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International Journal of Recent Scientific Research
Vol. 2, Issue, 2, pp.40-43, February, 2011

ISSN: 0976-3031

LOGGERGREN'S ADSORPTION DYNAMICS FOR THE REMOVAL OF LEAD USING EGG SHELL AS AN ADSORBENT

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Received 17th September, 2010; Accepted 25th November, 2011; Published online 15th February, 2011

Abstract

The removal of heavy metals from industrial effluents and from waste water has become a subject of keen interest. Earlier reports reveal that an extensive research work has been carried out with a view to analyze the various possible removal techniques. This present work deals with the removal of lead from its aqueous solution using very cheap waste material – egg shell as an adsorbent. The process of removal was carried out by column and batch mode techniques. Experimental results exhibit that the removal was found to be enhanced by increasing the dose of the adsorbent and decreasing the size of the adsorbent. The results are interpreted in the light of Loggergren's model.

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Key words: Adsorption dynamics; heavy metal; lead; egg shell; industrial effluent; Loggergren's model

INTRODUCTION

There has been an increasing concern in recent years over the discharge of industrial waste water containing dissolved species of heavy metal ions. Lead pollution arises mainly from automobile exhausts. Lead battery industries, metallurgical operation and industries manufacturing lead arsenate insecticides contribute a considerable amount of lead to environment (Trivedi and Goel. 1984). In early times, the use of utensils either made up of lead coated with lead glass was considered to be another source of lead. Lead is taken mainly from food even though the lead content in water is lesser than that in air. Lead adsorption is shown to be greater from the lungs rather than that from gut. After adsorption of lead food through the lungs, it enters the blood where 97% is taken up by the red blood cells (Ambasht, 1983). The half-life of lead in these cells is roughly three weeks. Some redistribution may also happen here and as a result, lead is transferred to some other parts like kidney or liver. This leads to either excretion into the bile or deposition in bone or teeth. Because of this kind of deposition in bone or teeth, it is possible to estimate the past exposure of lead. It is also possible to estimate the amount of lead from urine and blood analysis. Lead interferes with the synthesis of porphyrin. Myoglobin is also shown to be affected (Odum, 1971). The activity of enzyme is inhibited by lead and a correlation is available between blood lead level and the degree of inhibition.

Lead causes skeletal change. Acute exposure causes kidney damage whereas chronic exposure causes interstitial nephritis. Comparing inorganic lead with organic lead, the latter is found to be more toxic because it is lipid soluble. For instance, Tetraethyl lead is readily taken up through skin to brain, causing encephalopathy. Several procedures are available to remove heavy metals from aqueous solutions and Rouse has reviewed several metals removing techniques such as neutralization, precipitation, cementation, reverse osmosis, ion-exchange and adsorption (Natarajan, 1983.). However the method to be chosen is decided largely by economical factors as well as conditions of the effluent. In the present work, the removal of lead from waste water using egg shell as an adsorbent is attempted (Rao and Datta, 1987). Though many conventional adsorbents are used for the effective removal of heavy metal ions, we have chosen egg shells as adsorbents as they are thrown as kitchen, waste materials from hotels, restaurants and hostels of schools and colleges with an aim to use waste/ pollutant as adsorbents. Trichy is an industrial area, where a large number of small scale industries is located. These industries pollute the nearby soil and ground water with lead as a heavy metal. The present work is also aimed at fixing the optimal conditions such as adsorbent size, pH, equilibrium time (for batch mode technique) etc., for effective removal of lead.

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Inter. J. Rece. Sci. Res., Vol. 2, Issue, 2, pp. 40-43, February, 2011

MATERIALS AND METHODS

Reagents

All the chemicals used in the investigation were Analar grade. They were used without further purification unless specified otherwise.

Methods

Broken burette of height about 55 Cm and a diameter of about 0.5 Cm was chosen for the study. A stopper was provided at the bottom. At the bottom, a plug of cotton was inserted. A known weight of the adsorbent (pulverized egg shells) was added in small quantities with constant tapping. Care was taken to see that the adsorbent was closely packed. A cotton plug was inserted at the top. The height of the adsorbent column was measured. Pure water was admitted through the column. After some time, the stopper was adjusted so as to maintain a constant flow rate. The lead nitrate solution of known concentration was added, after draining of water in the tube. The flow rate of the influent was maintained constant. Its concentration was determined by titration against standardized EDTA solution. Adsorption tests were conducted batch wise by taking 25 ml of lead nitrate solution with a known weight of the adsorbent in a highly stopped clean take proof corning bottles in a rotary shaking machines in a constant speed of agitation. The progress of the adsorption process was noted by removing the bottles from the rotary shaking machine at a particular interval of contact times. After removing the bottles from the shaking machine, it was kept in a water bath at room temperature for a time and then filtered. The filtrate was titrated against standardized EDTA solution. The difference between the amount of lead nitrate present initially and that of at the end of a known interval time indicated by the amount of lead nitrate adsorbed by the chosen adsorbent for different concentration of lead nitrate solution and different weight of adsorbent. The experiments were repeated and the values were noted. Lead nitrate solution of known concentration (1000 ppm) was prepared. A known volume of the solution (20 ml) was pipetted out into a leak proof bottle, its pH was adjusted from 1-9 by adding hydrochloric acid and sodium hydroxide solution.

RESULTS AND DISCUSSION

Lead pollution arises mainly from automobile exhausts. Lead battery industry, metallurgical operations and industries manufacturing lead arsenate insecticides contribute a considerable amount of lead to the environment. Gasoline containing lead alkyl derivatives causes a significant lead pollution. Lead is taken in mainly from food even though the lead content in water is lesser than that in air. Children are reported to be more susceptible to lead than adults, because children can absorb greater amount of lead from their gastro intestinal tract. It also causes kidney dysfunctions, being due to impairment of energy metabolism. Removal of lead has been widely studied using various adsorbents such as wood, charcoal, leaves rice husk, coconut shell, saw dust, etc., Egg shell was used an adsorbent in the removal of the heavy metal lead in this present work. The adsorbent was prepared from dried, crushed and powdered egg shell material and it was sieved in different sizes. This powdered material was used as an adsorbent for the removal of lead in batch mode adsorption and column adsorption studies. The adsorption capacity was determined in both the methods. Column studies were also conducted and better results were obtained. The experimental data reveal the fact that the adsorption of lead by the egg shell was found to be the maximum of 69.5%. It is shown in Table 1.

Table 1. Influence of size of adsorbent on percentage adsorption of lead

Entry	Size of the adsorbent, μm	$[Pb]_{eq,}$ ppm	$[Pb]_{ads,}$ ppm	$[Pb]_{ads,}$%
01	75	1304.4	2970.5	67.48
02	150	2198.8	2076.1	48.56
03	212	2850.3	1424.6	33.32
04	300	2653.7	1621.1	37.92

Name of adsorbent: Egg shell $[Pb]_{ini}$ ppm : 4274.9
Weight of adsorbent: 40 g Temperature,°C : 29

Table 2. Influence of size of adsorbent on percentage adsorption of lead.

Entry	Size of the adsorbent, μm	$[Pb]_{eq,}$ ppm	$[Pb]_{ads,}$ ppm	$[Pb]_{ads,}$%
01	75	2563.3	1711.6	40.03
02	150	2748.5	1526.4	35.70
03	212	2850.3	1424.6	33.32
04	300	2959.9	1315.0	30.76

Name of adsorbent: Egg shell $[Pb]_{ini}$ ppm : 4274.9
Weight of adsorbent: 2.5 g Temperature,°C : 29
Time, min : 60

Table 3. Influence of the amount on percentage adsorption of lead

Entry	Weight of the adsorbent,g	$[Pb]_{eq,}$ ppm	$[Pb]_{ads,}$ ppm	$Pb]_{ads,}$%
01	0.5	3847.0	427.1	9.90
02	1.0	3847.8	427.1	9.90
03	1.5	3664.6	610.3	14.27
04	2.0	3345.9	929.0	21.73
05	2.5	2563.3	1711.6	40.03

Name of adsorbent: Egg shell $[Pb]_{ini}$ ppm : 4274.9
Size of adsorbent, μm : 75 Temperature,°C : 29
Time, min : 60

The influence of size of the adsorbent on the lead adsorption was studied by carrying out the experiment at various sizes 75,150,212 and 300μm. The maximum

Table 5. Influence of the initial concentration of lead on percentage adsorption of lead.

Entry	$[Pb]_{initial}$,ppm, (x)	$[Pb]_{final}$,ppm (y)	$[Pb]_{ads}$, ppm (x-y)	$[Pb]_{ads}$,% [x-y /x] ×100
01	5130.5	4526.9	603.6	11.7
02	3345.9	2748.5	597.4	17.8
03	1603.3	1452.0	151.3	9.4
04	1054.2	884.6	169.6	16.1
05	687.2	569.9	121.3	17.6
06	413.7	357.9	55.8	13.5
07	280.8	227.7	53.1	18.9

Name of adsorbent: Egg shell ; Ph : 8.0; Size of adsorbent, µm : 75 ; Temperature,°C : 29; Time, min : 60 ; Weight of adsorbent,g : 2.5

Table 6. Influence of Equilibrium time on percentage adsorption of lead

Entry	Time, min	$[Pb]_{eq}$, ppm	$[Pb]_{ads}$, ppm	$[Pb]_{ads}$,%
01	10	*3847.8*	427.0	9.90
02	20	*4809.8*	534.9	12.50
03	30	*3498.1*	776.8	18.17
04	40	*3206.5*	1064.4	24.99
05	50	*2850.3*	1424.6	33.32
06	60	*2482.5*	1792.4	41.92

Name of adsorbent: Egg shell $[Pb]_{ini}$ ppm : 4274.9; Size of adsorbent, µm : 75 Temperature,°C: 29; Time, min : 60; pH : 8.0; Weight,g:2.5

Table 7. Influence of Equilibrium time on percentage adsorption of lead

Entry	Time, min	$[Pb]_{eq}$, ppm	$[Pb]_{ads}$, ppm	$[Pb]_{ads}$,%
01	10	4809.8	320.6	6.2
02	20	4526.9	603.6	11.7
03	30	4275.4	855.0	16.6
04	40	4050.4	1080.2	21.0
05	50	3847.8	1286.6	25.0
06	60	3847.8	1286.6	25.0

Name of adsorbent: Egg shell $[Pb]_{ini}$ ppm: 5130.5; Size of adsorbent, µm : 75 Temperature,°C: 29; Time, min : 60; pH : 8.0; Weight,g : 2.5

Table 8. Influence of Equilibrium time on percentage adsorption of lead

Entry	Time, min	$[Pb]_{eq}$, ppm	$[Pb]_{ads}$, ppm	$[Pb]_{ads}$,%
01	10	587.5	99.7	14.5
02	20	583.0	104.2	15.2
03	30	578.6	108.6	15.8
04	40	574.3	112.8	16.4
05	50	570.1	117.1	17.0
06	60	570.1	117.1	17.0

Name of adsorbent: Egg shell $[Pb]_{ini}$ ppm : 687.2; Size of adsorbent, µm : 75 Temperature,°C : 29; Time, min : 60; H: 8.0; Weight,g : 2.5

Table 9. Influence of Equilibrium time on percentage adsorption of lead

Entry	Time, min	$[Pb]_{eq}$, ppm	$[Pb]_{ads}$, ppm	$[Pb]_{ads}$,%
01	10	265.4	15.4	5.5
02	20	256.5	24.3	8.6
03	30	252.5	28.5	10.1
04	40	248.3	32.6	11.4
05	50	244.3	36.5	12.9
06	60	244.3	36.5	12.9

Name of adsorbent: Egg shell $[Pb]_{ini}$ ppm : 280.8; Size of adsorbent, µm : 75 Temperature,°C : 29; Time, min : 60 pH: 8.0; Weight,g: 2.5

adsorption was found to be at the size 75µm.The experimental results are shown in Table-2. This can be attributed to the fact that as the size of the adsorbent decreases, the surface area of the adsorbent increases thereby increasing he extent of adsorption. Optimum pH for adsorption studies was found by conducting experiments at various pH (1-9) and maximum adsorption was found to be around 9. Experiments were further

Table 10. Application of Loggergren's Equation to adsorption of lead

Entry	Time, min	q mg/g	$(q_e$-q)mg / g	Log $(q_e$-q)
01	10	264.8	1456.4	3.1633
02	20	264.8	1456.4	3.1633
03	30	529.6	1191.6	3.0761
04	40	794.4	926.8	2.9669
05	50	1191.6	529.6	2.7239
06	60	1721.2	0	0

Name of adsorbent: Egg shell $[Pb]_{ini}$ ppm : 4274.9;Size of adsorbent, µm : 75 ; Temperature,°C : 29; Time, min: 60; pH : 8.0; Weight,g: 2.5; q_e :1721.2 mg /g

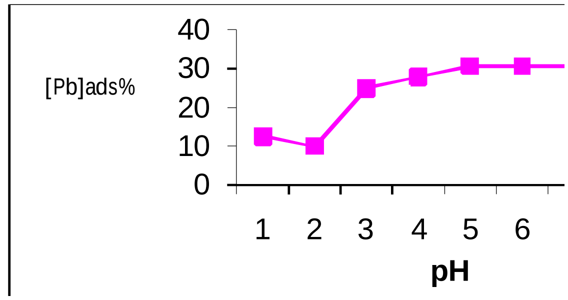

Fig .1. Influence of pH on percentage adsorption of Lead

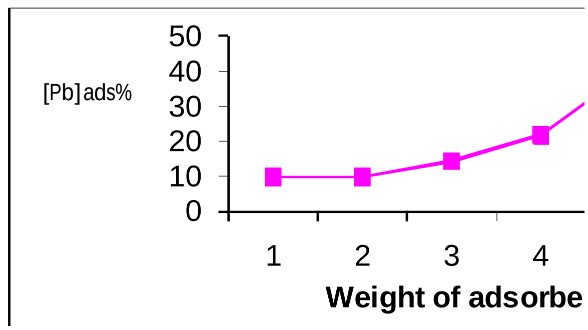

Fig.2. Influence of the amount of adsorbent on percentage adsorption of Lead

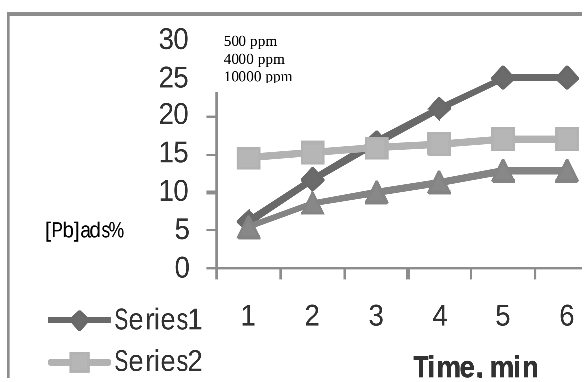

Fig .3. Plot of adsorption of Lead Vs time

carried out at this pH. The influence of PH on adsorption is represented in Table-3 and Fig.1. The effect of the weight of the adsorbent on the adsorption of lead was studied and the maximum adsorption was found to be at 250 mg /20 ml of lead. It is represented in Table-4 and

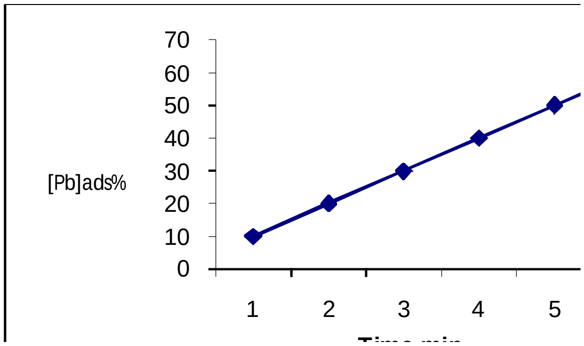

Fig .4. Laggergren's Plot for the adsorption of Lead

Fig.2. The data revealed the fact that the rate of adsorption increases with increase in the dose of the adsorbent. Effect of initial concentration of lead on adsorption was studied by carrying out the experiment at various initial concentrations around 500,1000,2000,4000 and 10,000 ppm of lead and weight of the adsorbent being around 250mg/20ml of lead. The influence of initial concentration of lead on percentage adsorption is shown in Table 5. The effect of time on the percentage of adsorption lead was studied and shown in Table 6-9 and Fig.3. It is known that this adsorbent has a capacity to remove the dissolved solute from the solution. Loggergren's equation [log $(q_e - q) = \log q_e - k_{ad}\, t /2.303$]was applied with a view to understand the nature of adsorption process. Log $(q_e - q)$ was plotted against the time and is shown in Table-10 and Fig 4. A linear relation was observed. It indicates the first order nature of adsorption process and also involves the formation of unimolecular layer adsorption. The k_{ad} calculated on the basis of Loggergren's equation and is found to be 0.008. The value was found to be with the reported value which again confirms the unimolecular layer formation and first order kinetics (Timbrell, 1979).

Conclusion

A cheap and convenient process for the removal of lead from its aqueous solution has been developed in this present investigation. This was achieved by the use of new, low cost adsorbent material, egg shell which is commonly available and economically feasible. The process of removal was found to be enhanced by increasing the dose of the adsorbent. The results were interpreted in the light of Loggergren's equation.

Acknowledgement

The author A.R thanks the Principal and the management of Sir Theagaraya College, Chennai-21 for their constant support and encouragement rendered.

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