 mole of Ca^{2+}, 4.0×10^{-4} mole of Fe^{2+} and 4.611×10^{-4} mole of Al^{3+} could be found in one gram of PES.

The nature of the 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 isotherms models, which include: Langmuir, Freundlich, BET, Temkin, Redlich-Peterson, Nerst and activated sludge isotherms. Due to inconvenience of evaluating three isotherm parameters, the two-isotherm-parameter equations (Langmuir, Freundlich, Temkin equation) are more widely used than the three-isotherm-parameter equation (Redlich-Peterson equation). Langmuir isotherm is 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 (Tebbutt, 1991):

$$q_e = \frac{abC_e}{1 + aC_e} \qquad (2)$$

Rearranging Eq. 2 to give Eq. 3 makes the equation to be linearised, from which the values of a and b can be determined from slope and intercept. Figure 1-3 show Langmuir model of Pb^{2+}, Ni^{2+} and Cd^{2+} ions adsorption onto PES.

$$\frac{1}{q_e} = \frac{1}{b} + \frac{1}{ab}\frac{1}{C_e} \qquad (3)$$

Estimated adsorption parameters by the Langmuir model are shown in Table 2. The Langmuir constants a and b (0.982 and 0.017; 0.281 and 0.007; 0.241 and 0.004 for

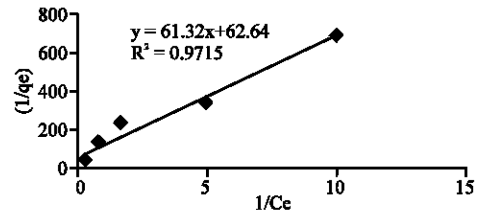

Fig. 1: Langmuir model of Pb^{2+} ion adsorption onto PES

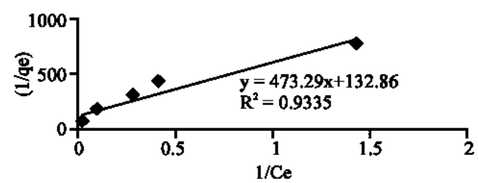

Fig. 2: Langmuir model of Ni^{2+} ion adsorption onto PES

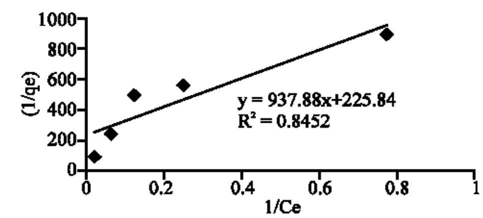

Fig. 3: Langmuir model of Cd^{2+} ion adsorption onto PES

Pb^{2+}, Ni^{2+} and Cd^{2+}, respectively) and the square of regression coefficient (R^2 = 0.9715, 0.9335 and 0.8452) suggesting that the adsorption of Pb^{2+} can be modelled well by Langmuir equation while adsorption of Ni^{2+} and Cd^{2+} could not be modelled well by the Langmuir isotherm. The values of b (1 mg of the adsorbent will require 0.0017, 0.007 and 0.004 mg of adsorbate) indicate that PES as an adsorbent may not be effective when initial concentrations of Pb^{2+} Ni^{2+} and Cd^{2+} are higher. These values of a and b are lower than the values obtained literature, but similar to values for HSAC (Kobya, 2004), which indicates that PES is a valuable adsorbent as HSAC (hazenut shell activated carbon). It is well documented that the essential characteristic of the Langmuir isotherm may be expressed in terms of the dimensionless parameter (R_L). R_L 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

Table 3: Adsorption parameters for multi component systems (synthetic waste waters)

	Langmuir model			Freundlich model			Temkin model			Redlich-Peterson model			
Pollutants	a (L mg^{-1})	b (mg mg^{-1})	R^2	K_f (mg mg^{-1})	N_f (L mg^{-1})	R^2	a_t (mg mg^{-1})	b_t (L mg^{-1})	R^2	α (mg mg^{-1})	β (L mg^{-1})	γ (L mg^{-1})	R^2
Pb^{2+}	0.461	0.007	0.91	0.0018	1.63	0.979	0.0009	0.0040	0.80	0.007	3.93	0.386	0.947
Ni^{2+}	0.234	0.0038	0.98	0.0011	3.38	0.743	0.0014	0.0007	0.71	0.0038	3.38	0.702	0.941
Cd^{2+}	0.122	0.0037	0.99	0.0007	2.73	0.891	0.0004	0.0007	0.97	0.0037	5.14	0.635	0.959

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

$$R_1 = \frac{1}{1+bC_o} \quad (4)$$

For individual and multi component synthetic wastewaters and natural water the R_L were found to be $0<R_l<1$ indicating that adsorption of Pb^{2+}, Ni^{2+} and Cd^{2+} ions on PES is favourable (Saswati and Gosh, 2005). 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+} ions onto PES agrees with adsorption studied by Mamdouth *et al.* (2004).

For multi-component synthetic wastewater the estimated adsorption parameters by the Langmuir model are shown in Table 3. The Langmuir constants a and b (0.461 and 0.007; 0.234 and 0.0038; 0.122 and 0.0037 Pb^{2+} Ni^{2+} and Cd^{2+}, respectively) and the square of regression coefficient (R^2 = 0.91; 0.98 and 0.99) suggested that the adsorption of Pb^{2+} Ni^{2+} and Cd^{2+} could be modelled by the Langmuir isotherm. Also the values of R^2 show that Langmuir equation can be used to describe removal of Ni^{2+} and Cd^{2+} ions by PES very well and averagely for Pb^{2+} ion adsorption ($0.75<R^2<0.95$, Loveday, 1980). The values of b (less than 1) indicates that PES as an adsorbent may not be effective when initial concentrations of Pb^{2+} Ni^{2+} and Cd^{2+} are higher. These values of a and b are lower than the values obtained for mono-component synthetic wastewater, which indicates that there are competitive adsorption between the ions (Igwe *et al.*, 2005).

For natural water estimated adsorption parameters by the Langmuir model are shown in Table 4. The Langmuir constants a and b (0.749 and 0.0197; 2.64 and 0.0008; 0.721 and 0.0016 Pb^{2+} Ni^{2+} and Cd^{2+}, respectively) and regression coefficient (R^2 = 0.91; 0.98 and 0.99) suggests that removal of Pb^{2+} Ni^{2+} and Cd^{2+} by PES from natural water could be modelled by the Langmuir isotherm (i.e., $R^2>0.95$,) (Loveday, 1980). The values of b for Pb^{2+} Ni^{2+} and Cd^{2+} indicate that PES as an adsorbent may not remove these ions effectively when initial concentrations of Pb^{2+} Ni^{2+} and Cd^{2+} are higher. These values of a and b are lower than the values.

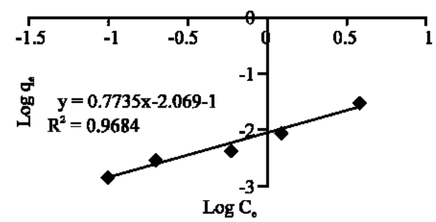

Fig. 4: Freundlich model of Pb^{2+} ion adsorption onto PES

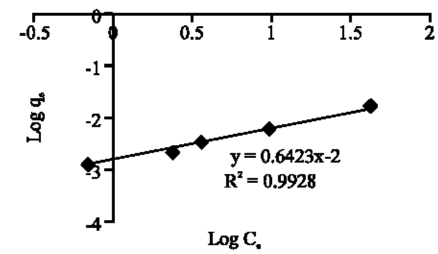

Fig. 5: Freundlich model of Ni^{2+} ion adsorption onto PES

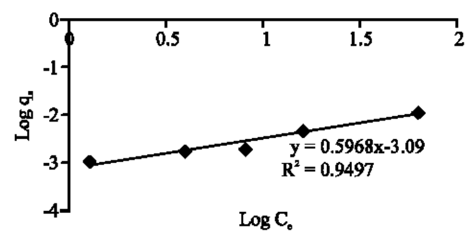

Fig. 6: Freundlich model of Cd^{2+} ion adsorption onto PES

It has been reported that Freundlich isotherm is an empirical relationship, which often gives a more satisfactory model of experimental data (Tebbutt, 1991). It can be expressed as shown in Eq. 5. Figure 4-6 show Freundlich model of the adsorptions.

$$q_e = K_f C_e^{1/N_f} \quad (5)$$

The values of K_f and N_f were obtained by plotting logarithms of adsorption capacity against logarithms of equilibrium concentration. Estimated adsorption parameters by the Freundlich model are shown in Table 2. High levels of K_f and high levels N_f values (greater than 1) from the Freundlich isotherm (Table 2) suggests that the adsorption capacity of PES was high and that any large

Table 4: Adsorption parameters for natural water

	Langmuir model			Freundlich model			Temkin model			Redlich-Peterson model			
Pollutants	a (L mg^{-1})	b (mg mg^{-1})	R^2	K_f (mg mg^{-1})	N_f (L mg^{-1})	R^2	a_t (mg mg^{-1})	b_t (L mg^{-1})	R^2	α (mg mg^{-1})	β (L mg^{-1})	γ (L mg^{-1})	R^2
Pb^{2+}	0.749	0.0197	0.98	0.0001	1.25	0.915	0.008	0.004	0.77	0.0197	3.36	0.293	0.982
Ni^{2+}	2.64	0.0006	0.96	0.00287	0.028	0.923	0.005	0.005	0.87	0.0008	3.35	0.953	0.968
Cd^{2+}	0.721	0.0116	0.98	0.0084	0.998	0.842	0.003	0.003	0. 59	0.0116	3.62	0.261	0.961

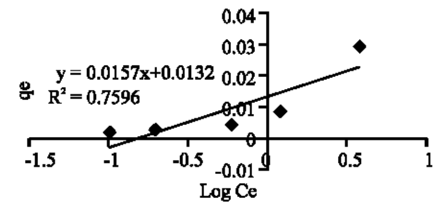

Fig. 7: Temkin model of Pb^{2+} ion adsorption onto PES

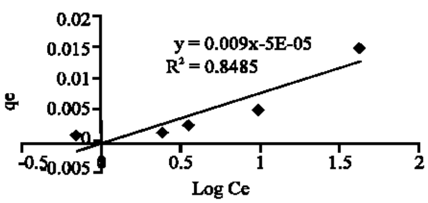

Fig. 8: Temkin model of Ni^{2+} ion adsorption onto PES

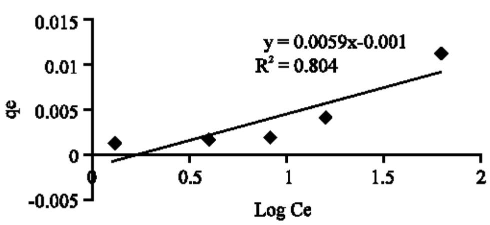

Fig. 9: Temkin model of Cd^{2+} ion adsorption onto PES

change in the equilibrium concentration of Pb^{2+}, Ni^{2+} and Cd^{2+} ions would not result in a marked change in the amount of Pb^{2+}, Ni^{2+} and Cd^{2+} ions adsorbed by PES. Also high values of N_f show that the forces which are exerted on the surface of PES during Pb^{2+}, Ni^{2+} and Cd^{2+} are weak forces, which are inorder of $Pb^{2+}>Ni^{2+}>Cd^{2+}$. The square of correlation coefficients (R^2) for Freundlich isotherm are 0.968, 0.993 and 0.950 representing a good fit ($R^2 \geq 0.95$) of the observed data. The values of R^2 also indicate that Freundlich isotherm describes adsorption of Pb^{2+}, Ni^{2+} and Cd^{2+} ion and the adsorption capacities are inorder of $Cd^{2+}<Pb^{2+}<Ni^{2+}$. This high correlation coefficient confirms Tebbutt (1991) statement on Freundlich isotherm. The values of K_f and N_f are different from the values documented in Mamdouth *et al*. (2004) and in Kobya (2004), which indicate that adsorption onto carbon is different from adsorption onto PES.

For multi-component synthetic wastewater estimated adsorption parameters by the Freundlich model are shown in Table 2. The values of K_f and N_f from the Freundlich isotherm (Table 3) suggest that the affinity of PES for Pb^{2+}, Ni^{2+} and Cd^{2+} ions was high and that any large change in the equilibrium concentration of Pb^{2+}, Ni^{2+} and Cd^{2+} ions would not result in a marked change in the amount of Pb^{2+} Ni^{2+} and Cd^{2+} ions adsorbed by PES. The squares of correlation coefficient (R^2) for Freundlich isotherm are 0.979, 0.743 and 0.891 representing a good and low fit of the observed data for Pb^{2+} Ni^{2+} and Cd^{2+} ion respectively. The correlation coefficients indicate that Freundlich isotherm describe Pb^{2+} ion adsorption well ($R^2>0.95$), fairly describe Cd^{2+} ion adsorption ($0.75<R^2<0.95$) and averagely describe adsorption of Cd^{2+} ions ($0.5<R^2<0.75$) onto PES. This low correlation coefficient for Ni^{2+} and Cd^{2+} does not confirms Tebbutt (1991) and Sawasti and Ghosh (2005) statement on Freundlich isotherm (the three-isotherm-parameters equations mostly provide a better fit of the isotherm data than a two-isotherm-parameters) (Loveday, 1980) and also show that analysis of multi component systems requires another model equation. The values of K_f and N_f are different from the values obtained for mono-component synthetic wastewater, which indicate that there are competitive adsorptions between the ions (Igwe *et al*., 2005).

Similarly, for natural water estimated adsorption parameters by the Freundlich model are shown in Table 4. The high level of K_f and a low $1/N_f$ values (less than 1) from the Freundlich isotherm (Table 4) suggests that the affinity of PES for Pb^{2+} Ni^{2+} and Cd^{2+} ions was high and that any large change in the equilibrium concentration of Pb^{2+} Ni^{2+} and Cd^{2+} ions would not result in a marked change in the amount of Pb^{2+} Ni^{2+} and Cd^{2+} ions adsorbed by PES. The squares of correlation coefficient (R^2) for Freundlich isotherm are 0.915, 0.923 and 0.842 representing average fits of the observed data for Pb^{2+} Ni^{2+} and Cd^{2+} ions, respectively. The correlation coefficients indicate that Freundlich isotherm describe Pb^{2+}, Cd^{2+} and Ni^{2+} ions adsorption onto PES averagely. It decreases inorder of $Ni^{2+}>Pb^{2+}>Cd^{2+}$. This low correlation coefficient for these ions does not confirms Tebbutt (1991) statement on the isotherm, but confirm Sawasti and Ghosh (2005) statement on Freundlich isotherm (the three-isotherm-parameters equations mostly provide a better fit of the isotherm data than a two-isotherm-parameters)

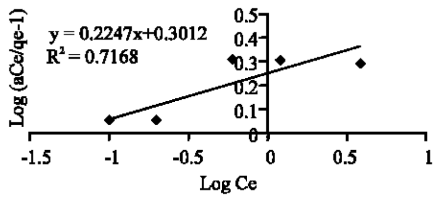

Fig. 10: R-Peterson model of Pb ion adsorption on onto PES

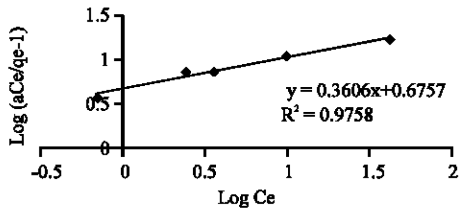

Fig. 11: R-Peterson model of Ni ion adsorption on onto PES

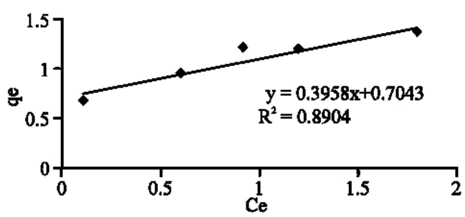

Fig. 12: Redlich Peterson model of Cd ion adsorption on onto PES

(Loveday, 1980) It also shows that analysis of multi component systems requires another model equation.

The Temkin isotherm is an empirical relationship, which often gives a more satisfactory model of experimental data (Saswati and Gosh, 2005). It can be expressed as shown in Eq. 6. Figure 7-9 show Temkin model of the adsorptions.

$$q_e = a_t + 2.3b_t \log C_e \qquad (6)$$

The values of a_t and b_t were obtained by plotting of adsorption capacity against equilibrium concentration. Estimated adsorption parameters by the Temkin model are shown in Table 1. The values of a_t and b_t from the Temkin isotherm (Table 2) suggests 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+} ions would result in a marked change in the amount of Pb^{2+}, Ni^{2+} and Cd^{2+} ions adsorbed by PES. The correlation coefficients (R^2) for Temkin isotherm are 0.760, 0.849 and 0.804 representing an average fit ($0.5<R^2<0.75$ and $0.75<R^2<0.95$) of the observed data. This medium correlation coefficients indicate that Temkin equation can not be used to model adsorption of Pb^{2+}, Ni^{2+} and Cd^{2+} ions onto PES correctly. The values of R^2, a_t and b_t were different from the values documented in Saswati and Ghosh (2005) which indicate that adsorption of Pb^{2+}, Ni^{2+} and Cd^{2+} ions PES cannot be model by Temkin equation unlike adsorption onto synthetic hydrous stannic oxide.

For multi-component synthetic wastewater estimated adsorption parameters by the Temkin model are shown in Table 3. The values of a_t and b_t from the Temkin isotherm (Table 3) suggest 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+} ions would result in a marked change in the amount of Pb^{2+}, $Ni^{2+}$and Cd^{2+} ions adsorbed by PES. The squares of correlation coefficient (R^2) for Temkin isotherm are 0.799, 0.71 and 0.97, representing an average fit of the observed data for Pb^{2+}, $Ni^{2+}$and Cd^{2+} ions, indicating that mono component isotherm equation cannot fit multi component system for Ni^{2+} and Cd^{2+} ions.

For natural water estimated adsorption parameters by the Temkin model are shown in Table 4. The values of a_t and b_t (less than 1) from the Temkin isotherm (Table 4) suggest 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+} ions would result in a marked change in the amount of Pb^{2+}, Ni^{2+} and Cd^{2+} ions adsorbed by PES. The squares of correlation coefficient (R^2) for Temkin isotherm are 0.771, 0.817 and 0.589, representing an average and a poor fit of the observed data for Pb^{2+}, $Ni^{2+}$and Cd^{2+} ions The correlation coefficients indicate that Temkin isotherm describe Pb^{2+} ion adsorption well, fairly describe Cd^{2+} ion adsorption and averagely describe adsorption of Cd^{2+} ions onto 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. This model has a linear dependence on concentration in the numerator and an exponential function in the denominator. It may be represented by the Eq. 7a. The Redlich-Peterson isotherm is an empirical relationship, which often gives a more satisfactory model of experimental data (Saswati and Gosh, 2005). Figure 10-12 show Redlich-Peterson model of the adsorptions.

$$q_e = \frac{\alpha_t C_e}{1+\beta_t C_e^{\gamma}} \qquad (7a)$$

For β_t = 1, the equation converts to the Langmuir isotherm; for $1 >> \beta_t C^{\gamma}_e$ it simplifies to Henry's law and for $1 << \beta_t C^{\gamma}_e$ it is identical with the Freundlich isotherm. The linear form is given in Eq. 7 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:

$$\frac{C_e}{q_e} = \frac{1}{\alpha_t} + \frac{\beta_t}{\alpha_t} C_e^{\gamma} \tag{7}$$

Equation 7 can be transformed to Eq. 8, which can be expressed as follows (Eq. 9):

$$\frac{\alpha_t C_e}{q_e} - 1 = \beta_t C_e^{\gamma} \tag{8}$$

$$\log\left(\frac{\alpha_t C_e}{q_e} - 1\right) = \log \beta_t + \gamma \log C_e \tag{9}$$

Plotting of logarithms of left hand side values against logarithms of equilibrium concentrations the unknown parameters will be found. The values of α_t γ and β_t can be obtained. Estimated adsorption parameters by the Redlich-Peterson model are shown in Table 2. The values of α_t γ and β_t (less than 1) from the Redlich-Peterson isotherm (Table 1) suggest 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+} ions would result in a marked change in the amount of Pb^{2+}, $Ni^{2+}$and Cd^{2+} ions adsorbed by PES. The correlation coefficient (R^2) for Redlich-Peterson isotherm are 0.7168, 0.9758 and 0.8904 representing a low fit of the observed data for adsorption $Pb^{2+}$and Cd^{2+} ions and a good fit of observed data for Ni^{2+} ions adsorption onto PES. The values of α_t and β_t are different from the values documented in Mamdouth *et al.* (2004) and in Kobya (2004), which indicate that adsorption onto carbon is different from adsorption onto PES.

For multi-component synthetic wastewater estimated adsorption parameters by the Redlich-Peterson model are shown in Table 3. The values of a_t and a low b_t from the Redlich-Peterson isotherm (Table 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+} ions would result in a marked change in the amount of Pb^{2+}, $Ni^{2+}$and Cd^{2+} ions adsorbed by PES. The correlation coefficients (R^2) for Redlich-Peterson isotherm are 0.947, 0.941 and 0.969 representing a good fit of the observed data. The values of α_t and β_t are different from the values for mono-component synthetic wastewater, which indicates that there are competitive adsorption between the ions.

For natural water estimated adsorption parameters by the Redlich-Peterson model are shown in Table 4. The values of a_t and a low b_t from the Redlich-Peterson isotherm (Table 4) 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+} ions would result in a marked change in the amount of Pb^{2+}, Ni^{2+} and Cd^{2+} ions adsorbed by PES. The square of correlation coefficients (R^2) for Redlich-Peterson isotherm are 0.982, 0.968 and 0.961 representing a good fit of the observed data. This high correlation coefficient confirms Tebbutt (1991) statement on Redlich-Peterson isotherm. The correlation coefficients indicate that Freundlich isotherm describe Pb^{2+} ion adsorption well, fairly describe Cd^{2+} ion adsorption and averagely describe adsorption of Cd^{2+} ions onto PES. This low correlation coefficient for Ni^{2+} and Cd^{2+} confirms Sawasti and Ghosh (2005) statement on Redlich-Peterson isotherm (the three-isotherm-parameters equations mostly provide a better fit of the isotherm data than a two-isotherm-parameters). The values of a_t and b_t are different from the values documented in Mamdouth *et al.* (2004) and in Kobya (2004), which indicate that adsorption onto carbon is different from adsorption onto PES.

EFFECT OF ADSORBENT DOSE

Table 5 shows adsorption parameters at various adsorbent dose. Statistical analysis of each of the

Table 5: Adsorption parameters for mono component systems (synthetic waste waters)

		Langmuir model			Freundlich model			Temkin model			Redlich-Peterson model			
Adsorbent dose (g)	Pollutants	a ($L\ mg^{-1}$)	b ($mg\ mg^{-1}$)	R^2	K_f ($mg\ mg^{-1}$)	N_f ($L\ mg^{-1}$)	R^2	a_t ($mg\ mg^{-1}$)	b_t ($L\ mg^{-1}$)	R^2	α ($mg\ mg^{-1}$)	β ($L\ mg^{-1}$)	γ ($L\ mg^{-1}$)	R^2
0.5	Pb^{2+}	1.61	0.015	0.91	0.008	1.71	0.807	0.013	0.0089	0.50	0.015	2.26	0.605	0.973
	Ni^{2+}	0.389	0.006	0.82	0.0018	2.74	0.978	0.0008	0.0017	0.94	0.006	3.29	0.641	0.989
	Cd^{2+}	0.086	0.006	0.51	0.0003	1.05	0.862	0.0086	0.0059	0.84	0.005	10.52	0.147	0.977
1.0	Pb^{2+}	0.982	0.017	0.97	0.009	1.29	0.968	0.0132	0.007	0.76	0.017	2.00	0.225	0.717
	Ni^{2+}	0.281	0.007	0.93	0.001	1.56	0.993	0.0001	0.004	0.85	0.007	4.74	0.361	0.976
	Cd^{2+}	0.241	0.004	0.85	0.001	1.68	0.950	0.0014	0.003	0.80	0.004	5.06	0.396	0.890
1.5	Pb^{2+}	20.51	0.006	0.92	0.007	2.37	0.888	0.013	0.0089	0.49	0.006	1.23	0.579	0.935
	Ni^{2+}	0.255	0.007	0.96	0.0012	1.53	0.981	0.0006	0.0029	0.88	0.007	5.80	0.348	0.948
	Cd^{2+}	0.267	0.004	0.92	0.0008	1.66	0.980	0.0004	0.0021	0.83	0.004	5.22	0.400	0.958

Table 6: Langmuir constants for the adsorption of Cd(II) onto different adsorbents

Adsorbent	Langmuir constants b ($mg\ g^{-1}$)	a ($dm^3\ mg^{-1}$)	References
Geothite	2.89	0.456	Krishnan and Anirudhan (2003)
Straw-based activated carbon	11.10	-	Krishnan and Anirudhan (2003)
Groundnut husk	42.71	0.027	Krishnan and Anirudhan (2003)
Activated bentonite	16.50	1.86	Krishnan and Anirudhan (2003)
Coconut shell-based activated carbon	124.76	0.02	Krishnan and Anirudhan (2003)
Apricot stone-based activated carbon	134.88	0.044	Krishnan and Anirudhan (2003)
Bituminous coal	6.47	0.015	Krishnan and Anirudhan (2003)
Kimberlite tailings	7.22	0.461	Krishnan and Anirudhan (2003)
Sphagnum peat moss	198.80	0.01	Krishnan and Anirudhan (2003)
Fe (III)/Cr (III) hydroxide waste	40.49	0.231	Krishnan and Anirudhan (2003)
Commercial activated carbon (F-400)	8.21	0.38	Krishnan and Anirudhan (2003)
Commercial activated carbon (E. Merck)	130.21	0.12	Krishnan and Anirudhan (2003)
SA-S(8.9)-C	149.93	0.161	Krishnan and Anirudhan (2003)
PES			
Mono component wastewater	4.00	0.241	Present study
Multi components wastewater	3.70	0.122	Present study
Natural water	11.60	0.721	Present study

isotherms parameters shows that there is a significant difference between the at 95% confidence level. This may be so because at higher doses there are might be more pores left unoccupied by the heavy metal ions and at lower adsorbent doses almost all the pores were fully utilized, which resulted in variation in the values of the same parameters at different adsorbent doses.

Comparison with other adsorbents: In order to justify the validity of PES as an adsorbent for Cd (II) adsorption, its adsorption potential must be compared with other adsorbents used for this purpose. The values of a and b for the adsorption of Cd (II) on different adsorbents reported in the literature compared with the adsorbent of the present study are summarised in Table 6. It may be observed that the uptake of Cd (II) on PES is very much greater than other adsorbent materials reported in the literature. However, it is clear from Table 6 that sphagnum moss peat shows much greater (1.33 times) adsorption potential. The high adsorption capacity for this material is probably related to the sorption mechanism including both ion exchange and complexation. Geothite has the lowest value of b indicating that PES is a better adsorbent than Geothite. 11.6 mg g^{-1} for natural water shows that PES is a better adsorbent than Geothite, Straw-based activated carbon, Bituminous coal, Kimberlite tailings and Commercial activated carbon (F-400)

Nomenclature

- a Langmuir isotherm parameter
- α_t Redlich-Peterson isotherm parameter
- C_e Equilibrium liquid-phase concentration of sorbate
- C_0 initial liquid-phase concentration of sorbate
- b Langmuir isotherm parameter
- K_f Freundlich isotherm parameter
- β_t Redlich-Peterson isotherm parameter
- M Adsorbent mass (mg)
- N_f Freundlich isotherm exponent
- q_e Equilibrium solid-phase concentration of sorbate (mg mg^{-1})
- R_L Langmuir equilibrium parameter
- V Volume of solution (L)
- γ Redlich-Peterson isotherm exponent

CONCLUSION

This study indicated that Pb, Ni and Cd ions could be removed by an inexpensive waste product-the powdered egg shell, there is a need to optimise the adsorbent dose and determine factors and interactions that can influence efficacy of the adsorbent.

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