Batch and Column Studies for Removal of Cu and Zn using Industrial Solid Waste as New Adsorbent

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Abstract: Chemical industries discharge both wastewater and solid waste laden with pollutants of environmental concern. This paper explores the reutilization of industrial solid waste, 'metal oxide slag' as new adsorbent for the removal of Cu and Zn from aqueous solutions through batch and column studies at fixed conditions of room temperature, acidic pH of 3.5, 8/14mesh adsorbent particle size. Through batch studies for three batch parameters of adsorbent dosage, time of contact and initial pollutant concentration, dynamics of adsorbent capacity, pollutant removal, Isomorphic ion-exchange mechanism, Langmuir and Freundlich isotherms, Lagergren rate, Weber diffusion and Elovich chemisorption were estimated. Similarly, at fixed feed flowrate, through column studies for two column parameters of bed depth and column feed concentrations, the column dynamics of breakpoint, pollutant removal, adsorptive capacity and adsorption rate were calculated. Chemically resistant PVC pipes were used in place of traditional glass columns. Standard S-shape breakthrough curves indicated the existence of constant liquid phase driving force upto bed exhaustion. Cu removal of 92.32percent and Zn removal of 74.57percent increased with increase in bed depth but decreased with increase in the feed concentration. A scale-up designed is proposed for treating large volumes of industrial effluents based on Bohrat-Adam's correlation and critical depth.

Keywords: adsorption, industrial wastewater, Cu, Zn, heavy metal, metal oxide slag, column studies, adsorbent.

I. INTRODUCTION

The chemical manufacturing industries are considered as one of the main sources that discharge solid wastes and wastewater laden with non-biodegradable pollutants like heavy metals and refractory organics [1]. At concentrations beyond permissible limits [2], their presence has toxic effects on aquatic life and indirectly, on human health. Thus, their disposal is a serious techno–economic problem. But with changing technology in today's chemical production, the discharge has reduced over time. However, cost effective and efficient methods are being explored that can be included as a support to the existing conventional treatment methods, that aim to be simple and eco-friendly with industrial feasibility and social acceptance [3]. This has led to an intensive examination and use of adsorption process. A literature review over the past three decades, for adsorption of two heavy metals, Cu and Zn, has indicated a constant quest for effective adsorbents [4] that aimed at the reutilization of abundantly available natural wastes [5,6], agricultural wastes [7,8], domestic wastes [9,10], a few types of industrial solid wastes [11,12] or activated carbons [13]. Though these adsorbents were reported to be effective in raw form, it was observed that the adsorbent potential was improved by chemical treatment [14,15] or by modifying them through charring to carbons [16,17]. However, to fit into the economics of the treatment methods, reuse of industrial solid wastes was explored. Flyash [18] is an effective option for many pollutants including Cu [19,20] and Zn [21]. In the recent past, an increased use of flyash for other beneficial productive activities like cement bricks has further interested researchers to explore the reuse potential of other such industrial solid wastes.

II. MATERIALS AND METHODS

The solid waste adsorbent selected for the present work is a waste byproduct of a local scrap iron industry that produced iron rods for construction purposes. The characteristics of this abundantly and easily available raw solid waste are presented in table-1. Similar to flyash [22], this solid waste also contained oxides of metals like silica, alumina and iron that could provide active sites on the surface [23] and may facilitate adsorption either through surface complexation or ion-exchange and will be referred as 'metal oxide slag' in this study. In order to avoid the use of chemicals that would further add to the existing pollution condition, the study aimed to promote the direct use of such industrial solid waste as adsorbent. The hard rock like material was crushed manually with a hammer to medium sized particles, further crushed in a ball mill and sieved using Indian standard screens. Keeping in view the sludge handling problems of finer particles and also the required surface area for the experiments, optimum uniform sized particles passing through '8mesh' and retained on '14mesh', graded as 8/14mesh size, were prepared and stored in polythene bags. It was observed from the characteristics of primary treated industrial wastewater [1,2] that Zn and Cu were

among the commonly present heavy metal pollutants in industrial wastewaters of printed circuit board, metal products, electroplating industries, to name a few.

The studies were carried out at industrial discharge conditions of room temperature and an acidic pH of 3.5 and their change was monitored until equilibrium. Such information would help in treating industrial wastewater at their existing discharge conditions of temperature, pH and pollutant concentrations.

Table-1: Significant adsorbent characteristics of 'metal oxide slag'.

	Metal oxide slag	Flyash
Characteristics	Present work	[24]
Physical and proximity analysis		
Particle bulk density, ρ_p (gm/cc)	2.053	—
Surface area, A_w, (m^2/gm)	11.096x10^{-4}	<2.0
Particle porosity, ε_p	0.42	—
Particle diameter, d_p, mm	1.765	+125μ
Chemical analysis (%)		
Loss on ignition (T=550°C)	33.5	26-30
Silica (SiO$_2$)	40.13	45-50
Alumina (Al$_2$O$_3$)	19.79	23-26
Iron (Fe$_2$O$_3$)	6.214	2-3
Calcium (CaO)	0.636	0.2-1.0
Sodium (Na$_2$O)	1.62	—
Magnesium (MgO)	0.752	0.05-0.5
Titanium (TiO$_2$)	—	0.5-1.5
Others	remaining	—

Batch experiments

A series of batch tests were carried out with laboratory prepared aqueous samples of the selected heavy metals Cu and Zn separately. From a standard stock solution, three different initial concentrations of 10mg/lit, 30mg/lit and 50mg/lit were prepared and studied. It was observed that the dosages of 8/14mesh size particles could not be measured as a mathematical round figure. Hence, the identified dosages were of 12gms, 23gms, 32gms and 41gms. Specific amount of the adsorbent was added and the test was continued for 3 hrs time to ensure equilibrium [5]. For reference, a blank test was also carried out using an equivalent dosage added to 100ml of distilled water and monitored for change in pH and for any seepage. The progress of adsorption in each batch sample was monitored upto equilibrium condition, at regular intervals of 15min of contact time. Experiments were conducted in duplicates for consistency. After use, the spent adsorbent or sludge laden with the adsorbed ions being considered hazardous, was further tested for any possibility of desorption or leaching under normal conditions. The sludge did not reflect any considerable desorption and however, was to be disposed by general procedure of TSDF (Treatment, Storage and Disposal Facility) for hazardous wastes. Other disposal options may also be explored.

Column experiments

Large volumes of wastewater discharged from industries are to be treated on continuous basis. So, a continuous flow adsorption system has to be designed. Packed bed columns are commonly preferred [34] for fixing the optimum column parameters and based on the obtained results, a scale-up design may be suggested for industrial application. The column studies aimed at two significant design objectives: a minimum contact time and maximum life of the adsorbent bed [25]. Laboratory prepared single component aqueous solutions of Cu and Zn were helpful to avoid interference. A series of column experiments were carried out at a fixed column feed flowrate of 20ml/min, while changing the column parameters of bed depth and feed concentrations. Accordingly, the feed concentrations for Cu were 5mg/lit, 10mg/lit and 15mg/lit and that of Zn were 10mg/lit, 20mg/lit and 30mg/lit. The volume throughput and remaining ion concentration were monitored upto column breakthrough condition using AAS. The results were analyzed for the column breakpoint, extent of removal, adsorptive capacity, rate of adsorption and critical bed depth.

Fixed bed columns

For large scale commercial application, fragile glass columns demand high installation and maintenance costs while glass-lined columns are expensive. With a view to promote the packed bed columns as cost effective systems for industries, an attempt was made through the present study to look for economic alternatives for glass columns. Chemically resistant hollow PVC pipes were available easily, unbreakable and were also comparatively economic. Hence standard PVC pipes of 4.6cm inner diameter, 2mm wall thickness and 60cm length were used for constructing the required columns. A large plastic container was positioned at a higher elevation as a feed tank and a volumetric feed flowrate of 20ml/min was made possible. No pump was used for feeding the column. For the column diameter of 4.6cm, a column feed flowrate was calculated as 1.2ml/min-cm^2. Three different bed depths [23,26] of 20cm, 30cm and

40cm, were designed for the column experiments. Separate experiments were carried out for each heavy metal solution taken at three different feed concentrations. Experiments were conducted in duplicates for consistency.

III. RESULTS AND DISCUSSION

The adsorptive potential of the industrial solid waste, 'metal oxide slag', as a new adsorbent for the removal of selected heavy metals, Cu and Zn, was estimated through these series of batch and column studies.

Batch studies

The effect of batch parameters: adsorbent dosage, time of contact and initial concentration of Cu and Zn was analyzed for their percent removal. Further, the adsorption behavior was analyzed through Langmuir and Freundlich isotherms, Lagergren's adsorption rate expression, Weber's intraparticle pore diffusion model and the kinetics of chemisorption was evaluated using Elovich rate equation.
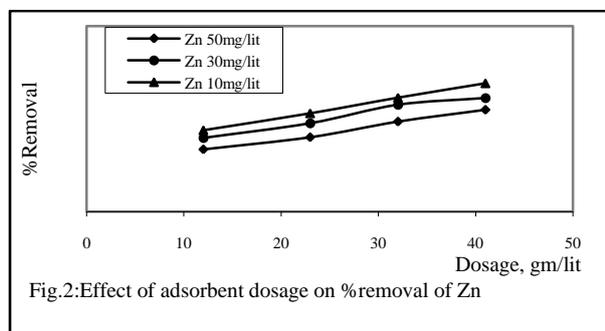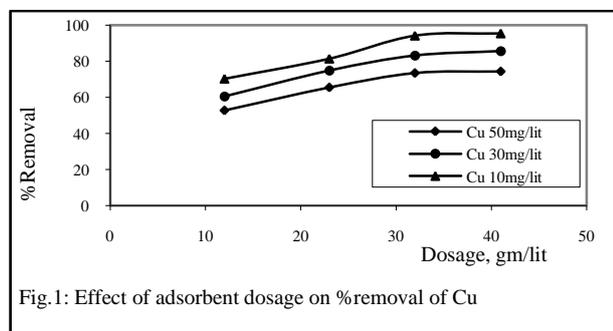
Effect of adsorbent dosage

Initial screening tests were carried out using different approximate adsorbent dosages of 12gms, 23gms, 32gms and 41gms and an optimum dosage was identified for carrying out the remaining batch experiments. The results are presented in table-2 for both Cu and Zn. The change in pH of the samples was also monitored upto equilibrium and mentioned in the table. For Cu removal, comparatively, a higher quantity of 41gm gave only a marginal increase in the percent removal as compared to that of the nearest dosage of 32gm. Similarly, for Zn removal, a maximum adsorbent dosage of 41gm gave an appreciable removal. But, keeping in view the bulk density of the adsorbent (2.053gm/cc), related sludge disposal problems and the observed trend in the percent removal for the studied dosages, experiments beyond a dosage of 41gm/lit were not carried out.

Table-2: Effect of dosage and initial concentration on equilibrium removal and pH change.

Dosage, gm/lit.	Percent removal at equilibrium			Selection of dosage
	At C_i = 50mg/lit	At C_i = 30mg/lit	At C_i = 10mg/lit	
Cu, pH variation - initial 3.52 to 5.07 at equilibrium				
12	52.84	60.51	70.24	Less
23	65.48	74.89	81.42	Less
32	**73.53**	**83.27**	**94.23**	**Optimum**
41	74.34	85.73	95.41	Excess
Zn, pH variation - initial 3.54 to 6.27 at equilibrium				
12	33.56	39.74	43.91	Less
23	40.13	47.62	52.97	Less
32	48.53	57.59	61.35	Less
41	**54.87**	**61.32**	**69.11**	**Selected**

For a fixed initial concentration, the increase in the percent removal with increase in the dosage is shown in fig.1(Cu) and fig.2(Zn).

Fig.1: Effect of adsorbent dosage on %removal of Cu

Fig.2:Effect of adsorbent dosage on %removal of Zn

Effect of contact time

The effect of contact time on the amount adsorbed upto equilibrium are shown in fig.3(Cu) and fig.4(Zn), as a comparison for the three initial concentrations studied. Smooth and continuous curves suggest a monolayer [27] formation on the adsorbent surface. During the initial time of contact, a linear curve indicated an appreciable rate of adsorption at the readily available adsorption sites and is the rapid adsorption stage. The second stage was of non-linear decreasing trend where the ions may have tried to reach the adsorption sites that existed in the inner pores of the adsorbent and thus was slow diffusion stage. The third part of the curve is almost parallel to the horizontal axis with no significant change in adsorption due to the diminishing driving force of the concentration gradient of the ions in the batch sample. This was the equilibrium stage. The batch studies at low initial concentrations have attained equilibrium earlier than at higher initial concentrations.
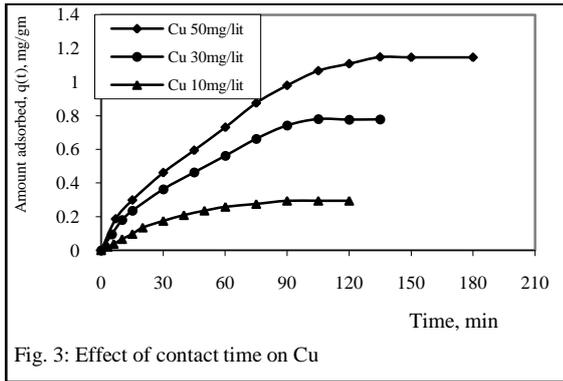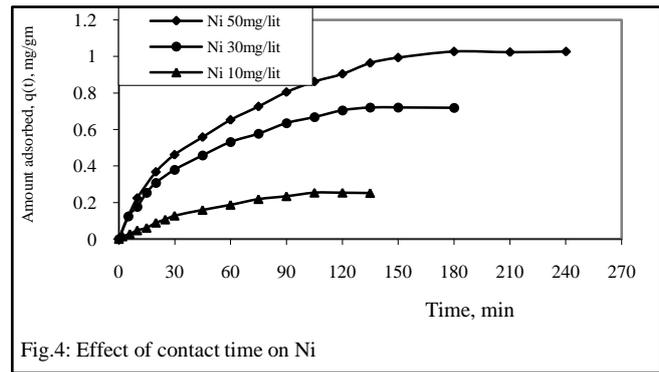
Fig. 3: Effect of contact time on Cu

Fig.4: Effect of contact time on Ni

Effect of initial concentration

The percent removal of the heavy metal ions at the three initial concentrations studied, was calculated from the test results and presented in fig.5(Cu) and fig.6(Zn).
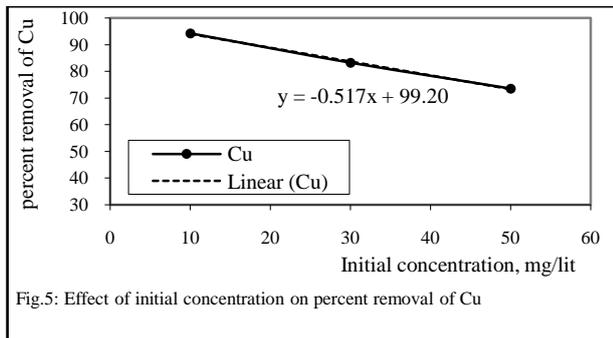

Fig.5: Effect of initial concentration on percent removal of Cu
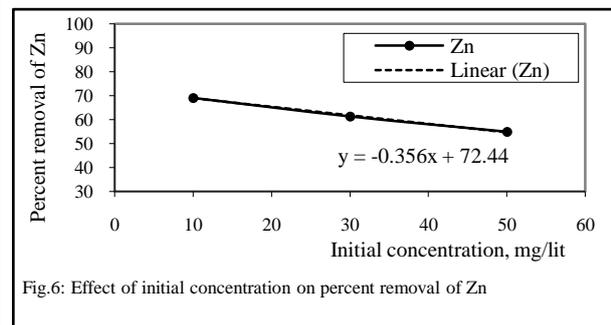

Fig.6: Effect of initial concentration on percent removal of Zn

At low initial concentration of 10mg/lit, equilibrium Cu removal was 94.23percent and that of Zn was only 69.11 percent with increase in initial concentration, the removal had decreased.

An attempt was made to correlate the non-linear removal trend, empirically [28]. The correlation for Cu removal could be explained by first order as:

$$\text{Percent removal} = - (0.517)\, C_i + 99.20$$

Similarly, the correlation for Zn removal could be fit to a
first order relation as:

$$\text{Percent removal} = - 0.356 C_i + 72.44$$

In either case study, a negative slope indicated a decrease in the percent removal of the ions with an increase in the initial concentration. These equations would be helpful to theoretically predict the possible removal at other initial concentrations, under approximately similar batch conditions.

Adsorption mechanism

If any adsorbent surface contains active sites, then in an aqueous medium the cations can undergo ion-exchange or can form surface complexes. Adsorption may be by interaction with anions that have free electrons or through electrostatic bonding or covalent bonding or isomorphic exchange of ions [27]. The characteristics of the adsorbent 'metal oxide slag' as presented in table-1 show the presence of double oxides of Si and Al along with small amounts of Fe, Ca and Na on the surface that promote the adsorption through coulomb forces. The presence of chloride (Cl^-) and sulphite (SO_3^-) groups further support isomorphic exchange of ions. In an aqueous solution, under acidic pH conditions, the inorganic cations like Ca and Na can undergo dissociation and move into the bulk aqueous medium simultaneously replace their position with that of heavy metal complex ions from liquid phase, by isomorphic ion-exchange. This would facilitate the adsorption and fixation of the complex ions. In the present study, the dissolution of CaO from 'metal oxide slag' through hydrolysis, at the initial acidic pH 3.5 was sufficient to cause the observed pH variation during the batch process. Such a variation could be explained by observing the chemistry between the adsorbed ions and the surface characteristics of the adsorbent. The mobility of the ions from the aqueous medium onto the solid surface is generally through coagulation [28] and depends on their existence in free or complex form.

The dissolution of CaO may be of the form:

$$CaO + H_2O \rightarrow Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$$

Similarly, the hydroxylate surface of the oxide sites of Si, Al or Fe may undergo amphoteric dissociation as:

$$[-M-O-]^{2-} \quad + \quad H_2O \quad \xrightarrow{\;H^+\;} \quad [-M-O-]^+ \quad\quad OH^-$$
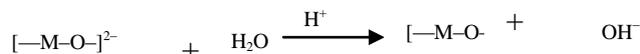
Cu adsorption

Depending on the pH condition, the divalent cation of Cu exists as complex [27] of the type $[Cu(OH)]^+$ through partial hydrolysis. The active oxide ends of the adsorbent may form surface complexes with the Cu complexes through electrostatic attraction as:
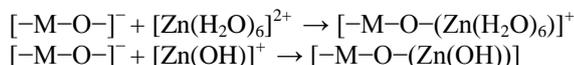
$$[-M-O-]^- + Cu(OH)^+ \rightarrow [-M-O-Cu(OH)]$$
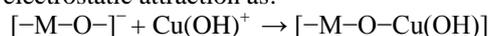
Simultaneously, there could be a possibility of inorganic oxide of Na^+ present on the surface of 'metal oxide slag', $[-Su-Na^+]$, to undergo isomorphic exchange of ions with $[Cu(OH)]^+$ complex ions in the aqueous solution. They may thus get fixed on the surface, simultaneously releasing Na^+ ions into the aqueous batch solution. This mechanism may be explained as:

$$[-Su-Na^+] + [Cu(OH)]^+ \rightarrow [-Su-(Cu(OH))^+] + Na^+$$
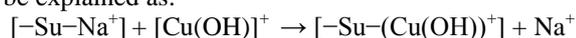
Zn adsorption

At acidic pH, the divalent cation of Zn exists as complexes [27] of the type: $[Zn(OH)]^+$ or $[Zn(H_2O)_6]^{2+}$ through partial hydrolysis. The active oxide ends of the adsorbent surface may form surface complexes with the Zn complexes through electrostatic attraction as:

$$[-M-O-]^- + [Zn(H_2O)_6]^{2+} \rightarrow [-M-O-(Zn(H_2O)_6)]^+$$
$$[-M-O-]^- + [Zn(OH)]^+ \rightarrow [-M-O-(Zn(OH))]$$

The possible adsorption mechanism on the surface of 'metal oxide slag' due to the presence of inorganic oxide of Na^+ may be represented by a simple formula as: $[-Su-Na^+]$. There could be a possibility of an isomorphic exchange of the Zn complex ions so as to get fixed on the surface, simultaneously releasing Na^+ ions into the aqueous batch solution. The presence of sulphite $(SO_3)^{2-}$ groups in the 'metal oxide slag' further supports the ion-exchange as:

$$[-Su-Na^+] + [Zn(H_2O)_6]^{2+} \rightarrow [-Su-(Zn(H_2O)_6)^+] + Na^+$$
$$[-Su-Na^+] + Zn(OH)^+ \rightarrow [-Su-(Zn(OH))^+] + Na^+$$
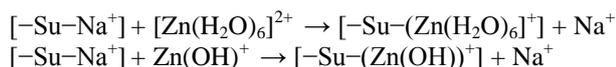
Adsorption isotherms

Adsorption isotherms are equilibrium relationship between the adsorbate concentration in the fluid phase (bulk solution) and that in the lesser solid phase (adsorbent particle) at a given temperature. For liquids, the remaining solute concentration in the solution provides an approximate estimation of the adsorptive capacity of the adsorbent.

Langmuir adsorption isotherm model:

Langmuir's Isotherm model indicates a basis that there are fixed number of active sites on the adsorbent surface [29]. For an easy graphical analysis, the equation is used in the double reciprocal form related as:

$$\frac{1}{q_e} = \left(\frac{1}{Q.b}\right)\frac{1}{C_e} + \frac{1}{Q}$$

Here, it has been applied to understand the monolayer, non-interactive binding mechanism by relating the degree of adsorption with the equilibrium condition and shown in fig.7(Cu) and fig.8(Zn). The resultant curve was fit to a straight line.
For Cu, as shown in fig.7, from the curve fit to a straight line, the monolayer adsorptive capacity, 'Q' was s 1.15mg/gm.

$$\frac{1}{q_e} = (1.462)\frac{1}{C_e} + 0.870$$

For Zn, as shown in fig.8, from the curve fit to a straight line, 'Q' was calculated as 1.21mg/gm.

$$\frac{1}{q_e} = (15.78)\frac{1}{C_e} + 0.828$$

In either of the case study, in comparison to the results of reported literature as shown in table-3, the removal of both Cu and Zn were appreciable. Similarly, a low value of 'b' of 0.06lit/gm that was close to zero had indicated a lesser demand of energy in order to facilitate the removal during the batch adsorption process.
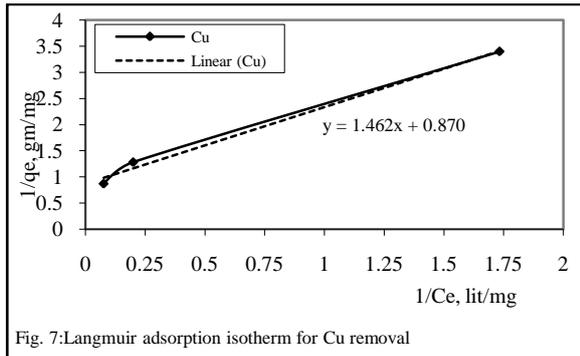
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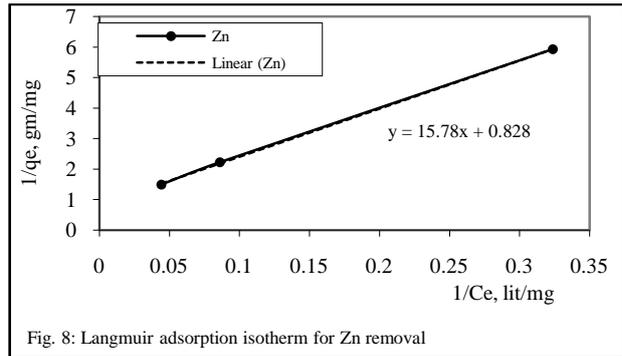
Fig. 7:Langmuir adsorption isotherm for Cu removal

Fig. 8: Langmuir adsorption isotherm for Zn removal

Further, the separation factor which explains the potential of the adsorbent, was observed to be in the range of $0<R_L<1$ thus indicating favorable adsorption of Cu and Zn at their batch conditions.

Freundlich adsorption isotherm model:

The possibility of multilayer adsorption phenomenon of solute from liquid phase on to the adsorbent surface was understood by the Freundlich isotherm model. The relation at equilibrium was expressed as:

$$q_e = k_f (C_e)^{\frac{1}{n}}$$

Here, 'k_f' is the multilayer adsorptive capacity, $[(mg/gm)/(mg/lit)^{1/n}]$ or simply (mg/gm) while '1/n' is the intensity of the adsorption process referring to the heat of adsorption. This relation has been applied for the batch tests as shown in fig.9(Cu) and fig.10(Zn). The resultant curve was fit to a power equation.

For Cu, as shown in fig.9, the curve was fit to a power equation of the form:

$$q_e = 0.377(C_e)^{0.437}$$

According to Freundlich, 'k_f' of 0.377mg/gm, a value less than 1.0, indicated a possibility of multilayer adsorption. The intensity of the adsorption process, '1/n' read as 0.437 has indicated 'n' value of 2.288 within the required range of 2.0 and 10.0. Hence, Cu complex may be easily formed inside the pores of the adsorbent which explains the observed high removal.
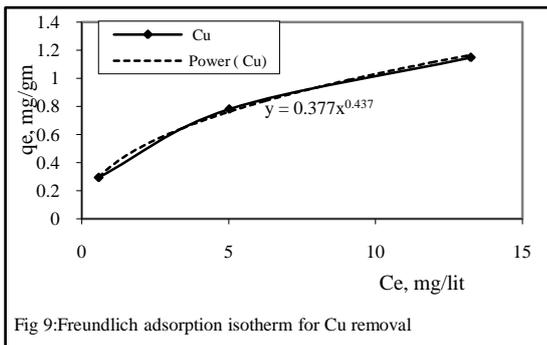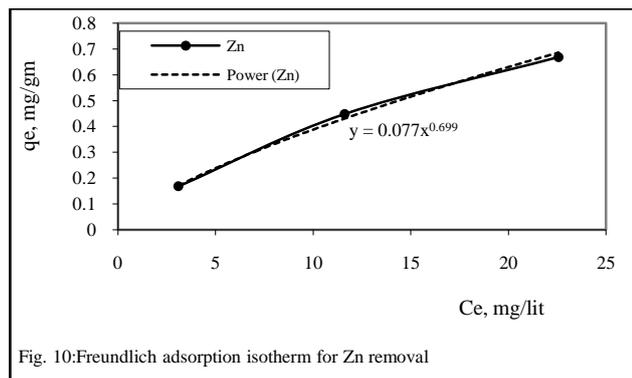

Fig 9:Freundlich adsorption isotherm for Cu removal

Fig. 10:Freundlich adsorption isotherm for Zn removal

Similarly, for Zn, as shown in fig.10, the curve was fit to a power equation of the form:

$$q_e = 0.077(C_e)^{0.699}$$

A very low value of 'k_f', 0.077mg/gm, close to zero had indicated that multilayer adsorption was more predominant during the adsorption process. The intensity of adsorption process, '1/n' read as 0.699. The reciprocal 'n' of 1.431 was very low value below the actual range of 2.0 to 10.0 and indicates heterogeneous adsorption. From the above discussion, it could be concluded that during the initial period of contact, the driving force for surface adsorption from the batch sample was high as explained by Langmuir isotherm. As the process approached equilibrium, the adsorption process slowed down indicating a possibility of porous diffusion, as explained by Freundlich isotherm.

Adsorption dynamics

Adsorption takes place as a result of solvent motivated forces that relate to surface tension or adsorbent motivated forces that combine chemical, electrostatic and physical interactions between adsorbate and adsorbent surface [27] or may be driven by a combination of both types of forces. In order to promote adsorption as a unit operation, the two important physicochemical aspects for parameter evaluation of the process are rate of sorption and equilibrium time of
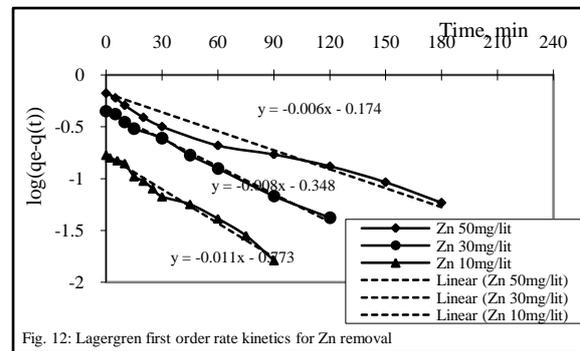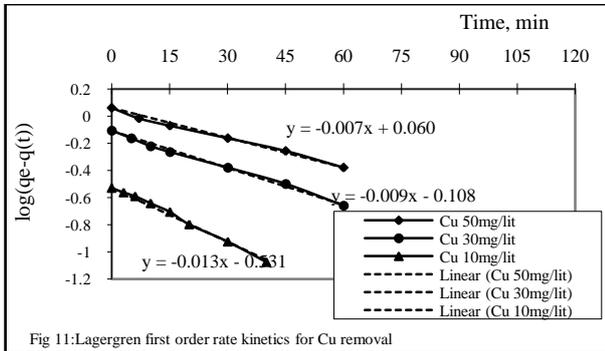
sorption. The rate of sorption describes the efficiency of solute uptake with reference to the time allowed for contact between the solid adsorbent and the adsorbate in the bulk liquid. Similarly, the equilibrium time defines the speed of sorption. The adsorption rate constant was estimated using Lagergren's first order rate expression, the possibility of pore diffusion was studied with Weber's relation and a possibility of chemisorption was evaluated using Elovich rate equation.

Lagergren's adsorption rate expression

The Lagergren's first order rate expression [30] was applied to understand the adsorption rate in batch studies. Accordingly, a linear curve suggests the adsorbate uptake to be of first order. For a perfect fit, the intercept read from the graph is supposed to be the same as that estimated from batch studies. The rate of adsorption should vary as the first power of concentration for a strict surface adsorption. However, the relationship between initial solute concentration and rate of adsorption will not be linear when pore diffusion limits the process. The batch experimental data were plotted as a comparison for all the three different initial concentrations and shown in fig.11(Cu) and fig.12(Zn).

$$\frac{(q_e - q)}{q_e} = e^{-k_1 t}$$

Only during the first half time of contact, the curves were linear, for both Cu and Zn, indicating a possibility of instantaneous adsorption and 'k_1', was as an average of $0.02 min^{-1}$. But a change to non-linearity after first half time of contact could be due to the ions adsorbed on the surface trying to reach the active sites inside the pores of the adsorbent thus indicating the possibility of pore diffusion towards equilibrium.


Fig 11:Lagergren first order rate kinetics for Cu removal

Fig. 12: Lagergren first order rate kinetics for Zn removal

Weber's intraparticle pore diffusion model

Adsorption generally starts on the outer surface of the adsorbent, through boundary (film) diffusion. Besides, there is a possibility of intraparticle diffusion of the adsorbate ions from the bulk of the outer surface into the pores of the adsorbent. Freundlich isotherm model also explains such a phenomenon. In order to understand the rate controlling parameters of the adsorption process, the Weber's Intraparticle Pore Diffusion Model [31] was applied as shown in fig.13(Cu) and fig.14(Zn):

$$q = k_p \sqrt{t} \ .$$

Here, the intraparticle transport rate constant, mg/gm-min$^{-\frac{1}{2}}$ is helpful to understand the rate controlling parameters of the process.

Fig .15: Intraparticle diffusion plot for Cu removal

Fig.14:Intraparticle diffusion plot for Ni removal
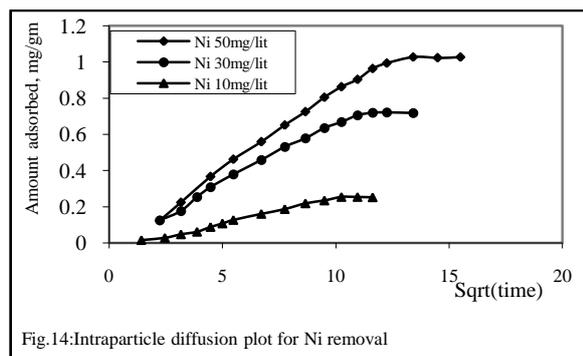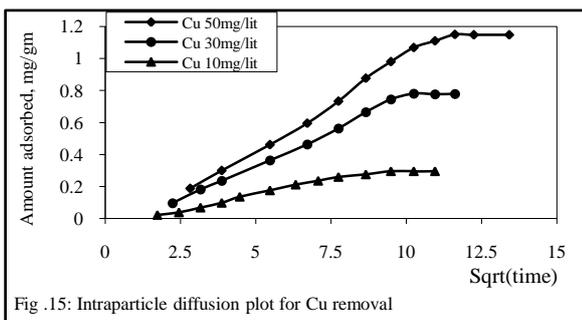
If the adsorption process was controlled only by the intraparticle diffusion, then the plot will be linear passing through the origin. Else, the existing intraparticle diffusion is not the only rate determining step. The rate constant cannot be estimated directly from the plots. Then the nature of the diffusion process can be further understood by calculating the 'coefficient of intraparticle pore diffusion' (D_p), using Michelsen's equation [32] where for pore diffusion to be predominant, D_p should be very low value of the order of 10^{-11} cm^2/sec.

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$$D_p = \frac{0.03r^2}{t_{\frac{1}{2}}}$$

In the present study, both for Cu from fig.13 and for Zn from fig.14, it was observed that only during the first half time of contact, the plots were linear but did not pass through the origin clearly indicating the dominance of boundary (film) diffusion on the adsorbent surface. As the process approached equilibrium, the nonlinearity in the curve clarified the possibility of intraparticle diffusion. 'D_p' for Cu was calculated as 2.0×10^{-4} cm^2/sec and for Zn 1.56×10^{-4} cm^2/sec indicating boundary (film) diffusion.
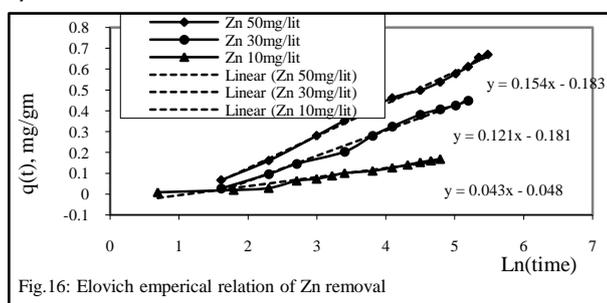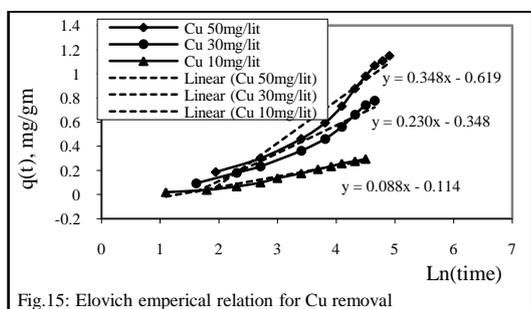
Table-3: Comparison of adsorption dynamics for removal of Cu and Zn by batch studies

Wastewater type	Adsorbent type	m (g/m/lit)	C_i (mg/lit)	pH	Q (mg/gm)	k_f (mg/gm)	k_1 (min^{-1})	D_p (cm^2/sec)	rem (%)	Ref
Cu removal										
Synthetic	**metal oxide slag**	32	10	3.5	1.15	0.377	0.021	0.0002	**94.23**	
Synthetic	flyash	1	500	5	—	2.23×10^{-12}	—	—	29.5	[19]
Synthetic	chemically activated Sawdust	90	60	4	—	0.00012	—	—	98.3	[15]
Synthetic	flyash	100	500	5	7.5	—	—	—	95	[24]
Zn removal										
Synthetic	**metal oxide slag**	41	10	3.5	1.21	0.077	0.018	0.00016	**69.11**	
Synthetic	flyash	100	500	5	3.4	—	—	—	95	[24]

Possibility of chemisorption using Elovich equation

The possibility of chemisorption was theoretically analyzed by applying the linear Elovich equation [33]. Fig.15(Cu) and fig.16(Zn) show a comparison for the different initial concentrations studied. Accordingly, for chemisorption to be significant the experimental data are to fit to a straight line that will have a positive intercept (greater than zero).

$$q = (-\frac{1}{\beta}Ln(t) + Ln(\alpha\beta))$$

Fig.15: Elovich emperical relation for Cu removal

Fig.16: Elovich emperical relation of Zn removal

But, in the present study, the curves were linear only during the initial period of one hour of contact and the intercept was not positive. The calculated values of α and β had decreased with increase in the initial concentration which indicated that there was no significant chemisorption between the heavy metal ions and the adsorbent 'metal oxide slag'. This was further evident from the low value of the product of the empirical constants, αβ, which was actually to be very high if the adsorption process was to indicate chemisorption.

Column studies

A series of column experiments were carried out in order to understand the effect of column parameters like bed depth (20cm, 30cm and 40cm); column feed concentrations (05mg/lit to 30mg/lit) at fixed column feed flowrate of 1.2ml/min-cm^2. At similar column operating conditions, the experimental results were analyzed for column breakpoint, percent removal of Cu and Zn, adsorptive capacity of 'metal oxide slag' in the column and interfacial adsorption rate.
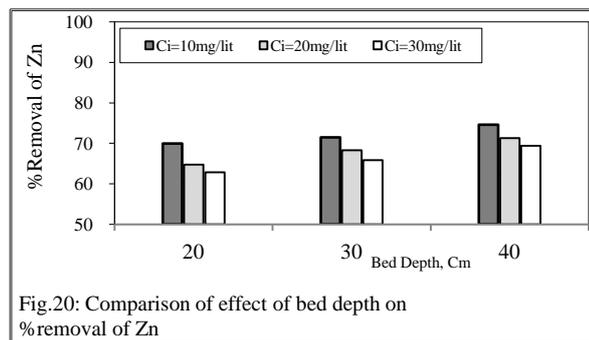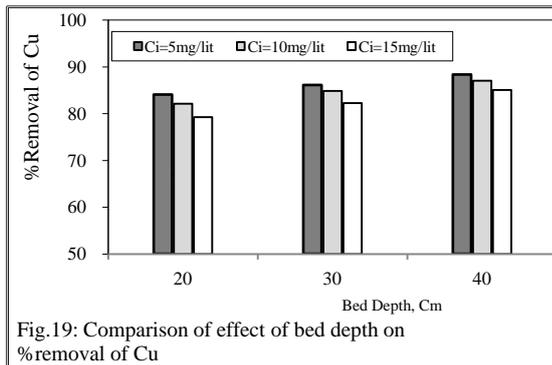
Construction of Breakthrough Curves

During column adsorption, the concentration of the adsorbate in the continuous liquid phase and the constant solid phase change with time as well as with the position in the bed [25]. Initially, most of the mass transfer takes place near the column inlet where the liquid contacts with fresh adsorbent.

As the liquid percolates, the decrease is observed with the distance traversed in the bed essentially to the maximum possible low value towards the end of the bed. The column experimental data were analyzed to understand the adsorbate-adsorbent behavior through breakthrough curves. Such studies are helpful to predict the related parameters for scale-up design. The breakthrough curves were compared for the three bed depths studied at column feed flowrate of 1.2ml/min-cm^2 as shown in fig.17(Cu) and fig.18(Zn). A similar trend was observed for higher initial concentrations also.

Fig.17: Breakthrough curves for removal of **Cu** at 5mg/lit

Fig.18: Breakthrough curves for **Zn** removal at **10mg/lit**
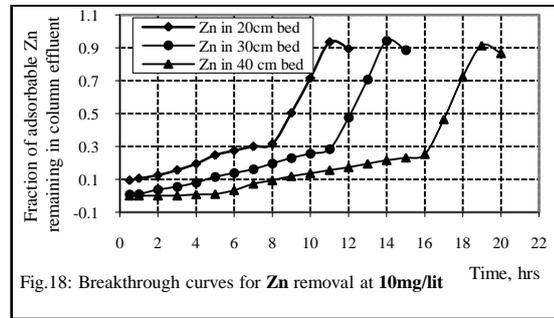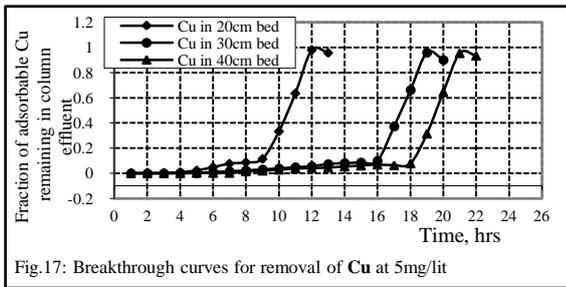
A constant wave pattern or a standard S-shape of all the curves had indicated the existence of a constant liquid phase driving force through the column till bed exhaustion condition. It was also observed that for a fixed feed concentration the time in which the column attained breakthrough condition has increased with increase in bed depth. This could be due to the availability of more amount of the adsorbent in the columns at higher bed depths. It is to be understood that a pollution problem is not considered to have been solved by merely transferring the pollutants from one phase of the ecosystem into another and still lurk on the final disposal problem. Hence, though a still higher bed depth could further increase the removal with an intention to reduce the production of final sludge further column bed depths were not studied.

Effect of feed concentration on pollutant removal at breakpoint

Fig.19: Comparison of effect of bed depth on %removal of Cu

Fig.20: Comparison of effect of bed depth on %removal of Zn

An increase in percent removal of Cu and Zn with increase in the bed depth are shown as a comparison for three different column feed concentrations studied, in fig.19(Cu) and fig.20(Zn).

At low column feed concentration of 5mg/lit of Cu, in comparison to the permissible limit of 2.0mg/lit, a removal of 88.54percent was achieved at breakthrough condition, using a 20cm bed. As the bed depth was increased to 30cm and 40cm, the removal increased to 90.08percent and **92.32percent** respectively. Similarly, with studies on Zn, in comparison to the permissible limit of 5.0mg/lit, a removal of 69.92percent was achieved at breakthrough condition with a 20cm bed. As the bed depth was increased to 30cm and 40cm, the removal also increased to 71.44percent and **74.57percent** respectively. However, for a fixed bed depth, the percent removal had decreased with increase in the column feed concentration, indicating a demand for higher amount of the adsorbent.

BDST curves and analysis of breakthrough condition

The experimental data obtained by simple laboratory scale column studies was analyzed to estimate the adsorptive capacity, N_0, of the 'metal oxide slag' in the column, using simple quantitative model proposed by Bohart-Adam [25] based on surface rate theory. Hutchins [34] introduced a graphical approach called 'bed depth-service time' (BDST) model to describe the movement of adsorption zone through the packed bed, defined as:

$$t_b = (\frac{N_0}{C_i v})X - \frac{1}{KC_i} Ln(\frac{C_i}{C_b} - 1)$$

Thus, the total service time of the bed, t_b, for the bed depths studied are shown in fig.21(Cu) and fig.22(Zn) as a comparison for the three different column feed concentrations studied.

Fig.21: BDST curves for removal of Cu

Fig.22: BDST curves for removal of Zn
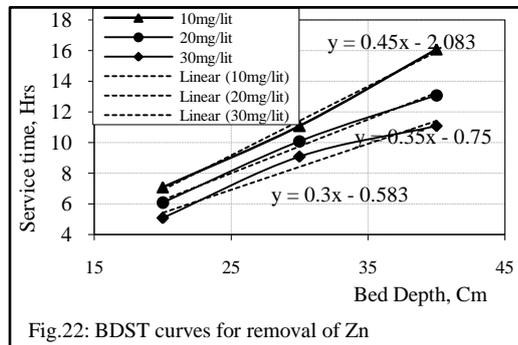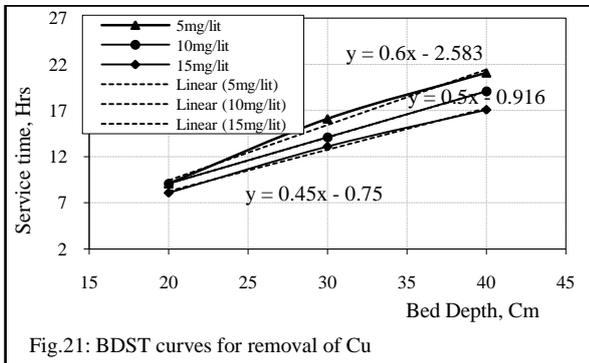
The linear curves were indicative of the applicability of the model. They were analyzed for estimating the adsorptive capacity N_0 mg/lit, the amount of heavy metal ions adsorbed in the bed, q mg/gm, adsorption rate constant K lit/gm-hr and critical bed depth X_c cm.

For a low Cu feed concentration of 5mg/lit, the calculated N_0 was 216.6mg/lit and 'q' was 0.281mg/gm. Similarly, for a low Zn feed concentration of 10mg/lit, the calculated 'N_0' was 324.9mg/lit and 'q' was 0.262mg/gm. In either case, these values were observed to increase with increase in the feed concentrations studied. An average adsorption rate constant 'K' of Cu was estimated as 0.175lit/mg-hr and for Zn it was 0.0306lit/mg-hr. A low value less than 1.0 was indicative of a non-linear adsorption trend at the solid-liquid-interface in the column.

Scale-up calculations

The estimated N_0 and K, collectively referred as Bohart-Adam's coefficients, are used to estimate critical bed depth, X_c. It is theoretical bed depth that is just sufficient to prevent penetration of a concentration excess of the permissible limit (P.L) of that solute, through a bed at zero time [25]. Under similar operating conditions of column feed flowrate, column feed concentration and bed depths, the critical bed depth, X_c for Cu was estimated as 35.93cm and for Zn it was 8.37cm.

These values help in predicting the possible breakpoint of higher bed depths for treating large volumes of industry discharged wastewater under similar column. Such large columns packed with large mass of the adsorbent are to be designed and studied at pilot plant level. At the same time, the distribution of the feed stream on the cross-section of the bed should be uniform. Hence, such columns are to be designed with a higher ratio of bed depth to bed diameter based on the results obtained from pilot plant columns.

Table-4: Comparison of column dynamics for the removal of Cu and Zn from single component synthetic wastewater

Ion	Adsorbent	X	column dia	W	Feed flow	feed pH	C_i	C_b	N_0	q	Removal	ref
		cm	cm	gms	ml/min		mg/lit	mg/lit	mg/lit	mg/gm	%	
Cu	metal oxide slag	40	4.3	960	20	3.5	5	0.384	216.6	0.122	92.32	-
Zn	metal oxide slag	40	4.3	960	20	3.5	10	2.543	324.9	0.15	74.57	-
Zn	flyash	2	3.0	_	2.0	6.5	0.92	0.35	-	-	61.95	[18]
Zn	flyash	2	3.0	_	2.0	6.5	0.55	0.18	-	-	67.3	[18]

IV.   CONCLUSION

Industrial solid waste containing active adsorption sites similar to flyash, termed 'metal oxide slag', was studied as an adsorbent for the removal of two selected heavy metals, Cu and Zn, from laboratory prepared aqueous solutions as wastewater. A series of batch and column studies were conducted to understand the adsorption dynamics. Keeping in view the sludge disposal problems, initial screening tests were conducted with an 8/14 mesh sized particles and an optimum batch adsorbent dosage was identified for the batch studies. Similarly, with a view to promote adsorption as a supportive treatment technique on industrial scale, the studies were conducted at room temperature and acidic pH of

3.5. For batch studies, at a low initial concentration of 5mg/lit, a Cu removal of **94.23**percent was achieved for an optimum adsorbent dosage of 32gm/lit. Similarly, Zn removal of **69.11**percent was achieved for a maximum adsorbent dosage of 41gm/lit. The pH of the batch samples had increased from an initial pH of 3.5 to an average of value 0f 6.0 towards equilibrium indicating a simultaneous release of OH^- ions. The results showed appreciable agreement with the standard adsorption isotherms indicating boundary (film) diffusion during the initial stages of adsorption followed by intraparticle diffusion towards equilibrium condition. An attempt was made to correlate the effect of initial concentration on the possible percent removal and also to explain the first order and non-linear adsorptive chemistry between Cu or Zn ions adsorbed and the surface characteristics of the adsorbent. Cost effective columns for industries need economic alternatives for glass columns. Chemically resistant hollow PVC pipes were used. For a fixed column feed flowrate of 1.2ml/min-cm^2, the effect of different bed depths and column feed concentrations on the column breakpoint, adsorptive potential, percent removal of Cu and Zn, adsorption rate constant and critical bed depth were estimated. Under similar column conditions, for a bed depth of 40cm and a low column feed concentration of 5mg/lit, in comparison to the permissible limit of Cu of 2.0mg/lit, a removal of **92.32percent** was achieved at breakthrough condition. Similarly, with studies on Zn, in comparison to the permissible limit of Zn of 5.0mg/lit, a removal of **74.57percent** was observed at breakthrough condition. In either case, the adsorbate removal had decreased with increase in column feed concentration. For removal of Cu, for a column feed concentration of 5.0mg/lit, the estimated N_0 was 216.6mg/lit and 'K' was 0.175lit/gm-hr. A 40cm bed as packed with 960gm of 'metal oxide slag' reached breakthrough after a throughput of about 30lit and the amount of Cu adsorbed was 0.122mg/gm. Similarly, for removal of Zn, for column feed concentration of 10mg/lit, N_0 was 324.9mg/lit and 'K' was 0.0306lit/gm-hr. A 40cm bed reached breakthrough after a throughput of 24lit and the amount of Zn adsorbed was 0.15mg/gm. Through these column studies, an attempt was made to estimate the demanded critical bed depth, 'X_c' which was observed to be an average of 30cm. Such data would be helpful for scale-up design and for predicting the breakpoint of higher bed depths, under similar column conditions.

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