

Kinetics of Industrial solid waste as a new adsorbent for removal of non-biodegradable pollutants

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Abstract: This paper discusses an attempt to explore the possibility of proposing a single treatment solution for dual pollution-problem in chemical industries which discharge wastewater and solid wastes. Batch and column studies were carried out to identify the adsorptive potential of a new adsorbent 'metal oxide slag', for removal of two common heavy metal pollutants, Cr and Ni, from laboratory prepared wastewater. The adsorbent characteristics and wastewater conditions were maintained similar to their existing discharge conditions. The effect of three batch parameters of dosage, initial concentration and time of contact on the possible removal and adsorption dynamics was studied and compared with industrial permissible limits. Further, the effect of column feed concentrations and bed depths were also studied and analyzed for breakpoint, adsorptive capacity and interfacial adsorption rate.

Keywords: metal oxide slag; adsorption; industrial wastewater; Cr; Ni; heavy metal; column studies.

I. Introduction

The presence of 'non-biodegradable' heavy metal ions in industrial wastewater [1,2] like chromium(Cr), cadmium(Cd), cobalt(Co), nickel(Ni), copper(Cu), zinc(Zn), iron(Fe) or manganese(Mn) and organic substances like surfactants, phenols, agricultural pesticides, color, dyes are proved to continuously hinder their beneficial use [3]. They are pernicious, generally refractory, non-nutritive, environmentally persistent, remain potentially active for a long time and thus are graded toxic to biological life [4]. The traditional treatment methods are a combination of various physical, chemical, biological unit operations and processes [5]. To fit into the economics of industrial treatment, adsorption technique was widely studied as a supportive method.

A review of reported literature for removal of Cr and Ni, over the past four decades indicated that there has been a constant quest for low cost and effective adsorbents [6,7] that aimed at the reutilization of the abundantly available natural wastes [8], agricultural wastes [9,10], domestic wastes [11], a few types of industrial solid wastes [12] or activated carbons [13]. The adsorbent potential was also improved through chemical treatment [14] or through charring [15]. As such modifications cannot be considered as energy efficient or eco-friendly, the reuse of abundantly available industrial solid wastes was also of interest to researchers. Flyash was studied in its raw and modified forms [16,17] for studies on removal of Cr [18] and Ni [19]. But, increased use of flyash for other beneficial activities has further interested researchers to explore the reuse potential of **other such industrial solid wastes**.

II. Materials and methods

With an objective to explore the possibility of proposing a single treatment solution for a dual pollution-problem of handling industrial solid waste and treating industrial wastewater, the solid waste adsorbent selected for the present work was a waste byproduct of a local recycle unit of scrap iron. The characteristics of the raw form of this solid waste which was available easily and in abundance are presented in table-1. Similar to the surface of flyash [20], the presence of oxides of silica, alumina and iron could provide active sites on the surface of this slag [21] and may thus facilitate adsorption through either surface complexation or ion-exchange, similar to that of flyash. No chemical treatment was applied for this slag to promote direct use and not to add more unwanted pollutants to the existing condition. The hard slag was crushed manually and in a ball mill and sieved to easily handled size of 8/14mesh Indian standard screens and stored in polythene bags.

In order to promote adsorption process for industrial wastewater treatment at their existing discharge conditions, the initial pH of all the samples was adjusted to an average acidic pH of 3.5. Further, no attempt was made to maintain the same but instead, the effect of the adsorption process on pH was monitored until equilibrium. The heavy metal ions present in all the samples, before and after study, was estimated using Atomic Adsorption Spectrophotometer (AAS) (ECIL-4136, India).

2.1. Batch experiments

Single component synthetic wastewater of Cr and Ni were prepared and used for all the experiments that helped to avoid inference of other co-existing pollutants. For, three different initial concentrations of 10mg/lit, 30mg/lit and 50mg/lit, the effect of slag dosages of 12gms, 23gms, 32gms and 41gms was studied. A blank test with distilled water was carried out to observe for any seepage of the adsorbent. Experiments were conducted in duplicates for consistency. After use, the spent adsorbent laden with the adsorbed non-biodegradable heavy metal ions are considered hazardous and were further tested for any possibility of desorption or leaching under normal conditions. No considerable desorption was observed. However, the sludge was to be disposed by general procedure of TSDF (Treatment, Storage and Disposal Facility) for hazardous wastes. Other disposal options may also be explored.

2.2. Column experiments

For industrial applications where large volumes of wastewater are to be treated especially on continuous basis, a continuous flow adsorption system has to be designed. Fixed bed packed columns is commonly preferred for fixing the optimum column parameters and based on the obtained results, the columns can be scaled up for industrial application. The design was based on two significant parameters: minimum contact time and maximum life of the adsorbent bed [22]. A series of column experiments were carried out at a fixed column feed flowrate and different column parameters of bed depth and feed concentrations of Cr (10mg/lit, 20mg/lit and 30mg/lit) and of Ni (10mg/lit, 15mg/lit and 20mg/lit). For adsorption to be considered as a cost effective and economic supporting method, an attempt was made through this study to replace the traditional glass columns with chemically resistant hollow PVC pipes. Standard pipes of 2mm wall thickness, 4.6cm inner diameter and 60cm length were used. Bed depths of 20cm, 30cm and 40cm were studied at a column feedflow of 1.2ml/min-cm².

III. Results and Discussion

The results of series of batch and single column studies were analyzed to understand the effectiveness of the industrial solid waste, 'metal oxide slag', as a new adsorbent for the removal of selected heavy metals, Cr and Ni, from their single component synthetic wastewater. The batch investigations were helpful for understanding the possibility of adsorption at the batch parameters of optimum dosage and equilibrium time. The column investigations were helpful for identifying the column breakthrough condition, adsorptive capacity and rate of adsorption.

3.1. Batch results

The effect of batch parameters of adsorbent dosage, time of contact and initial concentration of Cr and Ni 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.

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 Cr and Ni. Simultaneously, the change in pH was also monitored upto equilibrium. Further, it was observed that for a fixed initial concentration, as shown in fig.1(Cr) and fig.2(Ni), as a comparison for the three initial concentrations studied, there was a substantial increase in the percent removal with increase in the dosage. 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.

The effect of contact time on the amount adsorbed during the batch tests, upto equilibrium are shown in fig.3(Cr) and fig.4(Ni) as a comparison for the three initial concentrations studied. Smooth and continuous curves had suggested the formation of a monolayer [23] of the adsorbed heavy metal ions on the adsorbent surface. Further, it was understood that the adsorption has occurred in three significant stages. The initial linear curve indicated an appreciable rate of adsorption at the readily available adsorption sites and was *the rapid adsorption stage*. The non-linear decreasing trend explains that 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*. Towards equilibrium, 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. The batch studies at low initial concentrations have attained equilibrium earlier than at higher initial concentrations.

The effect of initial concentrations on the percent removal of Cr and Ni at the three initial concentrations studied is presented in fig.5(Cr) and fig.6(Ni). At low initial concentration of 10mg/lit, equilibrium Cr removal was 80.59percent and that of Ni was 81.15percent. But with increase in initial concentration, the removal had decreased.

An attempt was made to empirically correlate the non-linear removal trend [24] which would be helpful to theoretically predict the possible removal at other initial concentrations, under approximately similar batch conditions.

The correlation for Cr removal (1) was of first order dynamics as:

$$\text{Percent removal of Cr} = (-0.348) C_i + 84.04 \quad (1)$$

where a negative slope indicated a decreasing trend with increase in the initial concentration.

Similarly, the correlation for Ni removal (2) could be fit as a second order polynomial of the form:

$$\text{Percent removal of Ni} = 0.008(C_i)^2 + 0.088C_i + 81.43 \quad (2)$$

where, the negative coefficient of the second order term indicated a decreasing trend with increase in the initial concentration.

3.1.1. Adsorption mechanism

The characteristics of ‘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 isomorphous exchange of ions [23]. 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 replacing their position with that of heavy metal complex ions from liquid phase, by isomorphous ion-exchange. This would facilitate adsorption and fixation of the complex heavy metal ions.

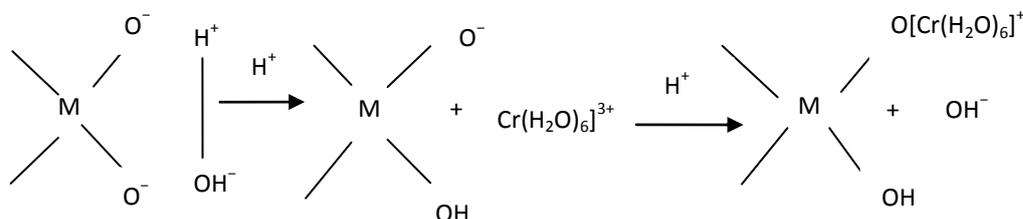
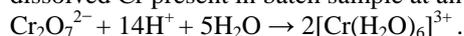
In the present study, the dissolution of CaO from ‘metal oxide slag’ through hydrolysis, at the initial acidic pH 3.5 was sufficient to cause the observed pH variation during the batch process. Such a variation could be explained by observing the chemistry between the adsorbed ions and the surface characteristics of the adsorbent. The mobility of the ions from the aqueous medium onto the solid surface is generally through coagulation [24] and depends on their existence in free or complex form. The dissolution of CaO may be of the form:



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

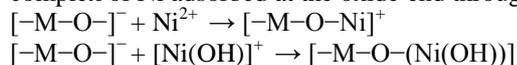


The adsorption of Cr can be explained depending on the pH condition. It is known from literature [25] that Cr had existed in several oxidation states when in water. The trivalent and the hexavalent were the most common forms. Below pH 6.5, CrO_7^{2-} was the dominant species. The formation of hydrolytic complex of the dissolved Cr present in batch sample at an acidic pH condition could be explained as:

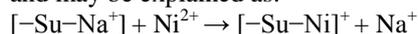


There is a possibility of chemical interactions through adsorbent surface complexation at the active oxide sites. Hence, the surface complexation of the hydrolytic Cr complex had led to an increase in the pH of the batch sample due to release of OH^- ions during adsorption.

The adsorption of Ni can be explained depending on the fact that it can exist as a divalent cation [23] or form complexes as $[\text{Ni(OH)}]^+$ or $[\text{Ni(OH)}_2]$ through partial hydrolysis. The surface of ‘metal oxide slag’ at the solid-liquid interface may be represented as $[\text{—Su—}]$ and the inorganic oxide of Na^+ present on the surface may be represented by a simple formula for explaining the possible adsorption mechanism as: $[\text{—Su—Na}^+]$. There is also a possibility of the inorganic oxide of Na^+ to undergo isomorphous exchange of ions such that Ni ions were fixed on the surface, simultaneously releasing Na^+ ions into the aqueous batch sample. The divalent cation complex of Ni adsorbed at the oxide end through electrostatic attraction may be:



The presence of sulphite (SO_3^{2-}) groups in the ‘metal oxide slag’ further supports the exchange of ions and may be explained as:



$[-\text{Su}-\text{Na}^+] + [\text{Ni}(\text{OH})]^{+} \rightarrow [-\text{Su}-\text{Ni}(\text{OH})]^{+} + \text{Na}^{+}$
 which explains the change in pH towards equilibrium.

3.1.2 Adsorption isotherms

Adsorption isotherms are equilibrium relationships 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 indicates a basis that there are a fixed number of active sites on the adsorbent surface [26]. The monolayer, non-interactive binding mechanism was understood by relating the degree of adsorption with the equilibrium condition and shown in fig.7(Cr) and fig.8(Ni) and the resultant curves were fit to a straight line of the form for Cr (3) as:

$$\frac{1}{q_e} = (0.8413) \frac{1}{C_e} + 0.758 \quad (3)$$

and for Ni (4) as:

$$\frac{1}{q_e} = (6.206) \frac{1}{C_e} + 0.558 \quad (4)$$

The monolayer adsorptive capacity was calculated as 1.32mg/gm for Cr and 1.79mg/gm for Ni. In either of the case study, in comparison to the results of reported literature as shown in table-3, the removal of Cr and Ni was appreciable. Similarly, the average demand of energy was estimated a low value of 0.09 lit/gm for both Cr and Ni. This value being close to zero had indicated a lesser demand of energy that facilitates removal during the batch adsorption process.

Freundlich adsorption isotherm model explains the multilayer adsorption of solute from liquid phase on to the adsorbent surface. Multilayer adsorptive capacity, ' k_f ', (mg/gm)/(mg/lit)^{1/n} and '1/n' intensity of the adsorption process referring to the heat of adsorption were estimated from the developed curves as shown in fig.9(Cr) and fig.10(Ni) that were fit to a power equation (5) for Cr and (6) for Ni removal.

$$q_e = 0.128(C_e)^{0.667} \quad (5)$$

According to Freundlich, for Cr, ' k_f ' of 0.128mg/gm, less than 1.0, indicated a possibility of multilayer adsorption. The intensity of the adsorption process, ' n ' was 1.497, a low value below the actual range of 2.0 to 10.0, explained a low speed of adsorption and that the Cr complex was not easily formed inside the pores of the adsorbent.

Similarly, for Ni, ' k_f ' of 0.182mg/gm, also indicated a possibility of multilayer adsorption. An ' n ' value of 1.567 explained a slow rate of heterogeneous adsorption and that the Ni complex was not easily formed inside the pores of the adsorbent.

$$q_e = 0.182(C_e)^{0.638} \quad (6)$$

From the above discussion, it could be concluded that during the initial period of contact, the driving force for surface adsorption of the heavy metal ions 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.

3.1.3. Adsorption dynamics

Adsorption can be explained by understanding the process to be 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 [23] or 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* 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 pollutants 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 first order rate expression [26] was applied to understand the adsorption rate in batch studies. Accordingly, a linear curve suggests first order uptake. 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(Cr) and fig.12(Ni). Only during the first half time of contact, the curves were linear, for both Cr and Ni, indicating a possibility of instantaneous adsorption. An average ' k_1 ', was 0.02min⁻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 thus indicating the possibility of pore diffusion towards equilibrium.

Weber's Intraparticle Pore Diffusion Model [28] helps in understanding the rate controlling parameters of the adsorption process. 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. If the adsorption process was controlled only by the intraparticle diffusion, then the plot will be linear passing through the origin. 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 [29]. In the present study, from fig.13(Cr) and Ni(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 Cr was calculated as $1.34 \times 10^{-4} \text{ cm}^2/\text{sec}$ and for Ni it was $1.17 \times 10^{-4} \text{ cm}^2/\text{sec}$. According to Michelsen, a very low D_p value of the order of $10^{-11} \text{ cm}^2/\text{sec}$ was indicative of intraparticle diffusion to be the rate determining step of the adsorption process while higher values indicated that boundary (film) diffusion is also involved.

Elovich equation was applied to theoretically analyze the possibility of chemisorption [29]. for the different initial concentrations studied, the curves in fig.15(Cr) and fig.16(Ni) show that 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, $\alpha\beta$, which was actually to be very high if the adsorption process was to indicate chemisorption.

3.2. 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 (10mg/lit to 30mg/lit) at fixed column feed flowrate of $1.2 \text{ ml}/\text{min}\text{-cm}^2$. At similar column operating conditions, the experimental results were analyzed for column breakpoint, percent removal of Cr and Ni, adsorptive capacity of 'metal oxide slag' in the column and interfacial adsorption rate.

During column adsorption, the concentration of the adsorbate in the continuous liquid phase and the constant solid phase change with time and with the position in the bed [30]. 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.

3.2.1. Breakthroughs curves

The developed curves were compared for the three bed depths studied at column feed flowrate of $1.2 \text{ ml}/\text{min}\text{-cm}^2$ and column feed concentration of 10mg/lit and as shown in fig.17(Cr) and fig.18(Ni). A similar trend was observed for higher initial concentrations also. 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. For a fixed feed concentration, the time of column breakthrough had increased with increase in bed depth due to the availability of more amount of the adsorbent. 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.

The effect of feed concentration on pollutant removal at breakpoint with increase in the bed depth are shown in fig.19(Cr) and fig.20(Ni), as a comparison for the three different column feed concentrations. At low feed concentration of 10mg/lit of Cr, in comparison to the permissible limit of Cr of 2.0mg/lit, a removal of 85.74percent was achieved at breakthrough condition using a 20cm bed. Under similar column conditions, the removal increased to 87.58percent and 91.35percent for bed depths of 30cm and 40cm respectively. Similarly, with studies on Ni, in comparison to the permissible limit of Ni of 3.0mg/lit, a removal of 85.42percent was observed at breakthrough condition with a 20cm bed. As the bed depth was increased to 30cm and 40cm, the removal increased to 87.85percent and 90.43percent 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. In either case, such an increase in attaining breakpoint could be indicative of the increased driving force per unit weight of the adsorbent in the column which had increased the rate of adsorption.

3.2.2. BDST curves

Bed depth-service time curves were developed based on Hutchins [31] graphical approach (7) to analyze the breakthrough condition. The adsorptive capacity, N_0 , of the 'metal oxide slag' in the column was estimated using Bohart-Adam model [22] based on surface rate theory and to describe the movement of adsorption zone through the packed bed.

$$t_b = \left(\frac{N_0}{C_i v}\right)X - \frac{1}{KC_i} \ln\left(\frac{C_i}{C_b} - 1\right) \quad (7)$$

Thus, the total service time of the bed, t_b , for the bed depths studied are shown in fig.21(Cr) and fig.22(Ni) as a comparison for the three different column feed concentrations. 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 Cr feed concentration of 10mg/lit, the calculated N_0 was 577.6mg/lit and ' q ' was 0.355mg/gm. Similarly, for a low Ni feed concentration of 10mg/lit, the calculated ' N_0 ' was 469.3mg/lit and ' q ' was 0.272mg/gm. In either case, these values were observed to increase with increase in the feed concentrations studied. An average adsorption rate constant ' K ' was estimated as 0.24lit/mg-hr for Cr and 0.14lit/gm-hr for Ni. A low value less than 1.0 was indicative of a non-linear adsorption trend at the solid-liquid-interface in the column.

3.3. Scale-up calculations

In the present study, under similar operating conditions of column feed flowrate, column feed concentration and bed depths, the critical bed depth, X_c was estimated as 38.08cm for Cr and 16.72cm for Ni. These values help in predicting the breakpoint of columns with higher bed depths, under similar column conditions. In order to treat the large volumes of industry discharged wastewater, columns of larger dimensions [22] that can hold 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 laboratory scale fixed bed columns.

IV. Conclusion

With an objective to explore the possibility of proposing a single treatment solution for a dual pollution-problem of handling industrial solid waste and treating industrial wastewater, the solid waste adsorbent selected for the present work was a waste byproduct of a local recycle unit of scrap iron. The characteristics of the raw form of this solid waste were observed to be similar to that of flyash. The adsorptive potential was explored for the removal of two selected heavy metals, Cr and Ni, from their single component synthetic wastewater through a series of batch and single column studies. 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, an acidic pH of 3.5 was identified. At a low initial concentration of 10mg/lit, **80.59percent** removal of Cr was obtained at a maximum adsorbent dosage of 41gm/lit. Similarly, **81.51 percent** removal of Ni was obtained at an optimum adsorbent dosage of 32gm/lit. An attempt was made to represent the effect of initial concentration on the percent removal. An increase in pH of the batch samples towards equilibrium had indicated a simultaneous release of OH^- ions. The results agreed with the adsorption isotherms. Initially boundary (film) diffusion was predominant followed by intraparticle diffusion towards equilibrium condition. The adsorption process was of first order and non-linear. An attempt was made to explain the chemistry between the adsorbed Cr or Ni ions and the surface characteristics of the adsorbent.

With a view to promote the columns as cost effective systems for industries, chemically resistant hollow PVC pipes that were unbreakable and easily available were tried as economic alternatives for glass columns. Results were analyzed for the effect of column bed depth and column feed concentration on the column breakpoint, adsorptive potential, percent removal, adsorption rate constant and critical bed depth. For a column feed flowrate of 1.2ml/min-cm², a bed depth of 40cm and a low column feed concentration of 10mg/lit, in comparison to the permissible limit of Cr of 2.0mg/lit, a removal of **91.35percent** was achieved at breakthrough condition. Similarly, with studies on Ni, in comparison to the permissible limit of Ni of 3.0mg/lit, a removal of **90.43percent** was observed at breakthrough condition. In either case, under similar column conditions, the adsorbate removal had decreased with increase in column feed concentration. For removal of Cr, for a column feed concentration of 10mg/lit, N_0 was 577.6mg/lit and ' K ' was 0.24lit/gm-hr. A 40cm bed packed with 960gm of 'metal oxide slag' reached breakthrough after a throughput of 28.9lit and the Cr adsorbed was 0.775mg/gm. Similarly, for removal of Ni, for column feed concentration of 10mg/lit, N_0 was 469.3mg/lit and ' K ' was 0.1204lit/gm-hr. A 40cm bed reached breakthrough after a throughput of 20.5lit and the amount of Ni adsorbed was 0.367mg/gm. In either case, the demanded critical bed depth, ' X_c ' was estimated to be an average

of 30cm which would be helpful for predicting the breakpoint of columns with higher bed depths, during scale-up design under similar column conditions.

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Table-1: Adsorbent characteristics of ‘metal oxide slag’.

Adsorbent	Metal oxide slag Present work	Flyash [17]
Characteristics		
Physical and proximity analysis		
Particle bulk density, ρ_p (gm/cc)	2.053	—
Surface area, A_w , (m^2/gm)	11.096×10^{-4}	<2.0
Particle porosity, ϵ_p	0.42	—
Particle diameter, d_p , mm	1.765	+125 μ
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	—

Table-2: Comparison of the effect of dosage of ‘metal oxide slag’ and initial concentration on the equilibrium removal.

Dosage, gm/lit.	Percent removal at equilibrium			Selection of dosage
	$C_i = 50mg/lit$	$C_i = 30mg/lit$	$C_i = 10mg/lit$	
Chromium, pH variation, initial 3.51 to 4.63 at equilibrium				
12	41.42	47.12	56.12	Less
23	53.81	60.23	67.56	Less
32	64.05	68.42	76.45	Less
41	66.67	73.55	80.59	Selected dosage
Nickel, pH variation initial 3.52 to 5.49 at equilibrium				
12	40.46	45.95	58.05	Less
23	56.67	69.81	73.73	Less
32	65.75	76.86	81.51	Selected dosage
41	69.13	79.45	82.16	Excess

Table-3: Comparison of adsorption dynamics for removal of Cr and Ni by batch studies

Wastewater type	Adsorbent type	m	C_i	pH	Q	k_f	k_1	D_p	removal	Reference
		gm/lit	mg/lit		mg/gm	mg/gm	min ⁻¹	cm ² /sec	%	
Cr removal										
Synthetic	metal oxide slag	41	10	3.5	1.32	0.667	0.022	0.000134	80.59	Present work
Synthetic	Activated neem bark	10	50	3	4.75	0.0032	—	—	83	[32]
Synthetic	chemically acti sawdust	90	60	4		0.0007	—	—	75	[14]
Synthetic	flyash	4	5	2	15.88	0.015	—	—	95.5	[18]
Synthetic	brick kiln ash	2	100	2	9.31	—	—	—	86.25	[33]
Synthetic	powdered acticarbon	2	100	2	9.47	—	—	—	93.57	[33]
Ni removal										
Synthetic	metal oxide slag	32	10	3.5	1.79	0.182	0.023	0.000117	81.51	Present work
Synthetic	chemically acti sawdust	90	60	4		0.0008	—	—	75	[14]
Synthetic	flyash	100	500	5	3.9	—	—	—	95	[17]

Table-4: Comparison of column dynamics for the removal of heavy metal pollutants from single component

Ion	Adsorbent	X	column diameter	W	Feed flow	feed pH	C_i	C_b	N_0	q	removal	Reference
		cm	cm	gms	ml/min		mg/lit	mg/lit	mg/lit	mg/gm	%	
Cr	metal oxide slag	40	4.3	960	20	3.5	10	0.865	577.6	0.355	91.35	Present work
Cr	flyash pellets	60	—	—	10	2.0	—	—	—	0.113	55.5	[16]
Cr	flyash pellets	80	—	—	10	2.0	—	—	—	0.154	82.7	[16]
Cr	brick kiln ash	—	2.5	10	2.0	2.0	100	—	—	9.47	—	[33]
Cr	powdered activated carbon	—	2.5	10	2.0	2.0	100	—	—	8.875	—	[33]
Cr	coal flyash	2	3.0	—	2.0	6.5	0.45	0.15	—	—	66.66	[34]
Ni	metal oxide slag	40	4.3	960	20	3.5	10	0.957	469.3	0.272	90.43	Present work

synthetic wastewater

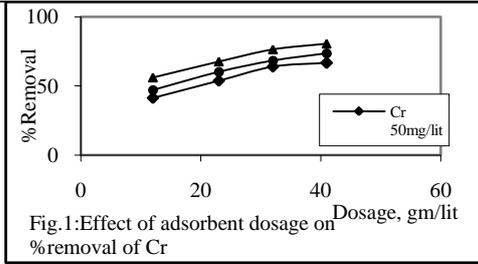


Fig. 1: Effect of adsorbent dosage on % removal of Cr

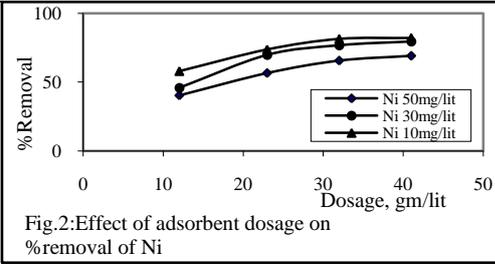


Fig. 2: Effect of adsorbent dosage on % removal of Ni

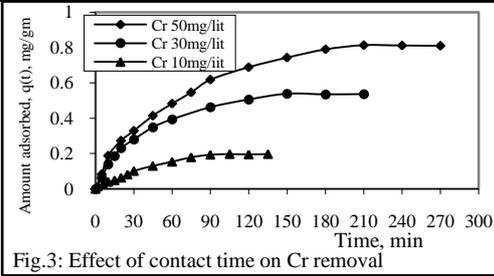


Fig. 3: Effect of contact time on Cr removal

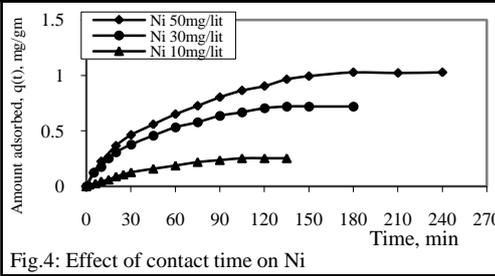


Fig. 4: Effect of contact time on Ni

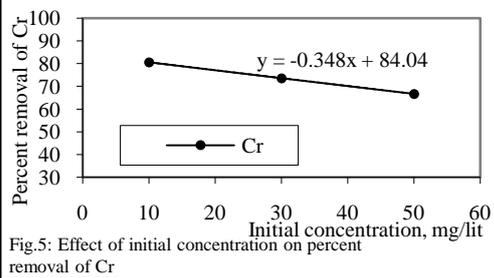


Fig. 5: Effect of initial concentration on percent removal of Cr

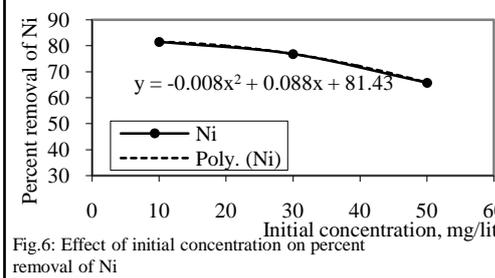


Fig. 6: Effect of initial concentration on percent removal of Ni

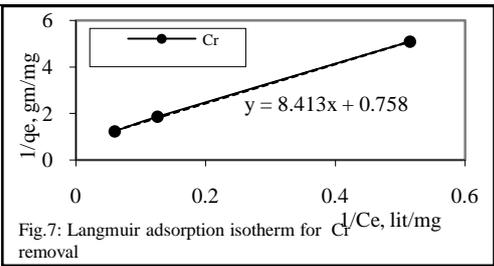


Fig. 7: Langmuir adsorption isotherm for Cr removal

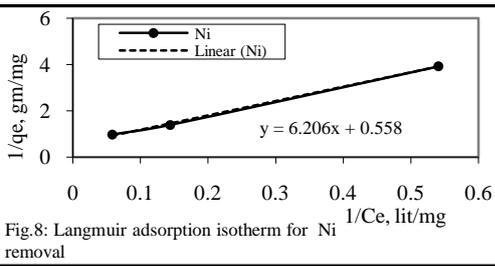


Fig. 8: Langmuir adsorption isotherm for Ni removal

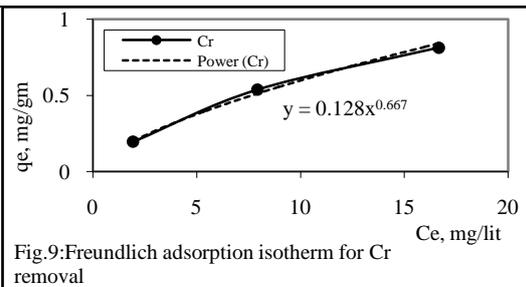


Fig. 9: Freundlich adsorption isotherm for Cr removal

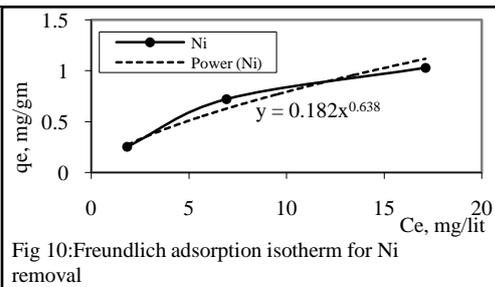


Fig. 10: Freundlich adsorption isotherm for Ni removal

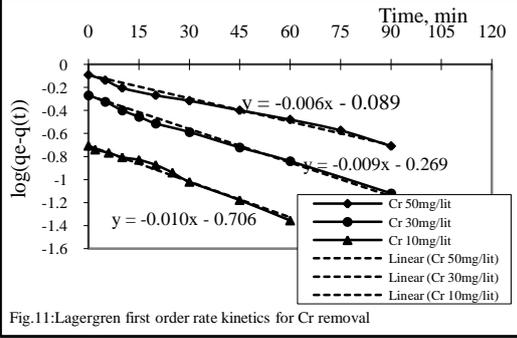


Fig.11:Lagergren first order rate kinetics for Cr removal

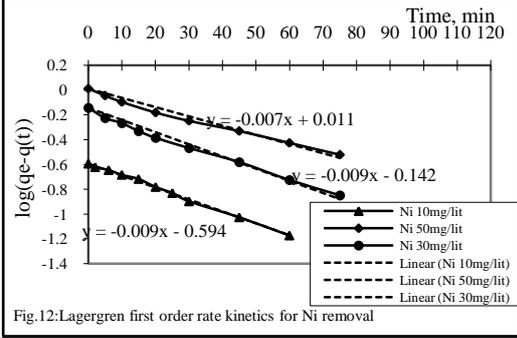


Fig.12:Lagergren first order rate kinetics for Ni removal

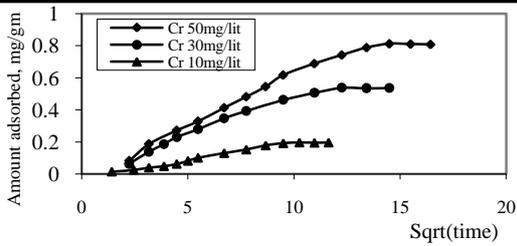


Fig.13:Intraparticle diffusion plot for Cr removal

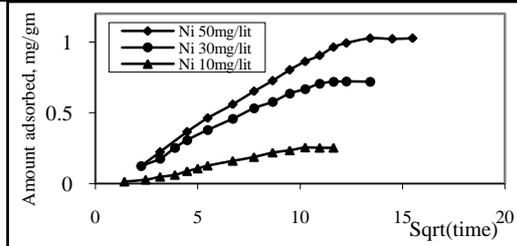


Fig.14:Intraparticle diffusion plot for Ni removal

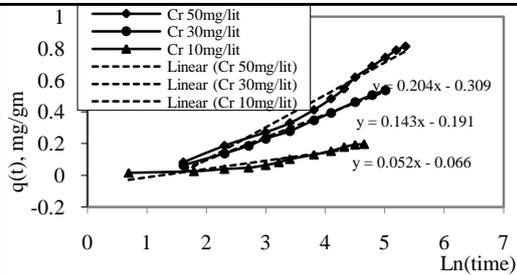


Fig.15:Elovich empirical relation for Cr removal

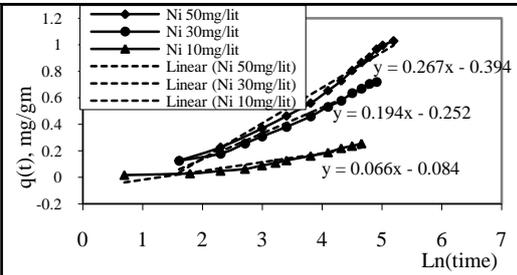


Fig.16: Elovich empirical relation for Ni removal

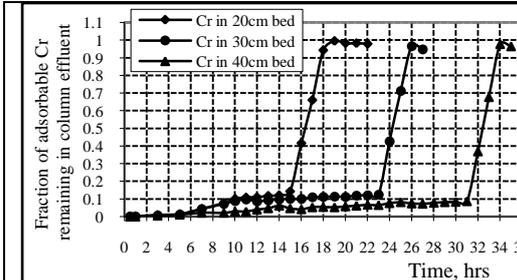


Fig.17: Breakthrough curves for Cr removal at 10mg/lit

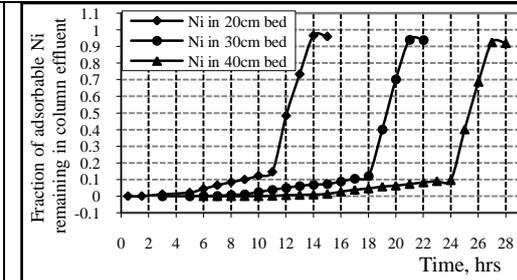


Fig.18: Breakthrough curves for Ni removal at 10mg/lit

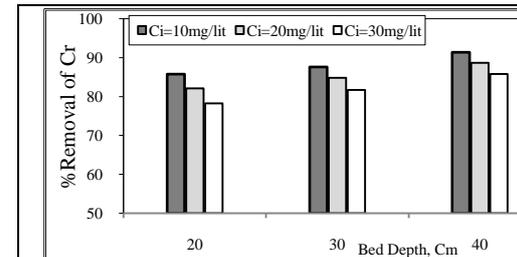


Fig.19 Comparison of effect of bed depth on %removal of Cr

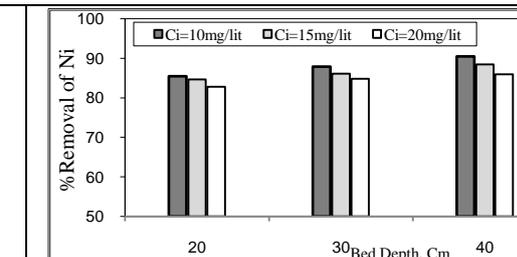


Fig.20: Comparison of effect of bed depth on %removal of Ni

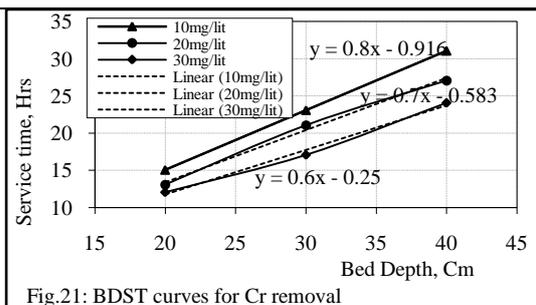


Fig.21: BDST curves for Cr removal

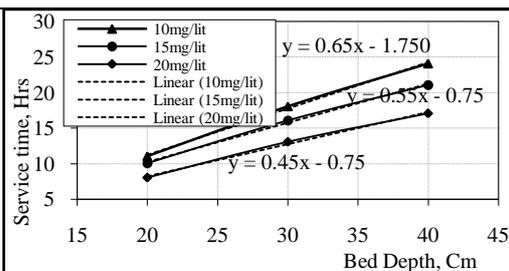


Fig.22: BDST curves for removal of Ni

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