Kinetic and Equilibrium Studies on the Removal of Copper and Zinc ions from Water using Eggshell Powder (ESP)

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Abstract—Adsorption is by far the most versatile and widely used method for the removal of pollutants due to its efficiency and ease of operation at large scale. In recent years various low-cost adsorbents derived from agricultural waste, industrial by-products or natural materials have been intensively investigated. The present work relates to the removal of Copper and Zinc ions by treatment with Eggshell powder (ESP) as an adsorbent. The adsorbent has been prepared by treatment of eggshells with NaOH. Removal has been studied at varying pH values for different times of contact, adsorbate concentrations and temperature. Removal is found to be pH dependent and maximum removal occurs at pH 3 and pH 7 for copper and zinc ions respectively, at a contact time of 210 min for both the ions. The results were found to be consistent with both Langmuir and Freundlich isotherm models. Kinetic studies show that the value of *n* (rate constant) determined at optimum pH is one within experimental error. This is further substantiated by applying the Lagergren model. Intra-particle diffusion has been studied by the Morris–Weber model and it is found to occur. Thermodynamic parameters suggest the process to be exothermic and spontaneous with increased randomness at the solid solution interface. Continuous flow column studies have also been undertaken. Desorption has been affected with 0.1M NaOH. The results suggest eggshell powder can be used as an effective adsorbent for the removal of copper and zinc ions.

Keywords—*Adsorption, Eggshell powder, kinetic, isotherm. Introduction*

I. INTRODUCTION

The presence of toxic contaminants in aqueous streams, arising from the discharge of untreated effluents into water bodies, is one of the most important environmental issues in the field of waste management [1]. Adsorption is by far the most versatile and widely used method for the removal of pollutants due to its high removal capacity and ease of operation at large scale [2]. As the current global trend towards more stringent environmental standards, technical applicability and cost-effectiveness become key factors in the selection of adsorbents for water and wastewater treatment. In recent years various low-cost adsorbents derived from agricultural waste, industrial by-products or natural materials have been extensively investigated. Several studies have been conducted to evaluate the adsorption ability of eggshell as low cost adsorbent, in artificial wastewater with mono or multi components. These studies show the effectiveness of this adsorbent in the removal of heavy metals [2,3] and other toxic compounds etc. Nevertheless, the optimization of parameters such as adsorbent dose and contact time remains [4] to be investigated. Arunlertaree et.al. [5] investigated the removal of lead from manufacturing wastewater by adsorption onto eggshell powder. They conducted batch studies at unadjusted pH, to reduce lead concentration. Later on, Park et al [6] studied the adsorption of chromium, cadmium and lead from a real electroplating wastewater treatment facility. They identified calcined eggshell as a good adsorbent for treatment of acidic wastewater with a considerable uptake for heavy metals. The present work relates to the removal of Copper and Zinc ions by treatment with Eggshell powder (ESP) as adsorbent. The effect of adsorbate concentration, contact time, pH and temperature on the removal has been studied.

II. EXPERIMENTAL

A. Preparation of the Adsorbent

Hen eggshells were procured. These were washed with distilled water several times, treated with NaOH to remove the proteinaceous matter, dried, crushed, and sieved. The particle size retained between 250-840 μm was used for the experiment.

B. Preparation of Adsorbate Solution

Stock solution of metal ions was prepared by dissolving required quantity of copper and zinc sulphate (Merck,A.R grade) in distilled water. Different initial metal ion concentrations were prepared by making suitable dilutions.

C. Batch Adsorption Studies

Batch experiments were carried out by agitating a known weight of adsorbent (250mg) placed in contact with 10mL of the metal ion solutions of different concentrations. The suspension was continuously stirred while maintaining a desired pH for a required time of contact. The effect of pH and initial metal ion concentration have been studied for the pH range 2.3-7.6 and 3-9 for copper and zinc ions respectively and for initial metal ion concentration ranging from 30 to 300mgL^{-1}, which corresponds to the concentration range of the metal ions found in effluents from related industries. The pH of the solution was adjusted by the addition of sulphuric acid and ammonium hydroxide in presence of ammonium chloride as the case may be The contact time was varied from 0.5 to 3.5 hr for all the pH values studied. The Zn^{2+} ion concentration in solution was determined titrimetrically by the reported method [7] using standard EDTA solution and Eriochrome black-T as indicator, the amount of metal ion adsorbed was subsequently calculated. To determine the concentration of Cu^{2+}ions in the solution, iodiometric titrations were carried out [7] using starch as an indicator**.** Each set of experiment was carried out in order to check the reproducibility of the results and values were found to differ by ±2% which is well within the experimental error.

D. Column Adsorption Studies

Column studies have been carried out using vertical columns[8]. A vertical column with an internal diameter of 4cm and height of 60cm was set up. The down flow mode has been used and the flow through the column was maintained using a centrifugal pump, a rotameter was employed to measure the flow. The adsorbent was packed up to a depth of 30cm in the column and the storage tank filled with copper sulphate and zinc sulphate solutions of desired concentration were passed through the column. The flow rate was adjusted to the desired value. Samples of the effluent were withdrawn at regular intervals, and analyzed for metal ion concentration. The concentration vs. time data is generated from these experiments.

III. RESULT AND DISCUSSION

A. Effect of pH

Effect of pH on the adsorption of metal ions on Eggshell powder (ESP) was determined in the pH range 2.3-7.6 and 3-9 for copper and zinc ions respectively. The study indicates that the system is strongly pH-dependent. Earlier reports have also indicated the pH dependence for maximum removal of Zn^{2+} on chemically modified rice (*Oryza sativa*) husk [8]. The amount adsorbed is maximum at pH 7 for zinc ions (Fig. 1) and pH 3 for copper (Fig. 2). Lesser removal of metal ions at lower pH in case of zinc is apparently due to the higher concentration of H^+ ions [9] present in the reaction mixture which competes with the M^{2+} ions for the adsorption sites of eggshell powder adsorbent. Decrease in sorption at pH higher than 7 is possibly due to the formation of soluble hydroxy complexes [9], while in case of copper more adsorption is due to formation of uncharged species and greater availability of adsorbing sites on adsorbent at pH 3.

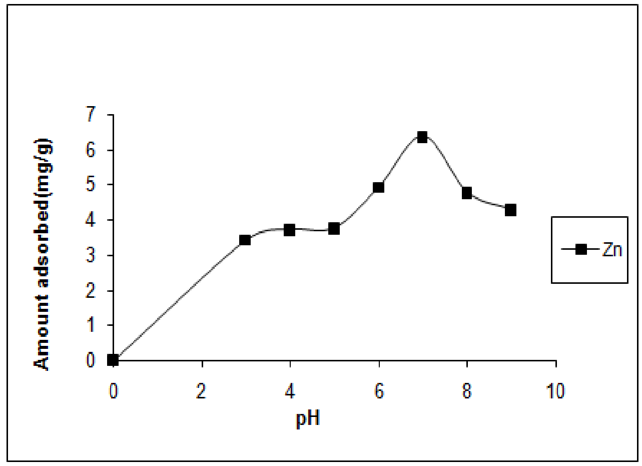

Fig. 1 Plot of amount of Zn2+ ions adsorbed on the egg shell vs different pH at final concentration of 300(mg)L)

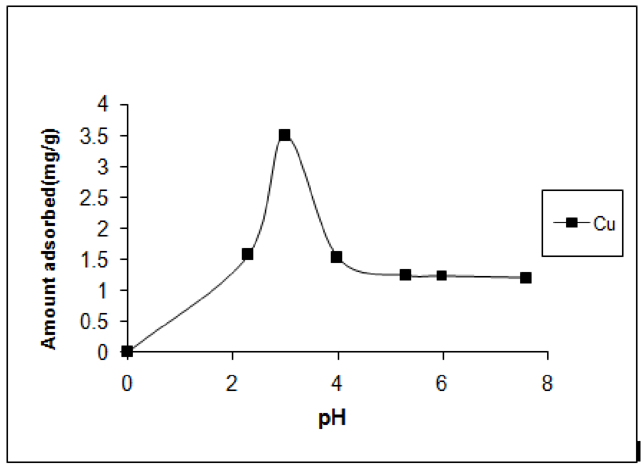

Fig. 2 Plot of amount of Cu^{2+} ions adsorbed on the egg shell vs different pH at final concentration of 300(mg)L)

B. Effect of Contact Time

Contact time is also an important factor affecting removal. Maximum adsorption occurs in the initial half hour and increases very slowly later [10]. Variation of time of contact from 0.5 to 3.5 h shows that maximum removal occurs for a contact time of 3.5h. for both the ions. A further increase in contact time tends to decrease in adsorption, probably due to desorption.

C. Effect of Initial Metal Ion Concentration

The amount of metal ions adsorbed increases with concentration (Fig. 3 and Fig.4). However, percentage removal increases with decrease in the concentration of Cu^{2+} and Zn^{2+} ions. The increase in percentage adsorption with dilution may be attributed to the availability of larger number of surface sites of the adsorbent for a relatively small number of adsorbing species at high dilution [11].

D. Adsorption Isotherm Studies

The data for the uptake of Cu^{2+} and Zn^{2+} by Eggshell powder have been analyzed by Freundlich and Langmuir isotherm models of adsorption and were found to be fitted well for both the models. The linearised form of the Freundlich equation can be given as [10]

$$\log q_e = \log K_f + 1/n \log C_e \quad (1)$$

where C_e is equilibrium concentration (mg L^{-1}) and q_e is the amount adsorbed (mg g^{-1}). The values of n and K_f were determined from slope and intercept of the linear plots of $\log q_e$ vs. $\log C_e$. The value of $1/n$ and K_f are 0.715 and 0.00692mg/g, 0.6907 and 0.074593mg/g for the Zn^{2+} and Cu^{2+} ions respectively. The values of $1 < n < 10$ indicate the effectiveness of the adsorbent [12].

The data is also consistent with the Langmuir model, the Langmuir equation may be described as

$$C_e/q_e = 1/Q_o b + C_e/Q_o \quad (2)$$

where C_e is the equilibrium concentration mgL^{-1}, q_e is the amount adsorbed at equilibrium mgg^{-1} and Q_0 and b are Langmuir constants related to adsorption capacity and energy of adsorption, respectively. The plot of C_e/q_e vs. C_e at pH 7 and pH 3 for the Zn^{2+} and Cu^{2+} ions, gives a straight line in both the cases, showing the applicability of Langmuir isotherm [12]. The applicability of the isotherm models and the high values of the correlation coefficients (R^2) suggest favorable and monolayer adsorption . The values of Q_0 as determined from the Langmuir plots are 11.035753 and 7.55287 and those for b are 0.675615 and 0.009377 for Zn^{2+} and Cu^{2+} ions respectively.

The essential characteristics of Langmuir isotherm can be described by the dimensionless parameter R_L; $R_L = 1/(1 + bC_0)$,where C_0 is the initial metal ion concentration. The factor R_L indicates whether adsorption is favourable or not. The values of R_L have been found to be between 0 and 1 which again suggests favourable adsorption [10].

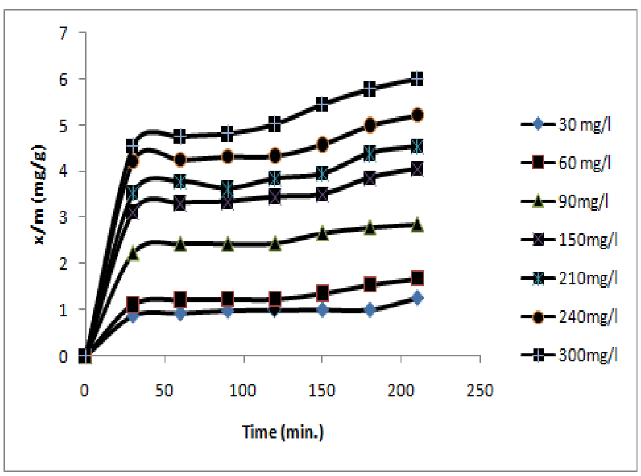

Fig. 3.Amount of Zn(II) ions adsorbed Vs contact time at different concentrations

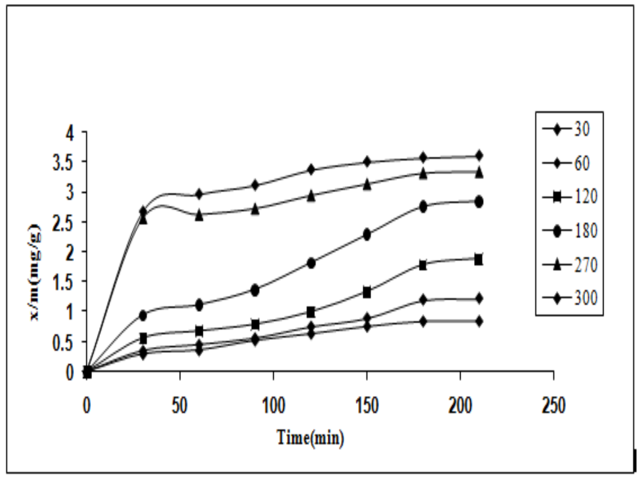

Fig. 4.Amount of Cu(II) ions adsorbed vs contact time at different concentrations at pH-3

E. Adsorption Kinetics

Kinetic studies for the adsorption of Cu^{2+} and Zn^{2+} ions on eggshell powder have been carried out by using the rate equation[13,14]

$$R = kC^n \quad (3)$$

where R is the rate of adsorption, k is the rate constant, C is the concentration and n is the order of the reaction. A plot of log R vs. log C was found to be a straight line in case of both the ions. The value of n as obtained from the slope of this plot indicates that the adsorption follows first order kinetics. The value of k has been calculated for different contact times and it is observed that the value of k decreases with increase in time of contact this may be attributed to the presence of lesser number of adsorption sites with increase in time of contact [15].

These results are further substantiated using Lagergren first-order equation [9]

$$\log (Q_e - Q_t) = \log Q_e - (K_{ad}/2.303)/t \quad (4)$$

where Q_e and Q_t (mg g^{-1}) are the amounts of metal ions adsorbed at equilibrium and at any time respectively, t (min) is the time of contact and K_{ad} the adsorption rate constant. A straight line plot obtained for $\log(Q_e - Q_t)$ vs. t indicates the applicability of first-order kinetics to the systems [9]. The rate constant K_{ad}(min^{-1}) values as obtained from plots at optimum pH are 0.013127 and 0.00942 for Zn^{2+} and Cu^{2+} respectively.

F. Intra-Particle Diffusion Study

Besides adsorption at the outer surface of the adsorbents there is also a possibility of intra-particle diffusion from the outer surface into the pores of the material [8]. The possibility was explored by plotting amount of Cu^{2+} and Zn^{2+} adsorbed per gram of adsorbent vs. $t^{1/2}$, according to Weber and Morris equation, $q_t = K_p \times t^{1/2}$ [8] where q_t is amount of Cu^{2+} and Zn^{2+} adsorbed at time t in mg g^{-1}, t is time of contact (min) and K_p is intra-particle diffusion constant (mg $g^{-1}min^{-1/2}$). The plots of q_t against time with half power (i.e. $t^{1/2}$) is a straight line which does not pass through the origin. This shows that intra-particle diffusion occurs but is not the rate determining step [8]. The K_p (mg $g^{-1}min^{-1/2}$) values at different concentrations of Cu^{2+} and Zn^{2+} ions are given in Table I .

G. Thermodynamic Studies

Effect of Temperature

The adsorption capacity of eggshell adsorbent increased with the increase in the temperature of the system from 30^0-40^0C.Thermodynamic parameter such as change in the free energy ΔG^0KJ/mol), enthalpy (ΔH^0) (KJ/mol) and entropy (ΔS^0) (J/K/mol) were determined using the following equation[12]

$$K_o = C_{solid}/C_{liquid} \quad (5)$$

(1)

$$\Delta G^0 = -RT \ln K_o \quad (6)$$

$$\log K_o = \Delta S^0/(2.303R) - \Delta H^0/(2.303RT) \quad (7)$$

Where K_0 is the equililibrium constant,C_{soild} is the solid phase concentration of equilibrium (mg/L),C_{liquid} is the liquid phase concentration at equilibrium (mg/L), T is the temperature in degree Kelvin and R is gas constant. Plots of $\ln K_o$ Vs 1/T give the values of enthalpy (ΔH^0) and entropy(ΔS^0) change from the slope and intercept of Van't Hoff plots respectively. The values of the parameter for Cu^{+2} are given in Table II.

From the results it is found that physisorption is much more favorable for the adsorption process.

The negative values of (ΔH^0) show the exothermic nature of adsorption. Because in the case of physical adsorption, while increasing the temperature of the system, the extent of ion adsorption increases, this rules out the possibility of chemisorption. The low (ΔH^0) value depicts that the ion are physisorbed onto eggshell powder.

The negative values of ΔG^0 shows the adsorption is highly favorable and spontaneous [16]. The positive value of ΔS^0 shows the increased disorder and randomness at the solid solution interface ion with eggshell, while the adsorption there is some structural changes in the Cu^{2+} ion and the adsorbent occur. The adsorbed water molecules, which have displaced by the adsorbate species, gain more translational entropy than is lost by the adsorbate molecules, thus allowing the prevalence of randomness in the system. The enhancement of adsorption capacity of the eggshell powder at higher temperatures was attributed to the enlargement of pore size and activation of the adsorbent surface.

TABLE I.

Values of Intraparticle diffusion constant for various concentrations of Zn and Cu ions in the adsoetion of metals on egg shell powder

Conc. (mg/l)	k_p(mg/g $min^{0.5}$) for Zn^{2+} ions	R^2	k_p(mg/g $min^{0.5}$) for Cu^{2+} ions	R^2
30	0.0369	0.572	0.0707	0.983
120	0.276	0.9269	0.1256	0.844
210	0.3066	0.853	0.2222	0.858
300	0.3801	0.8532	0.2032	0.995

TABLE II

Value of Thermodynamic Parameters for adsorption of Cu^{+2} ions on ESP

(1) (1)

Conc. (mg/l) (1)	Gibbs's Free energy change (1) (ΔG^0 (KJ/mol)			Enthalpy (ΔH^0) (KJ/mol)	Entropy ΔS^0 (J/ K/mol)
	Temperature				
	30^0C	35^0C	40^0C		
300	0.357821	-2.21246	-3.67192	-122.64	0.404177
240	-0.95727	-4.40177	-6.58946	-169.905	0.564579
180	-1.81378	-4.9086	-7.84975	-181.104	0.603763

H. Column studies

Column studies have been carried out for eggshell powder as adsorbent in order to study the adsorption capacity for dynamic adsorption. The break thought point can be obtained from plot of C_t/C_0 vs. t, where C_t is the concentration of effluent at any time; C_0 is the feed concentration and t is the time in hours. The break through time depends upon adsorbent, adsorbate and the operating parameters, i.e. column width, column height and flow rate. Studies have been carried out at different flow rates and it has been found that at higher flow rate due to lesser residence time of solution in bed, the mass transfer is lesser [17], i.e. lesser adsorption.

Effect of Metal Ion Concentration

In case of column studies concentrations viz. 200, 300 and 351mgL^{-1} were used in the experiment, maximum removal was observed at 200mg L^{-1} concentration for the copper ion. Removal efficiency decreases with increase in concentration of copper and zinc ions. Maximum adsorption obtained is 97.03% and 86.96% for copper and zinc ions respectively**.** This can be explained by the fact that as the concentration of ions increases, it causes an increase in number of ions coming in contact with the adsorbent during the same interval of time, whereas on the other hand the number of sites available for adsorption are constant for all concentrations. Hence at higher concentrations, the available sites for adsorption become fewer [18] hence the percentage of metal ions removed are dependent upon initial concentration.

Effect of Flow Rate

Maximum removal efficiency up to 97.03% and 86.96% for copper and zinc ions respectively has been observed when the flowrate is 1.02 L h^{-1} and decreases to 66.12 and 62.35% when the flowrate is increased to 1.38L h^{-1}.these observations may be explained on the basis that at higher flow rate due to lesser residence time of solution in bed, the mass transfer is lesser, i.e. lesser adsorption [19, 20].

I. Desorption/Regeneration of Adsorbent

For any adsorption process the recovery and regeneration of adsorbent are important factors. The adsorbed Cu^{2+} and Zn^{2+} ions can be eluted with the help of 0.1M NaOH, the recovery of the metal was to the extent of 89.33% in the first cycle and then reduced in the third cycle, the decrease in recovery may be attributed to the fact that some of the metal ions may be held to the adsorbent by stronger interactions [21] and this leads to lowering of removal efficiency. After each elution the adsorbent column was washed thoroughly with distilled water before reuse.

IV. CONCLUSIONS

Studies suggest that eggshell powder(ESP) can be effectively used as adsorbent for removal of Cu^{2+} and Zn^{2+} ions from aqueous medium. Batch adsorption studies show that removal is dependent upon process parameters like contact time, pH and metal ion concentration. Maximum removal of Cu^{2+} (to the extent of 93.63%) and Zn^{2+}(to the extent of 92.31%) takes place at pH 3 and pH 7 respectively for both the ions in 3.5 h in the concentration range 30–300mg L^{-1}. The sorption data obtained from batch studies at optimized conditions have been subjected to Freundlich and Langmuir isotherm studies and fit well to both the isotherm models indicating favourable and monolayer adsorption. The values of the Freundlich constants n and K_f and Langmuir constants Q_0 and b have been calculated. The values of $1 < n < 10$ indicate the effectiveness of the adsorbent. The dimensionless parameter R_L has also been calculated using the Langmuir constant b. The values of R_L have been found to be between 0 and 1 which again suggest favourable adsorption. The possibility of intra-particle diffusion has also been studied by using the Morris–Weber model. The effects of flow rate and metal ion concentration on the removal efficiency, in column studies, have been studied at the optimized conditions for adsorption on eggshell powder. Removal efficiency increases with decrease in flowrate and with decrease in metal ion concentration**.** Desorption has been affected with 0.1M NaOH. The results suggest eggshell powder can be used as an effective adsorbent for copper and zinc ions removal.

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