

Removal Of Lead From Water Using Eggshell Powder As An Adsorbent

Ajay Vikram Singh¹

Research Scholar

¹**Department of Chemistry,**

Shri Venkateshwara University, Gajraula, UP, India

Dr. Pradeep Kumar¹

Assistant Professor

¹**Department of Chemistry,**

Shri Venkateshwara University, Gajraula, UP, India

Considerable research has been carried out over the last decade on the protection against plant and animal life degradation. Several big cities contribute to increase this problem, as they are sources of industrial effluents. In order to reduce the environmental pollution, a number of studies have been considered to minimize the problems caused by the commonly employed treatment of metal bearing effluents [1]. The traditional methods for removing heavy metals have several disadvantages. Chemical precipitation leads to the production of toxic sludge. Due to the economics of dealing with large volumes of liquids and of solvent losses, solvent extraction is limited to streams containing more than 1 g/l of the targeted heavy metal. Application of the ion-exchange process is rather expensive due to the cost of synthetic ion exchange resins. Furthermore, they are not always selective enough to allow an effective recovery of heavy metals present in the waste [2].

Alternative methods of metals removal and recovery based on biological materials have been considered. Since commercial biotechnological

processes such as alginate extraction result in the production of large quantities of biomass and since this material is currently viewed as a low value by product, these industries represent an ideal source of non-living material for use as biosorbents [3]. In addition, since metal bio-sorption by non-living biomass is a metabolism independent process, it is not ruled by physiological restriction.

Mining and metallurgical waste are the most considerable sources of environmental pollution by heavy metals. Due to the health hazard presented by heavy metals, development of effective and economic removal technologies is necessary. In the case of removal of toxic metals from waste waters, biosorption has been involved. This method is based on the use of the metal binding capacities of various biological materials, including algae, fungi and bacteria [4,5].

Fungus belongs to groups of organisms with very well known heavy metal sorption capacity. It has been demonstrated that some fungi species are typically associated with heavy metal rich substrata and can be even considered as hyper accumulators of heavy metals [6]. Alternatively fungi can be exposed to heavy metals from the atmosphere and are very well known from biomonitoring studies focused on heavy metal pollution [7].

Heavy metals such as lead, mercury, arsenic, copper, zinc and cadmium are highly toxic when adsorbed into the body [9]. Lead one of the earliest metals recognized and used by humans, has a long history of beneficial use to humankind, but now been recognized as toxic and as posing a widespread threat to humans and wildlife [8]. Treatment of lead from polluted water and wastewater has received a great deal of attention. Treatment

process for metals contaminated waste streams include chemical precipitation, membrane filtration, ion exchange, carbon adsorption, and coprecipitation/adsorption. Cost effective alternative technologies or sorbents for treatment of metals contaminated waste streams are needed. Natural materials that are available in large quantities, or certain waste products from industrial or agricultural operations [10], may have potential as inexpensive sorbents. Due to their low cost, after these materials have been expended, they can be disposed of without expensive regeneration [11]. The effectiveness of sorption for the removal of heavy metals has been shown in a number of studies [9]. Natural materials that are available in large quantities, are certain waste products from industries, may have potential as inexpensive heavy metal sorbents

[11]. One cheap and easily available material having possibilities as suitable sorbent for heavy metal is *eggshell*. Due to their high calcium content, *eggshells* usually have no commercial importance. Disposal of eggshells is also a serious problem for egg processing industries due to stricter environmental regulations and high landfill costs [12]. In USA annually 120,000 tons of waste *eggshells* are generated and disposed in landfills [13].

In the present paper it is proposed to apply hen *eggshells* as low-cost sorbent of lead. The *eggshell* (which is almost entirely disposed of as waste) is currently used as source of calcium in animal feeds and human health supplements (i.e. for osteoporosis) [14]. Environmental parameters affecting the sorption process such as pH, contact time, metal ion concentration, sorbent

concentration and sorbent size were evaluated. The equilibrium sorption data were evaluated by Langmuir, Freundlich, Redlich-Peterson and Temkin isotherm models. **Materials and methods**

Sorbent

The sorbent used in the present paper is hen *eggshell powder*. Eggs are one of the first multifunctional food products, with various important gradients. They are well known for their whipping, gelling and emulsification properties in addition to their high quality protein [15]. The shell accounts for about 9-12 % by its total weight depending on egg size. It comprises about 94% CaCO_3 with small amounts of MgCO_3 , calcium phosphate and other organic matter including protein [16]. Most good quality eggshells from commercial layers contain approximately 2.2 grams of calcium in the form of

CaCO_3 weighing 5.5 grams. The average *eggshell* contains about 0.3 % phosphorous and 0.3 % magnesium and traces of sodium, potassium, zinc, manganese, iron and copper [17].

Preparation of sorbent

Eggshells were collected from Andhra University college of Engineering hostels, Visakhapatnam, Andhra Pradesh, India. Shells were washed with deionized water several times to remove dirt particles. The dried *eggshell powder* of 75-212 μm particle size was used as sorbent without any pretreatment for lead sorption.

Chemical

Analytical grades of $\text{Pb}(\text{NO}_3)_2$, HCl and NaOH were from merck, India. Lead ions were prepared by dissolving its corresponding Nitrate salt in distilled water. The pH of solutions was adjusted with 0.1

N HCl and NaOH. All the experiments were repeated five times and the average values have been reported. Also, blank experiments were conducted to ensure that no sorption was taking place on the walls of the apparatus used.

Sorption experiments

Sorption experiments were performed at room temperature (30 ± 1 °C) in a rotary shaker at 180 rpm using 250 mL Erlenmeyer flasks containing 30 mL of different lead concentrations. After one hour of contact (according to the preliminary sorption dynamics tests), with 0.1 g *eggshell* powder, equilibrium was reached and the reaction mixture was centrifuged for 5 min. The metal content in the supernatant was determined using Atomic Absorption Spectrophotometer (GBC A vanta Ver 1.32,

Australia) after filtering the adsorbent with whatman filter paper. The amount of metal sorbed by *eggshell* powder was calculated from the differences between metal quantity added to the sorbent and metal content of the supernatant using the following equation:

$$Q = (C_0 - C_f) \times \frac{V}{M} \quad (1)$$

Where Q is the metal uptake (mg/g); C_0 and C_f 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 sorbent (g). The pH of the solution was adjusted by using 0.1 NHCl and 0.1 N NaOH.

The Langmuir [18] sorption model was chosen for the estimation of maximum lead sorption by the sorbent. The Langmuir isotherm can be expressed as,

$$Q = \frac{Q_{\max} b C_f}{1 + b C_f} \quad (2)$$

Where Q_{\max} indicates the monolayer sorption capacity of sorbent (mg/g) and the Langmuir constant b (1/mg) is related to the energy of sorption. For fitting the experimental data, the Langmuir model was linearized as

$$\frac{1}{Q} = \frac{1}{Q_{\max}} + \frac{1}{b Q_{\max} C_f} \quad (3)$$

The Freundlich [19] model is represented by the equation,

$$Q = K C_f^{\frac{1}{n}} \quad (4)$$

Where K (mg/g) is the Freundlich constant related to sorption capacity of adsorbent and n is the Freundlich exponent related to adsorption intensity (g/L). For fitting the experimental data, the Freundlich model was linearized as follows,

$$\ln Q = \ln K + \frac{1}{n} \ln C_f \quad (5)$$

The Redlich-Peterson [20] model is represented by the equation,

$$q_e = \frac{A C_e}{1 + B C_e^g} \quad (6)$$

where A (1/g) and B (1/mg) are the Redlich-Peterson isotherm constants and g is the Redlich Peterson isotherm exponent, which lies between 0 and 1. The linearized form of equation is given by:

$$\ln \left(\frac{A C_e}{q_e} - 1 \right) = g \ln(C_e) + \ln(B) \quad (7)$$

Redlich-Peterson isotherm equation contains three unknown parameters A , B and g . Therefore a minimization procedure is adopted to maximize the coefficient of determination, between the theoretical data for q_e predicted from the linearized

from of Redlich-Peterson isotherm equation and the experimental data.

The Temkin [21] isotherm has generally been applied in the following form,

$$q_e = \frac{RT}{b_T} \ln (A_T C_e) \quad (8)$$

where A_T (1/mg) and b_T are Temkin isotherm constants.

Results and Discussion

The effect of contact time

The data obtained from the sorption of lead ions on the *eggshell powder* showed that a contact time of 60 min was sufficient to achieve equilibrium and the sorption did not change significantly with further increase in contact time. Therefore the uptake and unadsorbed lead concentrations at the end of 60 min are given as the equilibrium values (q_e , mg/g; C_{eq} , mg/L); respectively (Fig. 1) and the

other sorption experiments were conducted at this contact time of 60 min.

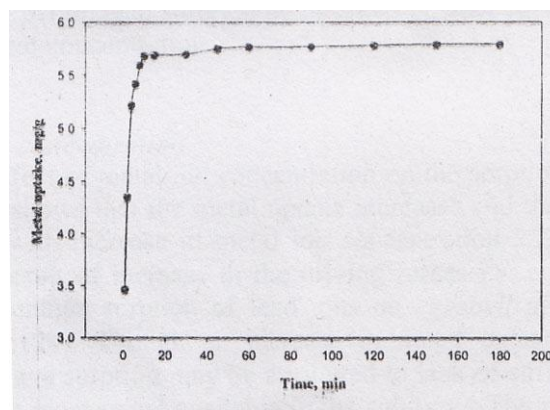
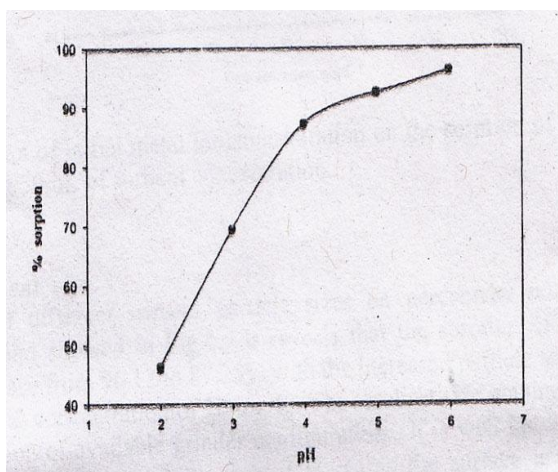


Figure 1: Effect of contact time of lead uptake by eggshell powder for 20mg/L of metal and 0.1g/mL of sobent concentration.

Effect of pH

It was found that lead uptake by *eggshells* was a function of solution pH. As shown in Fig. 2, the uptake of lead increased with increase in pH from 2.0 to 6.0. 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. At lower pH values

lead removal was inhibited, possibly as a result of the competition between hydrogen and lead ions on the sorption sites, with an apparent preponderance of hydrogen ions, which restricts the approach of metal cations as in consequence of the repulsive force. As the pH increased, the ligands such as carbonate groups in *eggshells* would be exposed, increasing the negative charge density on the sorbent surface, increasing the attraction of metallic ions with positive charge and allowing the sorption onto the cell surface.



Effect of metal ion concentration

Fig. 3. Shows the effect of

metal ion concentration on the sorption of lead by *eggshell* powder. The data shows that the metal uptake increases and the percentage sorption of lead decreases with increase in metal ion concentration. This increase (5.76 to 24.94 mg/g) is a result of increase in the driving forces i.e. concentration gradient. However, the percentage sorption of lead ions on *eggshell* powder was decreased from 96.12 to 83.12%. Though an increase in metal uptake was observed, the decrease in percentage sorption may be attributed to lack of sufficient surface area to accommodate much more metal available in the solution. The percentage sorption at higher concentration levels shows a decreasing trend whereas the equilibrium uptake of lead displays an opposite trend. At lower concentrations, all lead ions present in solution could interact with the binding sites and thus the percentage sorption was

higher than those at higher lead ion concentrations. At higher concentrations, lower adsorption yield is due to the saturation of adsorption sites. As a result the purification yield can be increased by diluting the wastewaters containing high metal ion concentrations.

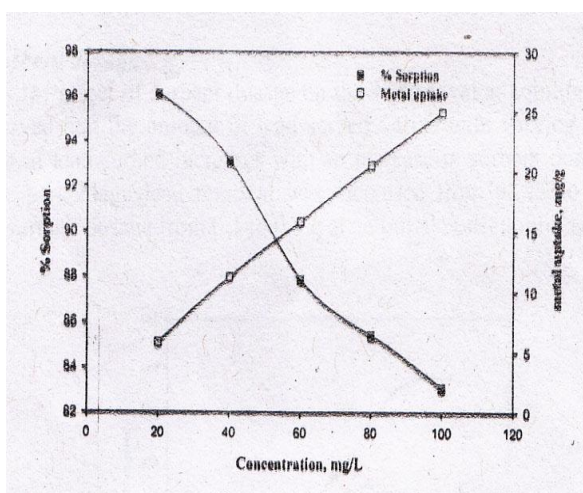


Figure 3: Effect of initial ion concentration on the sorption of lead by *eggshell* powder at 0.1g/30mL of sorbent concentration.

Effect of sorbent size

The effect of different sorbent particle size on percentage removal of lead is investigated and showed in fig. 4.

It reveals that the sorption of lead on *eggshell* powder decrease from 96.12 to 87.25% with the increased particle size from 75 to 212 μm at an initial concentration of 20mg/L. The smallest size obtained was 75 μm due to the limitation of available grinder configuration. It is well known that decreasing the average particle size of the sorbent increase the surface area, which in turn increases the sorption capacity.

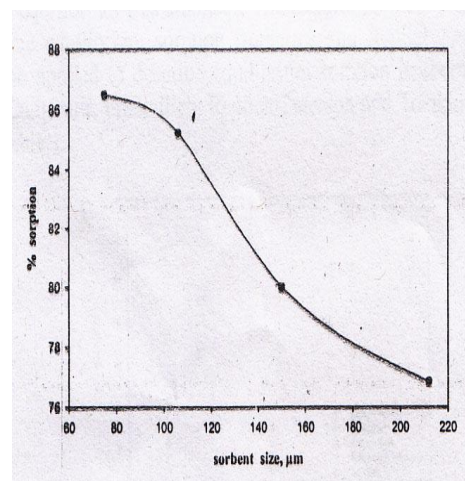


Figure 4: Effect of sorbent size on sorption of lead for 20 mg/L of metal and 0.1g/30mL of sorbent concentration.

Effect of sorbent dosage

Fig. 5 shows the effect of sorbent dosage on the % removal at equilibrium conditions. It was observed that the amount of lead sorbed varied with varying sorbent dosage. The amount of lead sorbed increase with an increase in sorbent dosage from 0.1 to 0.5g. The percentage lead removal was increased from 96.12 to 98.39% for an increase in sorbent dosage from 0.1 to 0.5g at an initial concentration of 20 mg/L.

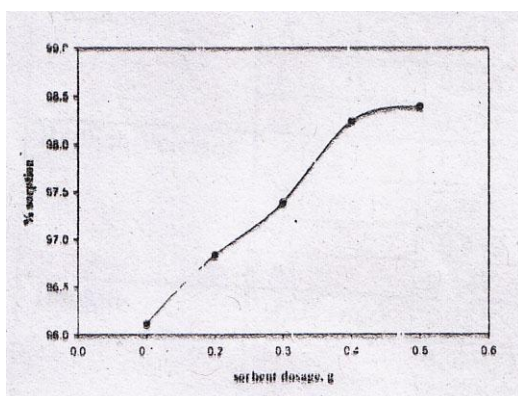


Figure 5: Effect of sorbent dosage on sorption of lead for 20mg/L of metal concentration.

Sorption equilibrium

The equilibrium sorption of lead on the *eggshell* powder as a function of the initial

concentration of lead is shown in Fig. 6. There was a gradual increase of sorption for lead ions until equilibrium was attained. The Langmuir, Freundlich models are often used to describe equilibrium sorption isotherms and Redlich-Peterson and Temkin models are also applied to describe equilibrium sorption isotherms. The calculated results of the Langmuir, Freundlich, Redlich-Peterson and Temkin isotherm constants are given in Table.1.

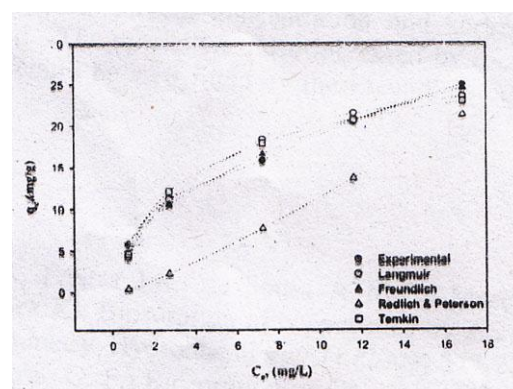


Figure 6: Equilibrium curves for lead onto eggshell powder.

Table 1: Langmuir, Freundlich, Redlich-Peterson and Temkin isotherm constants and correlation coefficients.

Langmuir	Q (mg/g)	29.878
	b(l/mg)	0.218
	R ²	0.959
Freundlich	K ₁ (mg/g)	6.613
	n (g/l)	0.464
	R ²	0.995
Redlich-Peterson	A (l/g)	1.988
	B(l/mg)	2.381
	g	-0.499
	R ²	0.129
Temkin	A _r (l/mg)	0.281
	b _r	424.922
	R ²	0.953

lead ions from aqueous solution. The effects of process parameters like pH, metal ion concentration, sorbent concentration and sorbent size on process equilibrium were studied. The uptake was also increased by increasing pH up to 6. The sorption isotherms could be well fitted by the Freundlich equation followed by Langmuir equation.

It is found that the sorption of lead on the *eggshell* powder was correlated well with the Freundlich equation and Langmuir equation as compared to Redlich-Peterson and Temkin equations under the concentration range studied. Examination of the Redlich-Peterson and Timkin data shows that these two isotherms are not modeled as well across the concentration range studied.

Conclusion

The present study shows that the *eggshell* powder was an effective sorbent for the sorption

References

1. de Carvalho R.P., Freitas J.R., de Sousa A. M.G., Moreia R.L., Punheiro M.V.B., Krambrock K.: Biosorption of copper ions by dried leaves: chemical bonds and site symmetry. *Hydrometallurgy* 71 (2003) 277-283.
2. Valdman E., Leite S. G. F. : Biosorption of Cd, Zn and Cu by *Sargassum* sp. waste biomass. *Bioprocess Engineering* 22 (2000) 171-173.
3. kratochvil D., Volesky R.,

- Demopoulos G.:
Optimizing Cu
removal/recovery in a
biosorption column. *Wat
Res.* 31 (1997) 2327-2339.
4. Bustard M., McHale A.P.:
Biosorption of heavy
metals by distillery-
derived biomass.
Bioprocess Eng. 19 (1998)
351-353.
5. Volesky B., Holan Z.R.:
Biosorption of heavy
metals. *Biotechnol. Prog.*
11, (1995) 235-250.
6. Veglio F., Beolchini F.:
Removal of metals by
biosorption: a review
Hydrometallurgy 44,
(1997) 301-316.
7. Purvis O.W., Halls C.: A
review of lichens in metal-
enriched environments.
lichenologist 28. (1996)
571-601.
8. Garty J.: Biomonitoring
atmospheric heavy metals
with lichens: theory and
application. *Critical
Reviews in Plant Sciences*
20, 309-371, 2001.
9. M.N. Rashed Fruit stones
as adsorbents for the
removal of Lead ion from
polluted water, <http://www.eea.gov/English/main/Env2003/day2/water/rashed.uniaswan>.
10. L. Friberg, G.F. Nordberg,
B. Vouk (Eds.), *Handbook
on the Toxicology of
Metals*, Elsevier, North-
Holland and Biomedical
press, Amsterdam, 1979.
11. M.J. Horsfall, A.A. Abia,
A.I. Spiff, Removal of
Cu(II) and Zn(II) ions
from wastewater by
cassava (*Manihot
esculenta* Cranz) waste
biomass, *African Journal
of Biotechnology.* 2(10)

- (2003) 360-364.
- 12.S.E.Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals. *Water Research* 33(11) (1999) 2469-2479.
- 13.K. Vijayaraghavan, J. Jegan, K. Palanivelu, M. Velan, Removal and recovery of copper from aqueous solution by egg shell in a packed column. *Minerals Engineering* 18 (2005_ 545-547.
- 14.Anonymus, valuable raw materials extracted from eggshells, *food eng. Int.* 25 (2) (2000) 45-49.
- 15.C. Davis, R. Reeves, High value opportunities from the chicken egg, A Report for the Rural Industries Research and Development Corporation. 2002.
- 16.G.D. Butcher, R. Miles, Concepts of Eggshell Quality, Fact sheet Vm-69, A series of the Veterinary Medicine Department, Florida Cooperative Extension service, Institute of food and Agricultural Sciences, University of Florida, 1996.
- 17.A. Schaafsma, I. Pakan, G.J.H. Hofstede, F.A.J. Muskiet, E. Vander Veer, P.J.F. De Vries, Mineral, amino acid, and hormonal composition of chicken eggshell powder and the evaluation of its use in human nutrition, *Poultry sci.* 79 (2000) 1833-1838.
- 18.I. Langmuir, the adsorption gasses on plane surface of glass, mica and platinum, *J. Am Chem. Soc.* 40 (1916) 1361=1368.
- 19.H.M.F. Freundlich, Over the adsorption in solution,

J. Phys. Chem. 57 (1906)
385-470.

20.O. Redlich, D.L. Peterson,
A useful adsorption
isotherm, J. Phys. Chem.
63 (1959) 1024.

21.C. Aharoni, M. Ungarish,
Kinetics of activated
chemisorption-Part 2.
Theoretical models, J.
Chem. Soc. Far. Trans. 73
(1977) 456-464.