REMOVAL OF HEAVY METALS FROM TANNERY WASTEWATER USING POWDERED EGG SHELLS (PES)

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Abstract

This research focuses on the evaluation of the capability of powdered egg shells (PES) in removal of three heavy metals (chromium, zinc and arsenic) from tannery wastewater. The study was carried out as a batch process and for the different doses of PES (0.25 g, 0.50 g and 1.0 g) used, the highest dose of 1.0 g gave the highest percentage removal for all the three heavy metals. Also, the experiment was carried out at different contact times and the optimum contact time was found to be 90 min. At these optimum conditions, PES had 95.62%, 94.08%, and 75.67% reductions for As, Cr, and Zn ion,s respectively. The performance level of the adsorption models used to model the removal of each of the three heavy metals studied showed that the Langmuir model performance was 0.930, 0.366 and 0.994, respectively for As, Cr and Zn while the Freundlich isotherm model performance was 0.967, 0.908 and 0.921, respectively for each of these metals. The study indicated that the removal of As, Cr and Zn could be achieved by the use of powdered egg shells.

Keywords: *Adsorption, powdered egg shells, tannery wastewater.*

INTRODUCTION

It has been reported that at least 20 metals are classified as toxic and half of these are emitted into the environment in quantities that pose risks to human health (Kortenkamp *et al.*, 1996). The source of environmental pollution with heavy metals is mainly industry i.e metallurgical, electroplating, metal finishing industries, tanneries, and chemical manufacturing (Matheickel & Yu 1997). Heavy metals such as chromium, lead, mercury, arsenic, copper, zinc and cadmium are highly toxic when absorbed into the body (Eamsiri *et al.*, 2005). Exposure to chromium at high levels has been shown to result in chronic toxic effects such as dermatitis, ulceration of skin or liver, and kidney damage in animals and humans by ingestion. Arsenic compounds have been shown to have acute and chronic effects which include systemic irreversible damage. It is also listed as a carcinogen (www.watersafetestkits.com).

Up to date, the treatment methods applied for the removal of heavy metals from waste water include chemical precipitation (Noyes, 1994; Mahvi *et al.*, 2005; Oke & Okuofu, 2000); solvent extraction, ultra filtration, biochemical treatment, ion exchange and adsorption (Metcalf & Eddy, 2003). Of these various methods, adsorption, which is considered as a third stage -wastewater treatment process, has been preferred over other processes because of the low technological concepts involved and the ease of adopting local materials as its adsorptive media (Metcalf & Eddy, 2003). Recently, heavy metals removal from industrial wastewater have become particularly difficult because of the more stringent laws that control the concentration of pollutants in effluents discharged into waters and soils on the level lower than 1 mg/kg (Katarzyna, 2005). Most of the studies on heavy metals removal by adsorption are carried out on synthesized solutions of the heavy metals and only few studies actually make use of wastewater contaminated with heavy metals (Demirbas *et al*., 2004; Otun *et al*., 2006; Kalyani *et al*., 2009; Ismail *et al.*, 2009; Adie *et al*., 2010). The effectiveness of adsorption for the removal of heavy metals has been shown in a number of studies (Demirbas *et al*., 2004; Otun *et al*., 2006 & Kalyani *et al*., 2009). However, an adsorbent will be accepted commercially only when its cost can compete with the existing technologies. Hence, low cost adsorbents become a crucial factor when considering practical application of adsorption.

Waste materials from food and agricultural industry in this regard are appropriate in terms of cost and availability, and should be considered for use as low-cost adsorbents. This study therefore considers the use of powdered egg shells (PES) as a low-cost adsorbent for the removal of some heavy metals from tannery wastewater. The effect of contact time and dose of adsorbent were evaluated and the used PES was analyzed to determine the actual proportion of the total removal that was adsorbed. The data obtained were evaluated using the Langmuir and Freundlich isotherm models.

MATERIALS AND METHODS

Adsorbent Preparation

The egg shells used were soaked for 4 h, thereafter were washed three times with tap water. The egg shells were dried for 2 h and placed in an aluminum foil inside a hot-air oven maintained at 65^0C. Thereafter the egg shells were allowed to cool at room temperature and were ground to powder using local mortar and pestle. The powdered egg shells used were sieved through 300 μm particle size sieve.

Dose of Adsorbent Analysis

100 ml of the wastewater were added into three 600 ml beakers. 0.25 g, 0.50 g and 1.00 g of powdered egg shells was added into each of the beakers and the magnetic stirrer was adjusted to 120 rpm and stirred for 1h at pH range of 6.0 – 9.5. Concentrated hydrochloric acid and 1M sodium hydroxide was used to control the pH. Treated wastewater was filtered through Whatman filter paper, and then the metal concentration was determined using the double beam Atomic Absorption Spectrophotometer (AAS) (Shimaduzu A.A. 650)

Contact Time Analysis

1.00 g of powdered egg shells was added into the 600 ml beaker containing 100 ml of tannery wastewater at a controlled pH range of 6.0 - 9.5. The magnetic stirrer was adjusted at 120 rpm for 60, 90 and 120 minutes. Treated wastewater was filtered through Whatman filter paper, and then the metal concentration was determined using AAS.

Batch Studies with the Adsorbents on the Wastewater

Adsorption experiments were performed in three 600 ml beakers each containing 300 ml of the tannery wastewater. 3 g of powdered egg shell was added into each of the beakers, respectively and then stirred continuously with an electromagnetic stirrer at 120 rpm. At intervals of 12 minutes, the pH of the mixture was checked using a digital pH meter and was regulated between pH of 6.0 – 9.5 using concentrated hydrochloric acid at room temperature. After the procedure, the heavy metal content in the effluent was determined using Atomic Absorption Spectrophotometer (Shimaduzu A.A. 650) after filtering the adsorbent with whatman filter paper. The process was repeated in a second run of the experiment to achieve a better removal of the heavy

Adsorption Isotherm Study

The data obtained from the experiment in were used to study adsorption isotherm for determining the adsorption capacities of the adsorbents. Langmuir's, and Freundlich's adsorption isotherms were tested for the description of the adsorption data obtained. The amount of metal adsorbed by adsorbent was calculated from the differences between metal quantity in the wastewater and metal content of the supernatant using the following equation:

$$Q = \frac{(Co - Ce) \times V}{m} \qquad (1)$$

Where Q is the metal uptake (mg/g); C_o and C_e are the initial and equilibrium metal concentrations in the solution (mg/L), respectively; V is the solution volume (ml); and m is the mass of adsorbents (g).

The removal efficiency (%) was also determined using the following equation:

$$\frac{A-B}{A} \times 100 \qquad (2)$$

Where A = Initial concentration (mg/l), B = Final concentration (mg/l)

Application of Adsorption Isotherm

The experimental data obtained was used to obtain the adsorption isotherm using the Langmuir and Freundlich models.

The Langmuir equation is linearised for application as follows:

$$\frac{Ce}{Q} = \frac{1}{ab} + \frac{Ce}{a} \qquad (3)$$

Plotting C_e/Q against C_e, gives a straight line with slope 1/a and an intercept 1/ab. The 'b' value is the ratio between adsorption and desorption rates. 'a' could be used to determine the removal efficiency of the adsorbent.

Linearization of the Freundlich equation for application is written in logarithmic form as:

$$\text{Log } Q = \log K_f + \frac{1}{n} \log C_e \qquad (4)$$

Plotting Log Qe against log Ce, a straight line plot is obtained, slope is 1/n and intercept is log K. The calculated n value was qualitative related to the distribution of site bonding energies. K values could be used to compare the removal efficiency of the adsorbent (Samuel & Osman, 1987). The square of regression coefficient (R^2) is used to determine how well processes such as adsorption can be modeled by a given equation. Adsorption parameters are considered to be well modeled when $R^2 > 0.95$; averagely modeled when $0.75 < R^2 < 0.95$; and cannot be modeled by the given equation when $R^2 < 0.75$. (Loveday, 1980)

RESULTS AND DISCUSSION

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wastewater is as shown in Table 1. The effect of various concentrations (0.25 g, 0.5 g, and 1.00 g) of the adsorbent on removal efficiency of heavy metals from the wastewater using PES is shown in Table 2. Results from Table 2 showed that the percentage removal of the heavy metals increased as the concentration of the adsorbent was increased. This is expected due to the fact that the higher dose of adsorbent in the solution, the greater the availability of exchangeable sites for the ions. The percentage of removal of chromium, zinc and arsenic increased from 32.39 % to 50.70 %, 23.88 % to 50.75 % and 27.97 % to 67.03 %, respectively as the concentration of PES was increased from 0.25 g to 1.00 g.

Table 1: Physico-chemical characteristics of the sampled tannery wastewater

Parameter	Value
Colour (mg Pt/l)	75.00
pH	8.400
Total Dissolved Solids (TDS) [mg/L]	7250
Electric Conductivity (µmhos/cm)	7500
Chromium (mg/L)	0.710
Zinc (mg/L)	0.670
Iron (mg/L)	0.800
Cadmium (mg/L)	0.260
Manganese (mg/L)	0.100
Nickel (mg/L)	0.140
Magnesium (mg/L)	6.200
Arsenic (mg/L)	0.640

Table 2: Effect of quantity of adsorbent used on heavy metals removal efficiency (at 120 rpm for 1 h)

Quantity of Adsorbent (grams)	0.25		0.50		1.00	
	(mg/l)	Removal Efficiency (%)	(mg/l)	Removal Efficiency (%)	(mg/l)	Removal Efficiency (%)
Cr	0.480	32.39	0.410	42.25	0.350	50.70
Zn	0.510	23.88	0.420	37.31	0.330	50.75
As	0.461	27.97	0.304	52.50	0.211	67.03

Effect of contact time on heavy metals removal

The effect of contact time on the adsorption process is shown in Fig. 1. The removal efficiency of PES increased with increase in contact time. From the Fig. 1, the optimum contact time is 90 minutes. This result is consistent with the study of Pawebang & Sukcharoen (1999), who reported that the equilibrium time to remove lead in synthetic wastewater by egg shell could be reached at about 80 minutes and that of Lee *et al*. (1998) on the removal of lead by crab shell particle showed that the necessary contact time to reach equilibrium was about 90-120 minutes.

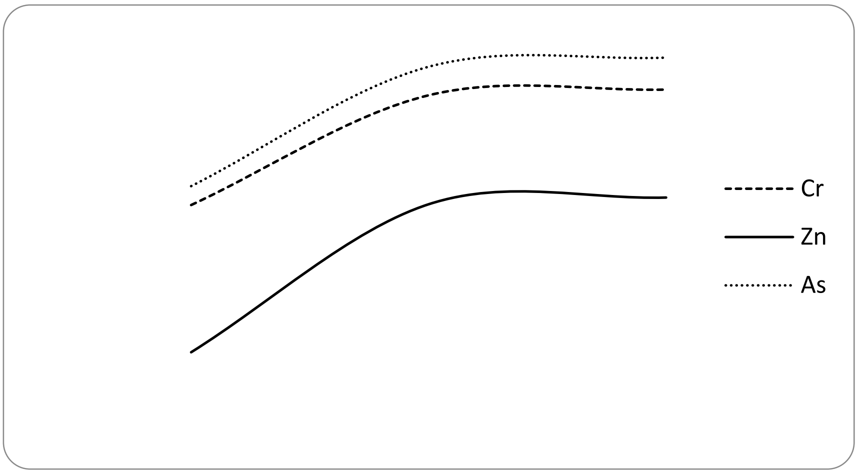

Fig. 1: Effect of contact time on heavy metals removal efficiency

Percentage removals of heavy metals from wastewater

The percentage of heavy metals removed from the wastewater after the first and second run as well as the total removal are as shown in Table 3. The results showed that As and Cr were better removed compared to Zn. Also, the percentage removals in the second run are much lower than that obtained in the first run which shows that the concentration of adsorbate affects the rate of adsorption by the adsorbent. This is further buttressed by the fact that Zn which had the lowest percentage removal (53.73 %) in the first run had the highest removal of 21.94 % in the second run because it had the highest percentage remaining followed by Cr with 18.03 % and then As 9.84 % removal in the second run.

Table 3: Percentage removals of heavy metals from wastewater (using 1.0 g of PES and at 90 minutes contact time)

Heavy metal	1st Run (%)	2nd Run (%)	Total removal (%)
Cr	76.05	18.03	94.08
Zn	53.73	21.94	75.67
As	85.78	9.84	95.62

Analysis of heavy metals removal

The comparison of the percentage of heavy metals removed using (1.0 g of PES and 90 minutes contact time) from the wastewater with that adsorbed onto the adsorbent are represented in Fig. 2. The experiment was carried out initially in a first run and repeated on the effluent in a second run in order to determine if a better effluent could be obtained. From the figure, it is observed that Cr, Zn, and As ions where adsorbed, this is due to nature of the pore structure of the adsorbent and the functional group i.e. carboxyl group of the adsorbent. The uptake of these metals as reported from literature might be of more than one type of mechanism (Vijayaraghavan *et al.*, 2005). The figure shows that the removal of Cr by PES was entirely by adsorption as the percentage adsorbed was more than the percentage removed. The removals of Zn, and As by PES were not by adsorption alone, part of their removal from the wastewater could be through precipitation initiated by the hydrolysis of $CaCO_3$ which is primary in the composition of PES in the wastewater. The hydrolysis of $CaCO_3$ increases the pH of the solution and making the metal ions insoluble by forming hydroxides of the metals (Brown and Lemay, 1985) which might have been filtered out with the Whatman filter paper.

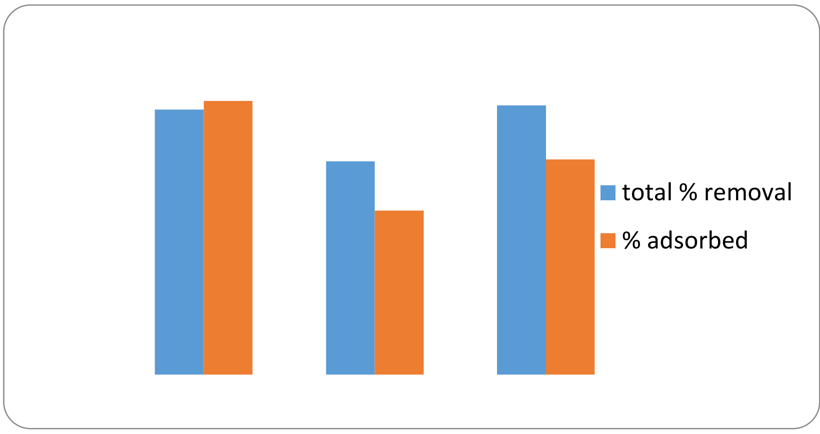

Fig. 2: Comparison of total percentage removal and percentage adsorption

Adsorption Isotherm

The adsorption isotherm constants and their correlation coefficients are shown in Table 4 and Figures 3-8. The values of the correlation coefficients indicate that the adsorption of Zn could be modeled by Langmiur model ($R^2 > 0.95$) (Loveday, 1980), As could be modeled averagely ($0.75 < R^2 < 0.95$) while Cr adsorption ($R^2 < 0.95$) could not be modeled by Langmuir model. The correlation coefficients for Freundlich isotherm are 0.967, 0.908 and 0.921 for As, Cr and Zn respectively, representing a good fit for As and an average fit for Cr and Zn.

Table 4: Adsorption isotherm constants and the correlation coefficients

Heavy metals	Langmuir model a (L mg^{-1})	b (mg mg^{-1})	R^2	Freundlich model K_f (mg mg^{-1})	N_f (L mg^{-1})	R^2
As	0.083	0.909	0.930	0.363	0.500	0.967
Cr	0.250	0.645	0.366	0.100	1.187	0.908
Zn	0.086	8.241	0.994	0.091	3.508	0.921

CONCLUSION

This study indicated that removal of As, Cr and Zn was possible using PES, however only Cr was removed entirely by adsorption. The adsorption process was dependent on adsorbent dose (up to 1.0 g) and the optimum contact time was found to be 90 minutes. The study also showed that re-run of the adsorbate through the adsorption process could result in better removal of heavy metals from industrial wastewater. It was found that the adsorption of Zn could be modeled by the Langmuir model while the Freundlich model gave a good fit for As adsorption and an average fit for Cr.

Langmuir model while the Freundlich model gave a good fit for As adsorption and an average fit for Cr.

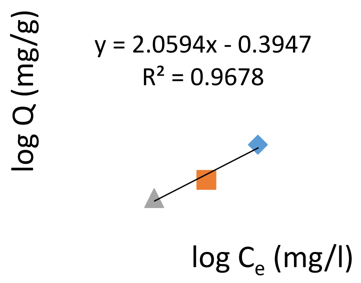

Fig. 3: Langmuir model of Cr adsorption onto PES

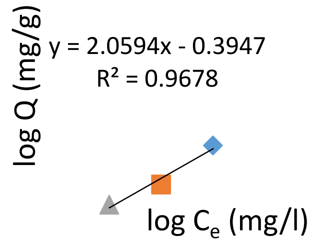

Fig. 4: Freundlich model of Cr adsorption onto PES

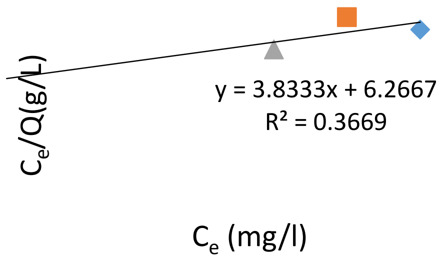

Fig. 5: Langmuir model of Zn adsorption onto PES

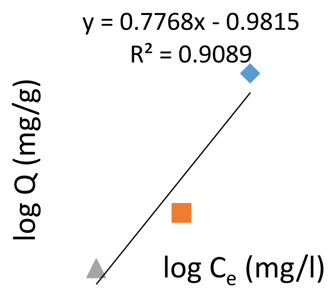

Fig. 6: Freundlich model of Zn adsorption onto PES

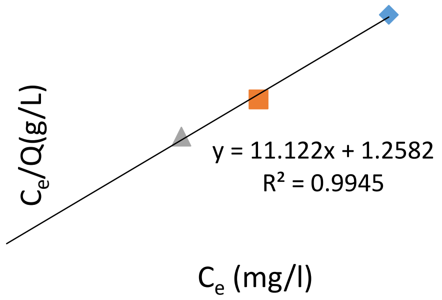

Fig. 7: Langmuir model of As adsorption onto PES

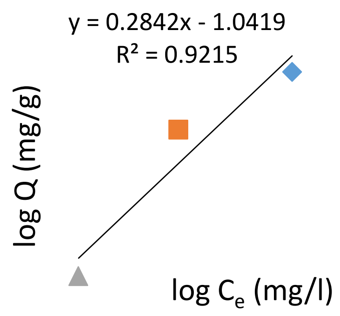

Fig. 8: Freundlich model of As adsorption onto PES

REFERENCES

Brown, T. L. & Lemay, H. E. Jr. (1985). Chemistry the Central Science Health, Prentice-Hall Publishing, New Jersey.

Demirbas, E., Kobya, M., Senturk, E. & Ozkan T. (2004). Adsorption kinetics for the removal of chromium(vi) from aqueous solutions on the activated carbons prepared from agricultural wastes. Water S. A, 30 (4): 533-539.

Eamsiri, A., Arunlertaree, C. & Datchaneekul, K. (2005). Removal of heavy metals in synthetic wastewater by adsorption on bentonite, Envi. and Natural Res., 3: 21-30.

Hamidi, A., Mohd, S. Y., Mohd, N. A., Nurul–Hidayah, A. & Salina, A. (2004). Physico-chemical removal of iron from semi-aerobic landfill leacheate by limestone filter. Waste Management, 24(4): 353-358.

Ismail, A., Adie, D. B., Oke, I. A., Otun, J. A., Olarinoye, N. O., Lukman, S. & Okuofu, C. A. (2009). Adsorption kinetics of cadmium ions onto powdered corn cobs. Can. J. Chem. Eng., 87: 896-909.

Kalyani, G., Babu, R. G., Vijaya, S. B. & Prasanna, K. Y. (2009). Equilibrium and Kinetic studies on biosorption of Zinc onto *Gallus domesticus* shell powder. ARPN Journal of Engineering and Applied Sciences, 4(1): 39-49.

Katarzyna, C. (2005). Biosorption of Cr(III) ions by eggshells, Journal of Hazardous Materials, B., 121: 167-173.

Lee, M., Lee, S., Shin, H. & Kajiuchi, T. Y. (1998). Characteristics of lead removal by crab shell particles. Process Biochem., 33(7): 749-753.

Loveday, R. (1980). Statistics, A Second Course in Statistics. 2nd Edition, University Press, Cambridge.

Mahvi, A. H., Dariush, N., Forugh, V. & Nazmara, S. (2005). Teawaste as an Adsorbent for Heavy Metal removal from Industrial Wastewaters. Am. J. applied Sci., 2: 372-375

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