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Sorption and Desorption Studies on Toxic Metals From Brewery Effluent Using Eggshell as Adsorbent

Ayodele Rotimi Ipeaiyeda[a],*; Godswill Okeoghene Tesi [a]

[a] Department of Chemistry, University of Ibadan, Ibadan, Nigeria.
* Corresponding author.

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Abstract

The adsorption capacity of eggshell in removing Pb^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+} and Co^{2+} from standard solution and consolidated brewery effluent was investigated in this study. The sorption process dependent on pH, contact time, initial metal ion concentration and sorbent dosage with pH 7.0 being the optimum value, and maximum sorption was attained within the first 60 minutes. The equilibrium sorption data followed the Langmuir and Freundlich isotherms with R^2 ranges of 0.834 – 0.993 and 0.939 – 0.998 respectively. The kinetic data were best described with pseudo second order kinetic. Desorption of sorbed metal ions was efficient with 3.0 mol/L NaOH. The affinity of metal ion sorption was in the order of $Co^{2+} > Pb^{2+} > Ni^{2+} > Zn^{2+} > Mn^{2+}$. The percentage adsorptions of Mn^{2+} and Zn^{2+} from the brewery effluent were 95.86% and 44.29% respectively, while the corresponding percentage desorption of Mn^{2+} and Zn^{2+} were 19.94% and 35.48% respectively.

Key words: Eggshell; Brewery effluent; Sorption; Desorption; Toxic metals.

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INTRODUCTION

Excessive discharge of toxic metals to water bodies due to ever increasing industrialization has become a major environmental problem in recent years. Due to inefficient industrial effluent treatment techniques, many rivers and streams are serving as receptacles for industrial effluent containing hazardous materials including heavy metals. Because of their high solubility, heavy metals make enormous detrimental impact on the quality of river water and associated aquatic lives. These heavy metals include cadmium, manganese, copper, lead, nickel, cobalt and chromium, which are highly toxic when ingested into the body through food web (Vieira & Volesky, 2000; Ahalya, Ramachandra, & Kanamadi, 2003). Because of the toxicological effects of these metals, their monitoring and subsequent removals from effluent during treatment become expedient. A number of innovative technologies have been in practice for heavy metals removal from industrial effluent. These technologies include chemical coagulation, electro-chemical precipitation and ion exchange. These conventional methods have several disadvantages. For instance, chemical precipitation leads to the production of toxic sludge (Basha, Selvi, Ramasamy, & Chellammal, 2008). Due to huge capital investment on dealing with large volumes of liquids and occurrence of high solvent losses, solvent extraction is limited to streams containing more than 1g L^{-1} of the targeted heavy metals. Application of the ion-exchange process is economically not feasible due to the cost of synthetic ion-exchange resins. Adsorption method is noted to be more effective in removing toxic heavy metals from effluents, (Tseng & Tseng, 2005; Liu, Zhang, Zhang, Wang, & Li, 2010) but sometimes found to be expensive and time consuming especially when the adsorbent is of mineral and organic origin.

However, several studies suggest that a relatively new technology involving the use of agricultural wastes as adsorbent, can provide a cost-effective means of recovering metals from aqueous solutions including industrial effluent (Nakajima & Sakaguchi, 1993). Earlier investigations have revealed that the eggshell membrane

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is capable of binding various metal ions from aqueous solutions (Ishikawa, Suyama, Arihara, & Itoh, 2002). However, its application as sorbent of chromium only from aqueous solution has been reported (Chojnacka, 2005). In this study, the eggshell was utilized as a biological sorbent of other heavy metals such as Zn(II), Co(II), Mn(II), Pb(II) and Ni(II) from aqueous solutions. The effects of process parameters, such as initial pH, metal ions concentrations, contact time, sorbent concentration, on adsorption process and kinetics were equally studied. In addition, its application for the removal of some of these potentially toxic metals from brewery effluent was also investigated. This application has environmental benefit in terms of the reuse of hen eggshell, which is dispose of usually as waste in Nigeria.

1. EXPERIMENTAL

1.1 Characterisation of the Eggshell

The FT-IR spectrum of the raw eggshell was obtained using the KBr disk technique. The eggshell was ground in a mortal for 5 min after drying it for 2 hours at 60 ^oC. Dilution and homogenization to 0.01 % (w/w) with KBr (spectroscopic grade) were carried out. The disk was pressed in a hydraulic KBr press. The transmission FT-IR spectrum was then recorded between 400 and 4000 cm^{-1} using a Perkin – Elmer Spectrum RX 1 FT-IR system.

1.2 Preparation of Sorbent

Hen eggshells were collected from some kitchens on University of Ibadan campus. The eggshells were washed with tap water several times and afterwards with double distilled water four times. Then they were oven dried at 60 ^oC. The dried eggshells were crushed, milled and sieved using a 100 µm sieve.

1.3 Preparation of Metal Ions Solutions and Reagents

Stock solutions of 1,000 mg L^{-1} each of the standardized Zn^{2+}, Ni^{2+}, CO^{2+}, Pb^{2+} and Mn^{2+} were prepared from $ZnSO_4.7H_2O$, $NiSO_4$, $CO(NO_3)_2.6H_2O$, $Pb(NO_3)_2$ and $MnSO_4$ respectively. Working standard solutions of these metal ions were further prepared by serial dilution of the stock standard solutions with double distilled water. All reagents used in the experiments were of analytical grade. Solutions of 2 mol L^{-1} each of HNO_3 and NaOH were prepared by adequate dilution of concentrated HNO_3 and adequate weighing of NaOH pellets respectively. All the glassware and polyethylene bottles used in experiments were firstly soaked with 10 % nitric acid for at least 24 h and cleaned with double distilled water. The glassware was dried in a clean oven and polyethylene bottles were air dried in the laboratory before use.

1.4 Effect of Initial pH

Metal ions standards of different pH ranging from 4 to 9 were prepared by adjusting the pH of 5 mg L^{-1} metal ions standards using either 2 mol L^{-1} HNO_3 or NaOH solution. A weighed amount (1.0 g) of eggshell was gently agitated with 25 mL each of the metal ions solutions for 1 h at 30^oC on a rotary shaker. It was known from previous studies that biosorption as well as desorption reached equilibrium within 1 h. (Ishikawa, Suyama, Arihara, & Itoh, 2002; Ishikawa & Suyama, 1998) Samples were immediately filter through No. 1 paper filter before Atomic Absorption Spectrophotometry (AAS) measurement using Perkin Elmer (A Analyst 200) was done. Each equilibration was done in triplicate and a maximum deviation of 20 % was usually obtained. Mean values were used for the plotting of curves.

1.5 Effect of Contact Time

The effect of contact time was investigated by agitating 1.0 g portions of eggshell with 25 mL each of the metal ions standards at pH 7 for time intervals of 15, 30, 45, 60, 75, and 90 minutes. The mixtures were filtered at the end of each time interval and the metal ions concentrations were determined using AAS.

1.6 Effect of Initial Metal Ion Concentration and Dosage

Several concentrations of metal ions standards ranging from 5 to 30 mg L^{-1} were prepared. A known weight (1.0 g) of eggshell was shaken with 25 mL of each set of metal ions standards at pH 7 for 1 h on a rotary shaker. The agitation was done at 30 ^oC and the mixtures were filtered.

The effect of dosage was equally investigated by agitating weighed amounts of eggshell ranging from 0.2g to 1.2 g with 25 mL of metal ion standards at pH 7 for 1 h on a rotary shaker. The mixtures were then filtered. The metal ions concentrations in the filtrates were determined by AAS.

1.7 Adsorption Equilibrium and Kinetics of Metal Ions Adsorption

The amount of metal ions in solutions adsorbed (q_e) by eggshell (adsorbent) were calculated from the initial ion concentration, CO (mg L^{-1}) and the equilibrium concentration of metal ion in solution, Ce (mg L^{-1}) using the formula given in equation (1). V is the volume of the solution (L) and W is the dry mass of the eggshell used (g).

$$q_e = V(CO - Ce)/W \tag{1}$$

Two well-known equilibrium adsorption isotherm models were employed to facilitate the estimation of adsorption capacities at various concentrations of metal ions. These models are Langmuir and Freundlich (Gazcó, 2001; Acar & Malkov, 2004), whose linear forms are given by equations 2 and 3 respectively:

$$\frac{Ce}{qe} = \frac{1}{Q_m K_a} + \frac{Ce}{Q_m}, \tag{2}$$

$$\log(q_e) = \log(K_f) + \frac{1}{n}\log(C_e). \tag{3}$$

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In Equation (2), *Ka* is the Langmuir constant which is for the intensity of the adsorption process (L mg^{-1}), and *Qm* is a constant related to the area occupied by a monolayer of adsorbate (eggshell) to reflect the adsorption capacity (mg g^{-1}). In equation (3), K_f is a constant for the system, related to the bonding energy. It can be defined as adsorption or distribution coefficient and represents the quantity of metal ions adsorbed onto eggshell for a unit equilibrium concentration. The slope 1/n, ranging between 0 and 1, is a measure of the adsorption intensity or surface heterogeneity.

The essential characteristic of the Langmuir isotherm was expressed by the dimensionless constant called equilibrium factor or separation factor, which is defined by the following equation:

$$K_R = \frac{1}{1+K_a C_o}, \tag{4}$$

Two kinetic models were applied to examine the controlling mechanism of the sorption process. The models are pseudo first order and pseudo second order whose expressions are given by equations (5) and (6) respectively. K_1 and K_2 are pseudo first order and pseudo second order rate constants respectively. The second order rate constant is used to calculate the initial sorption rate (h) as given in equation (7):

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t, \tag{5}$$

$$\frac{t}{qt} = \frac{1}{kq_e^2} + \frac{t}{q_e}\,t, \tag{6}$$

$$h = k_2 q_e^2 \tag{7}$$

1.8 Desorption Experiment

Desorption studies were performed with varying concentrations (2 mol L^{-1}, 4 mol L^{-1} and 6 mol L^{-1}) of NaOH and HNO_3 solutions. The hen eggshell previously exposed to metal ions standard solution was pulled up from the solution and mixed with 25 mL of each of NaOH and HNO_3 solutions. The agitation was performed on the rotary shaker for 1 hr. The metal ions concentrations were measured with atomic absorption. The desorption efficiency was calculated using the following formula:

$$\text{Desorption efficiency (\%)} = \frac{\textit{released matal concentration}}{\textit{intiallysorbed metal concentration}} \times 100$$

1.9 Application to Real Industrial Effluent

Industrial effluent samples were collected along Omi Asoro river in Ilesa, Nigeria, for sorption experiment. The river receives wastewater from Consolidated Brewery that is situated near the river. Before sorption and desorption experiments, the samples were filtered and stored at 4 ^oC in a refrigerator. 25 mL each of the effluent samples whose pH had been adjusted to 7 was gently agitated with 1.0 g of eggshell on a rotaory shaker for 1 h at 30 ^oC. Before AAS analysis, the mixtures were immediately filtered through No 1 paper filter. The desorption study on the adsorbent was also carried out. All the experiments were carried out in triplicate.

2. RESULTS AND DISCUSSION

2.1 Fourier Transform Infrared Spectroscopy Analysis

The presence of certain functional groups in the eggshell powder is found in the FTIR spectrum. The peak positions at 3331.96 cm^{-1} and 1797.58 cm^{-1} which are due to N-H and *C*=0 stretching respectively are present on the

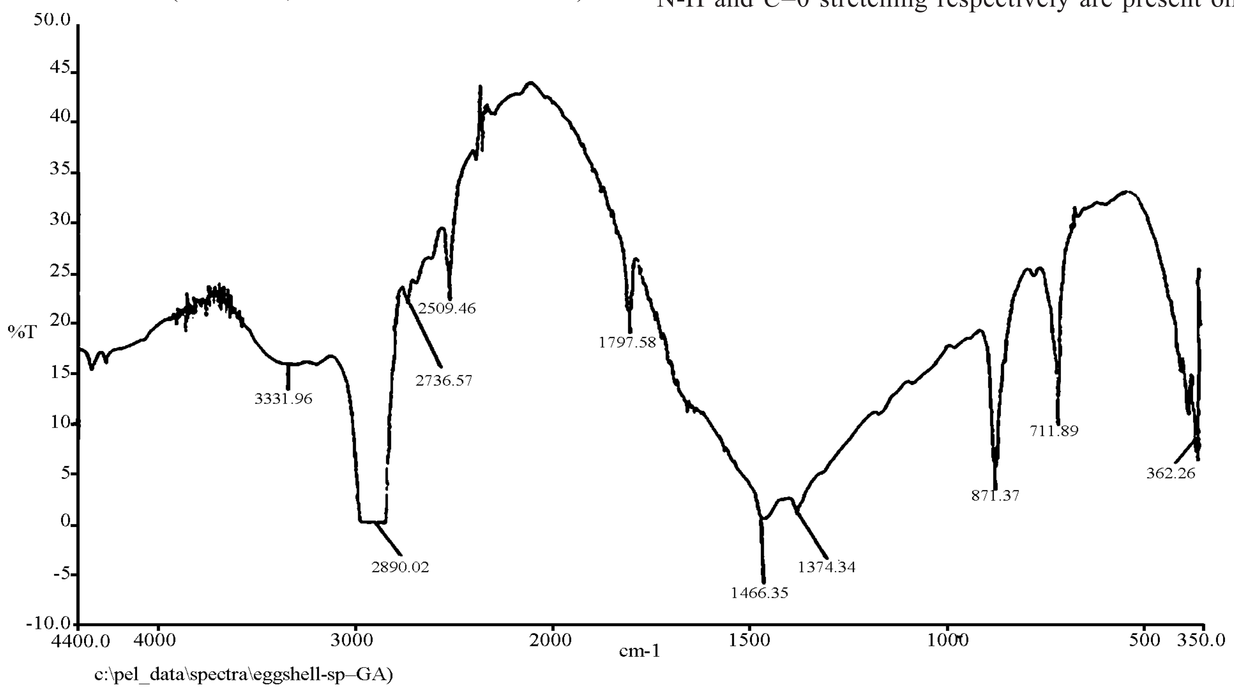

Figure 1
FTIR Spectrum of Adsorbent Eggshell in the Range 350 – 4400 Cm^{-1} (coded as C:\pel_data\spectra\eggshell-sp–GA)

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eggshell. Out-of-plane bending for aromatic hydrogen atom (C-H) gives characteristic absorption band at 871.37 cm^{-1}. The presence of an alkanal C-H stretch is revealed by significant peak at intensity of 2890.02 cm^{-1}. The band of 711.89 cm^{-1} may correspond to *SiO*=H vibration for the eggshell (Figure 1). This is similar to the observation of a characteristic peak in the FTIR analysis reported by He et al. (He, Ma, He, Zhao, & Yu, 2002) during the photooxidation of azo dye in aqueous solution.

2.2 Effect of pH

pH is an important process parameter in sorption of metal ions from aqueous solutions since it is responsible for protonation of metal binding sites, calcium carbonate solubility and metal speciation in the solution (Chojnacka, 2005). The influence of pH on the biosorption capacity of eggshell for the different metals is shown in Figure 2.

The sorption of Pb, Ni, Mn, Zn and Co by eggshells increased with increase in pH from 4 to 7. The rate of sorption at pH 7 was significantly higher than at other pH of standards. Beyond pH 7 there is no much further increase in sorption efficiency.

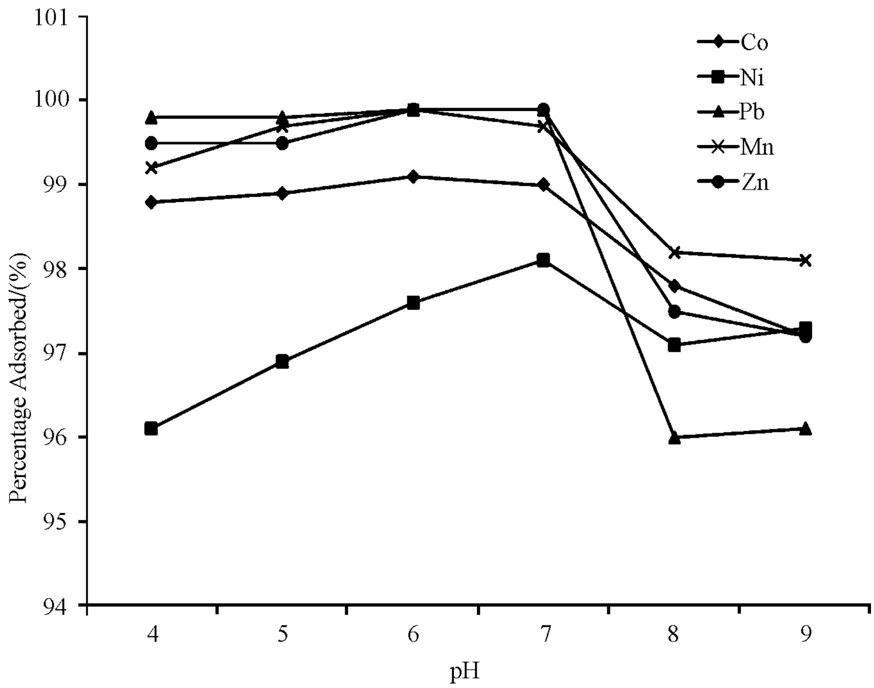

Figure 2
Effect of pH on Metal Ions Sorption by Eggshell Powder for 5 mg L^{-1} of Metals and 1g in 25 mL of Sorbent Concentration at 30 ^{o}C

Similar results were also reported in literatures for different sorbent systems. (AjayKumar, Darwish, & Hilal, 2009; Rashed, 2006; Sajidu, Henry, Persson, Masamba & Kayambazinthu, 2006; Sharma, Kumari, Srivastava, & Srivastava, 2007; Rao, Kalyani, Rao, Kumar, Mariadas, Kumar, Vijetha, Pallavi, Sumalatha, & Kumaraswamy, 2010) This implies that when considering biosorption kinetics and equilibrium, it is advantageous to carry out sorption at pH 5. The effect of pH can be explained by ion-exchange mechanism of sorption in which the important role is played by carbonate groups that have cation-exchange properties. (Chojnacka, 2005) At lower pH, metals (Pb, Ni, Mn, Zn, and CO) sorption was less, possibly as a result of the competition between hydrogen and metal ions on the sorption sites. With an apparent preponderance of hydrogen ions at lower pH, more carbonate groups are bound with hydrogen and less carbonate groups are available to metal ions. Moreover, the surface charge of eggshell is dependent on pH. The positively charged sites are formed on the eggshell surface under acidic media, (Wang, Chen, Huang, & Cao, 2010) which would probably make metal ions badly adsorbed on or repel by the surface of eggshell. (AjayKumar, Darwish, & Hilal, 2009; Chojnacka, 2005; Rao, Kalyani, Rao, Kumar, Mariadas, Kumar, Vijetha, Pallavi, Sumalatha, & Kumaraswamy, 2010) When solution becomes neutral as pH is 7, it seems more carbonate groups in eggshell are made available to metal ions, which are expected to interact more strongly with the negatively charged binding sites. Therefore, the optimum pH 7 was used for other sorption experiments.

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2.3 Effect of Contact Time

The removal efficiency increases from 98.4 % to 98.8 % for Pb, from 97.7 % to 98.3 % for Ni, from 99.4 % to 99.8 % for Mn, from 99.4 % to 99.9 % for Zn, and from 99.3 % to 99.5 % for Co as the contact time increases from 15 to 90 minutes (Figure 3). The results exhibited that satisfactory sorption of metal ions were attained within the first 60 min of contact time. Further increase in contact time led to no significant sorption of metal ions by eggshell. Therefore, the contact time of 60 min was selected as the optimal contact time for further investigation. The equilibration time required by the eggshell used in this study is less compared to time required by some other biosorbents such as pericarp of pecan (24 h at 150 rpm) reported by Hernández-Montoya et al. (Hernández–Montoya, Mendoza–Castillo, Bonilla–Petriciolet, Montes–Morán, & Perez–Cruz, 2011) Since short equilibration time is essential for having economical treated water, this shorter contact time exhibited by eggshell has beneficial effect of reducing operation cost in wastewater treatment plant.

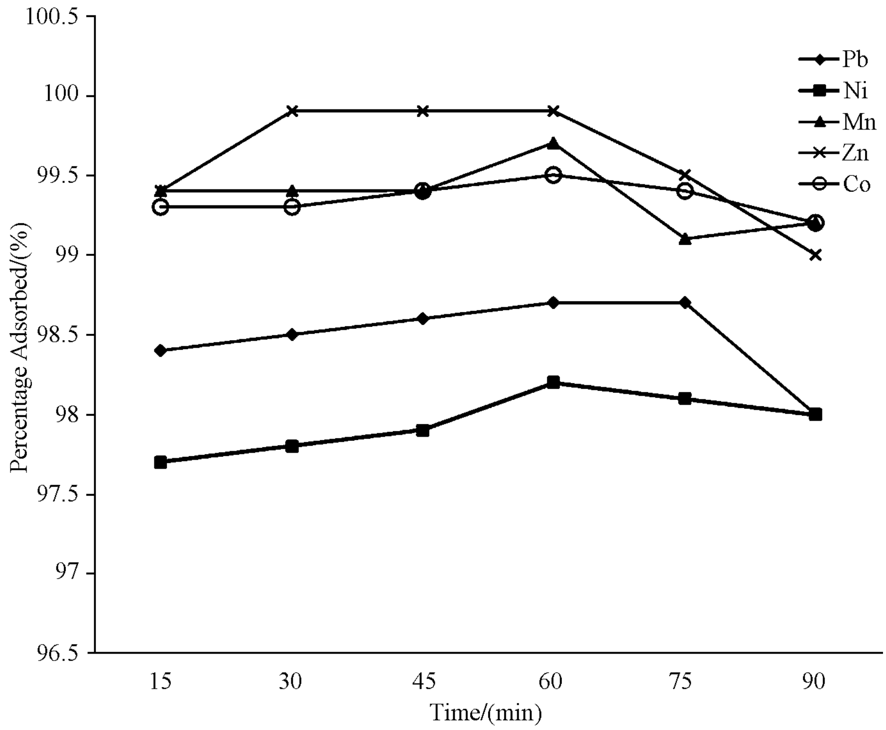

Figure 3
Effect of Contact Time on Metal Ions Sorption by Eggshell Powder for 5 mg L^{-1} of Metals and 1 g in 25 mL of Sorbent Concentration at 30 ^oC

2.4 Effect of Initial Metal Ion Concentration

The initial metal ion concentration provides an important force to overcome all mass transfer resistances of the metal ions between aqueous and solid phase (Aksu & Akpinar, 2000). The removal efficiency decreases for Pb from 99.8 % to 98.9 %, for Ni from 99.5 % to 97.9 %, for Mn from 99.8 % to 95.5 %, for Zn from 99.9 % to 98.7 %, and CO from 99.3 % to 98.6 % as the initial metal ions concentration increases from 5 mg L^{-1} to 30 mg L^{-1} (Figure 4). The Figure revealed that all metal ions present in solution interacted more with the binding sites at lower metal ions concentrations than at higher concentrations. Thus higher percentage sorption was obtained at lower metal ions concentrations. Low percentage sorption at higher metal ion concentration suggests agglomeration of adsorbent particles (AjayKumar, Darwish, & Hilal, 2009). Such agglomeration leads to a decrease in the total surface area of the egg particles available for adsorption, and an increase in the diffusion path length. (Yasemin & Tez, 2007) This observation agrees with the findings of Rao *et al*. and Chojnacka. Similar observation was reported when wild cocoyam and sugar cane bagasse pith were utilized as adsorbent (=AjayKumar, Darwish, & Hilal, 2009; Horsfall, & Spiff, 2004; Krishnan, & Anirudhan, 2003).

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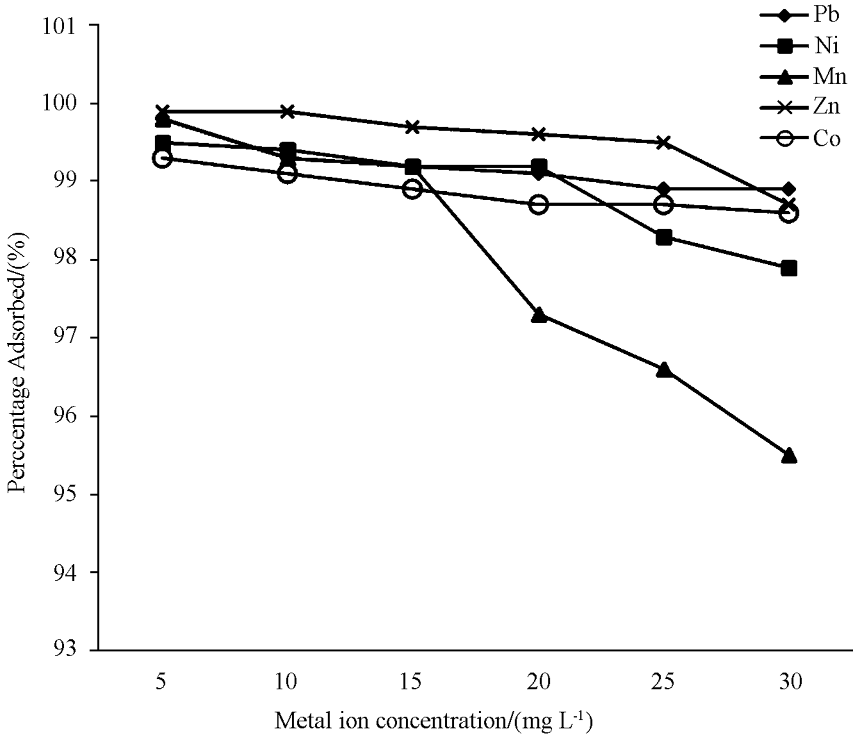

Figure 4

Effect of Initial Metal Ion Concentration on the Sorption of Metal Ions by Eggshell Powder at 1g in 25mL of Sorbent Concentration at 30 °C

2.5 Effect of Dosage

The plot of the amount of metal ions adsorbed (q_e) against the adsorbent dosage employed is shown in Figure 5. The Figure reveals that the amounts of metal ions increase with an increase in the quantity of eggshell from 0.2 g to 1.2 g at an initial metal ion concentration of 5 mg L^{-1}. It implies that the corresponding removal efficiency increases for Pb from 98.5 % to 99.5 %, for Ni from 88.6 % to 93.1 %, for Mn from 77.0 % to 95.4 %, for Zn from 83.0 % to 96.1 %, and for Co from 90.2 % to 94.8 %. These increases in the sorption of the amounts of metal ions are obvious due to increasing sorbent surface area and number of binding sites for the ions (Rao, Kalyani, Rao, Kumar, Mariadas, Kumar, Vijetha, Pallavi, Sumalatha, & Kumaraswamy, 2010; Al-Qodah, 2006; Makata, Sajidu, Masamba, & Mwatseteza, 2010). It seems that at high sorbent dosage, the available metal ions are sufficient to cover all the exchangeable sites on the eggshell usually resulting in high metal ions uptake. Similar trend was also observed in by Gong et al. (Gong, Ding, Liu, Chen, & Liu, 2005) and Oboh et al.(Oboh, Aluyor, & Audu, 2009).

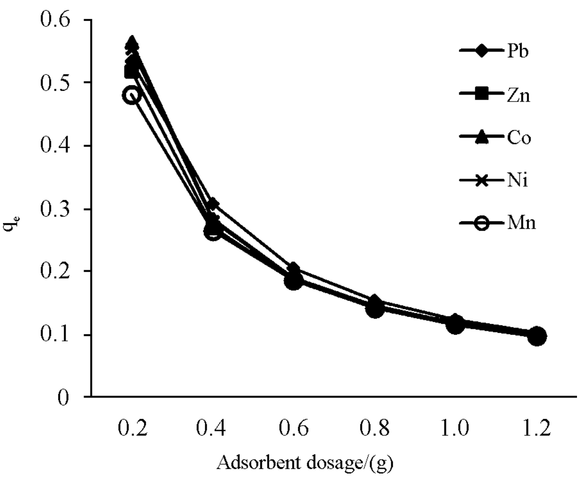

Figure 5

Effect of Adsorbent Dosage on Metal Ions Sorption by Eggshell Powder for 5 mg L^{-1} of Metal at 30 °C

2.6 Adsorption Equilibrium and Kinetics of Metal Ions Adsorption

The quantification of the adsorption features of eggshell as sorbent must be established via Langmuir and Freundlich models for proper evaluation (Vecchio, Finoli, Di Simine, Andreoni, 1998).

2.6.1 Langmuir Isotherm

The Langmuir isotherm provides a good model for the adsorption process as indicated by the regression coefficient (R^2) ranging from 0.834 to 0.990 (Table 1). The sorption capacity (Qm), shows that the order of adsorption affinity for metal ions on eggshell is Co^{2+} > Pb^{2+} > Ni^{2+} > Zn^{2+} > Mn^{2+} with values ranging from 0.7 to 1.4 (Table 1). A metal with high electronegativity exhibits higher adsorption tendency than that with low electronegativity. (Lim, Kang, Kim, & Ko, 2008) Considering the electronegativities of Pb^{2+}, Ni^{2+}, Mn^{2+},

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Zn^{2+} and CO^{2+} which are 2.33, 1.91, 1.55, 1.65 and 1.88 respectively, the observed adsorption affinities of metal ions arising from Qm values disagreed with this order of electronegativity. This implies that other factors such as initial metal ions concentrations would have contributed to the adsorption process of these metals. The observed order of adsorption affinity for metal ions on eggshell in this study is in agreement with the findings of Lim et al. (Lim, Kang, Kim, & Ko, 2008).

The order of favourable energy of adsorption for the metals is Zn^{2+} > Mn^{2+} Pb^{2+} > Ni^{2+} > CO^{2+} as revealed by the adsorption coefficient (*Ka*), which is related to the apparent energy of sorption. The energy of sorption is more favourable for Zn^{2+} than other metals due to its highest K_a value. Also, the isotherm shape as indicated by K_R value is useful to predict whether a sorption is either favourable or unfavourable (Venkata, Ramanaiah, Rajkumar, & Sarma, 2007). The shape of the isotherm can be assessed by the following classification: K_R > 1 indicates unfavourable adsorption, K_R=0 indicate linear adsorption, K_R > 0< 1 indicate favourable adsorption, K_R< 0 indicate irreversible adsorption. (Venkata, Rao, & Karthikeyan, 2002) This shows that adsorption of all these metal ions on the eggshell is favourable as K_R ranged from 0.01 to 0.08 (Table 1).

2.6.2 Freundlich Isotherm

A linear relation was observed among the plotted parameters for Freundlich isotherms whose graphs were not included in this paper. The general capacity of metal ions adsorbed onto eggshell for a unit equilibrium concentration is represented by K_f. The K_f and 1/*n* values

Table 1
Langmuir and Freundlich Isotherms Parameters for the Adsorption of Metal Ions by Eggshell

	Langmuir isotherm parameters				Freundlich isotherm parameters			
	K_a	Q_m	K_R	R^2	*N*	1/*n*	K_f	R^2
Pb	6.5	1.0	0.03	0.834	1.98	0.51	1.16	0.969
Ni	6.4	0.9	0.03	0.990	1.88	0.53	1.05	0.949
Mn	7.2	0.7	0.03	0.972	2.89	0.35	0.65	0.979
Zn	27.7	0.8	0.01	0.993	2.54	0.39	1.26	0.939
Co	2.5	1.4	0.08	0.914	1.41	0.71	1.34	9.998

Obtained from the Freundlich isotherms ranged from 0.65 to 1.34 and 0.39 to 0.71 respectively (Table 1). The adsorption capacities (K_f) obtained for all the metal ions show that the order of adsorption is Co^{2+}>Zn^{2+} > Pb^{2+} > Ni^{2+} > Mn^{2+}. The values of n between 1 and 10 represent beneficial adsorption (Zheng, Feng, Lam, Lam, Ding, & Yu, 2009). The n values in this study ranged between 1.41 and 2.89. Thus, the absorption of metal ions by eggshell is beneficial. The obtained values of 1/n are less than unity which is an indication that significant adsorption takes place at low metal ions concentrations. Noteworthy is the fact that increase in the amount of metal ion adsorbed with concentration becomes less significant at higher concentration and vice versa (Makata, Sajidu, Masamba, & Mwatseteza, 2010).

2.7 Kinetics of Metal Ions Sorption

The pseudo-first order parameters k_1, q_e (calculated) and the regression coefficient (R^2) are shown in Table 2. The R^2 values obtained indicated that the first-order model was not appropriate to describe the adsorption process. The observed rate constant k_1 for Ni^{2+} was the highest followed by that for Pb^{2+}, Mn^{2+}, Zn^{2+} and lastly for CO^{2+}. The calculated q_e for all the metal ions differs significantly from those of the experimental. This is expected since the pseudo-first order is not appropriate to describe the adsorption process. This result agrees with Rao et al., (Rao, Kalyani, Rao, Kumar, Mariadas, Kumar, Vijetha, Pallavi, Sumalatha, & Kumaraswamy, 2010) that in most cases, the pseudo-first order equation for liquid/solid sorption

Table 2
Pseudo-First and Second Order Parameters for the Adsorption of Metal Ions by Eggshells

	Pseudo first order parameters				Pseudo-second order parameters			
Metal	q_e(exp) / (mg g^{-1})	q_e(cal) / (mg g^{-1})	k_1 / (min^{-1})	R^2	q_e(exp) / (mg g^{-1})	*h* / (mg g^{-1} min)	k_2 / (g mg^{-1} min)	R^2
Pb	0.1235	$3.48E*10^{-5}$	-0.06	0.250	0.1239	0.51	33.00	0.999
Ni	0.1224	$4.25E*10^{-2}$	0.07	0.338	0.1220	-0.23	-15.50	0.999
Mn	0.1248	$4.24E*10^{-5}$	-0.06	0.311	0.1249	0.90	57.59	1.000
Zn	0.1249	$7.36E*10^{-3}$	-0.07	0.428	0.1250	2.49	159.20	1.000
Co	0.1244	$9.27E*10^{-6}$	-0.14	0.719	0.1245	2.06	133.02	1.000

Notes. exp = experimental; cal = calculate

system does not fit well for the whole range of contact time and is generally applicable over the initial 20 to 30 minutes of the sorption process. On the other hand, the correlation coefficients (R^2) of pseudo second order kinetic ranged between 0.999 and 1.000, and were higher than the corresponding coefficients for first order kinetic model. The values for q_e (calculated) using pseudo second kinetic model were about the corresponding values for q_e (experimental) (Table 2). Therefore, the kinetics of the metal ions sorption is well best described by pseudo second order kinetic model rather than pseudo first order. The order of h and k_2 magnitudes is Zn^{2+} > CO^{2+} > Mn^{2+} >

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Pb^{2+} > Ni^{2+}. This implies that Zn^{2+} is better adsorbed than other metal ions in solution by eggshell, and it is similar to the findings in the literatures (Lim, Kang, Kim, & Ko, 2008; Zheng, Feng, Lam, Lam, Ding & Yu, 2009; Rao, Kalyani, Rao, Kumar, Mariadas, Kumar, Vijetha, Pallavi, Sumalatha, & Kumaraswamy, 2010; Ho, 2003; Singha & Das, 2011).

2.8 Desorption Studies

Desorption of metal ions from loaded eggshell was carried out using different concentrations of NaOH and HNO_3 solutions. Table 3 showed that the desorption efficiency increased with the increase in nitric acid concentration to 6.0 mol L^{-1}. However, desorption efficiency with sodium hydroxide generally increased with increase in concentration to 3.0 mol L^{-1}, above which the efficiency decreased. This trend in desorption efficiency was only observed for Ni^{2+}, Mn^{2+}, Zn^{2+} and Co^{2+}. The resultant desorption phenomenon observed in both NaOH and HNO_3 might be attributed to ion exchange type interaction rather than chemical sorption (Venkata, Rao, & Karthikeyan, 2002).

2.9 Application Studies Using Real Industrial Effluent

Application studies using real brewery effluent was carried out to determine the suitability of eggshell as adsorbent at optimum batch condition and the result are shown in Table 4. The adsorption studies on brewery effluent using eggshell as sorbent showed adsorption efficiency of 95.86 % and 44.29 % for Mn and Zn respectively. The adsorption efficiency obtained in this study agreed with those obtained by Singha and Das (Singha & Das, 2011) using wastewater of an electroplating unit and different natural adsorbents. On the other hand, the percentage desorption of Mn with 3.0 M NaOH were 19.94 % and 35.48 % for Mn and Zn respectively.

Table 3
Desorption of Metals From Loaded Eggshells Adsorbent

Strength of NaOH / (mol L^{-1})	*Percentage desorption / (%)				
	Pb	Ni	Mn	Zn	Co
1.0	6.24	25.60	1.97	14.31	22.61
2.0	9.84	28.26	2.24	14.86	23.40
3.0	12.80	28.52	2.34	15.20	24.10
4.0	11.50	23.73	2.04	15.79	23.89
5.0	12.85	21.45	2.04	13.64	23.52
6.0	17.13	21.73	2.06	12.34	24.02
Strength of HNO_3 / (mol L^{-1})					
1.0	49.60	13.01	2.21	18.20	20.51
2.0	53.80	13.53	2.76	23.20	22.73
3.0	54.20	17.40	6.52	23.71	22.31
4.0	55.63	22.32	11.87	25.21	22.94
5.0	57.90	23.74	15.31	26.51	25.40
6.0	60.57	25.33	19.02	28.05	26.67

Notes. *Mean values of triplicate analysis

Table 4
Percentage Adsorption and Desorption of Metals From Brewery Effluent

Metal	Percentage adsorption/%	Percentage desorption/%
Pb	<0.001	<0.001
Ni	<0.001	<0.001
Mn	95.86	19.94
Zn	44.29	35.48
Co	<0.001	<0.001

Notes. *Mean values of triplicate analysis

3. CONCLUSION

Eggshell has been successfully applied in this study as a cheap and effective adsorbent for the removal of Pb^{2+}, Ni^{2+}, Mn^{2+}, Zn^{2+} and CO^{2+} from standard aqueous solutions, and for Mn and Zn in particular from brewery effluent. pH had a clear influence on the sorption capacity of eggshell for the removal of heavy metals in which the optimum pH of 7 was established. Adsorption of heavy metal ions by eggshell was very rapid in the first 30 minutes and the equilibrium time of 60 minutes was obtained. Adsorption capacity of eggshell was found to decrease with increase in initial metal ions concentrations. The data pertaining to the sorption fitted well into both Langmuir and Freundlich isotherms. The adsorption kinetics data were best described by pseudo-second order model, and was found to be in good agreement with the experimental data. This study revealed that NaOH and HNO_3 were sufficiently useful for desorption of these metal ions from adsorbents. However, desorption is well suited with 3 mol L^{-1} NaOH.

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