Adsorption of zinc by waste industrial sludge

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ABSTRACT

Industrial effluents with their heavy metals like copper, zinc, cadmium, lead pollute the inland water sources. Attempts have been made in this paper to study the adsorption process for removal of zinc from a synthetic solution of zinc nitrate and sodium nitrate. An industrial sludge collected from TISCO Jamshedpur has been used to make the adsorption studies. Different parameters like initial metal concentration, pH, particle size of the adsorbent, sorbent dose, rate of agitation, effect of ionic strength of the solute and presence of different anionic ligands have been studied.
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INTRODUCTION

Effluents from metallurgical, chemical and other plants contain different heavy metals like copper, zinc and cadmium. It is necessary that these metals are removed before the water is discharged or reused. The process can be carried out by various methods of chemical precipitation, ion exchange, reverse osmosis and adsorption. Out of this adsorption has advantage over other methods because of low investment and simple design. Though active carbon is used in many cases as an adsorbent, newer materials are being tried for lower cost and easy availability.

In this work waste sludge, collected from a steel plant has been used to study the adsorption process. It may be mentioned here that above sludge was generated after treatment of steel plant effluents. Presently this sludge is being dumped and its successful utilization will be an added advantage.

Characterization of adsorbent

Adsorbent characterization plays an important role to determine the mechanism of adsorption, and is used to find out the design parameters of the process variables in the batch and continuous systems. Therefore, the following physical and chemical characteristics of waste sludge were studied.

01. Bulk density.
02. Specific gravity.
03. Porosity (Void fraction).
04. BET Surface area.
05. Chemical Analysis.
06. pH_{zpc} (pH at zero point charge)
07. SEM. EDAX Analysis - The topography of three states of waste sludge was examined by scanning electron microscope such as undisturbed fresh waste sludge sample, metal-ion adsorbed waste sludge sample and the desorbed of waste sludge sample.

Waste sludge samples used in the experiments were procured from the industrial (steel industry) wastewater treatment plant, TISCO, Jamshedpur (Jharkhand, India) with the prior permission of the concerned authorities. The dried sludge samples were ground in a ball mill and sieved.

The characteristics of the sludge are given in the following tables.

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TABLE 1 : Physical characteristics of waste sludge

SL. NO.	Parameter	Values**
		(Geometric mean)
1	Diameter of the particle	
	(i) 75 to 150 μm (W_1)	106.06 μm
	(ii) 150 to 425 μm (W_2)	252.48 μm
	(iii) 425 to 850 μm (W_3)	601.04 μm
	(iv) 850 to 1700 μm (W_4)	1202.08 μm
2.	Bulk density.	0.85 g / cm³
3.	Specific gravity.	1.15
4.	Porosity (Expressed as the ratio of weight of water adsorbed after 24h to oven-dried. Weight.	0.091
5.	Loss of weight after washing with distilled water.	2 to 3%
6.	Specific surface area (BET method) for size	
	W_1	7.65 m² /g
	W_2	7.51 m² /g

TABLE 2 : Chemical characteristics of waste sludge

Sl.No.	Consultants	Wt.(%)
1.	Carbon	23
2.	Iron	21
3.	Calcium	18
4.	Magnesium	9
5.	Silica	3
6.	Sulphur	19.5
8	Aluminum	2.5
9	Manganese	0.5
10	Sodium	1.5
11	Others	2

Procedure

All the glassware used was of borosilicate make and all the chemicals were of analytical grade. For the batch kinetic experiments mechanical stirrers (M/s. Remi Motors, India) with speed regulators and tachometers were used. Isotherm experiments were conducted in the rotary shakers. Systronics model 243 combined electrode pH meter was used for the measurement of pH of the solution.

The metal-ion concentrations in the solution were analyzed using Perkin Elmer 3100 atomic absorption spectrophotometer (AAS). Waste sludge samples used in the experiments were procured from the industrial (steel industry) wastewater treatment plant, TISCO, Jamshedpur (Jharkhand, India) with the prior permission of the concerned authorities. The dried sludge samples were ground in a ball mill and the range of particle size were designated in the order 75 μm > W_1 > 150 μm > W_2 >425 μm > W_3 > 850 μm > W_4 >1700 μm The sludge had bulk density 0.85g/cm² and specific gravity 1.15.

Solutions of metal ions were prepared with nitrate salts of $Zn(NO_3)_2$ to eliminate the aionic effects on the adsorption as faced by some previous investigators[1,2]. Sodium nitrate solutions of different molarities were used for changing ionic strength of the solution. The required pH could be adjusted by adding dilute HNO_3 or NaOH solution.

Experiments were conducted with one liter of solution at the original solution pH with one gram of waste sludge. The size of the waste sludge was W_1 and initial metal-ion concentration was 20 mg/1. The samples were withdrawn after 0.5, 1.2, 5, 10, 35, 60, 90, 120, 150 and 180 minutes as there was no adsorption after 3 hours. Sag et al., (1995)[3] in the adsorption studies collected samples at 5 minutes interval initially and at 30 minutes interval after the equilibrium was attained. From the results of preliminary experiments it was decided to maintain 1 liter solution volume, 2g/l waste sludge, pH 5.0, 20 mg/l initial metal concentration, particle size W_1, agitation 400 rpm and 3 hrs contact time for all the kinetic studies. Temperature was maintained at 20-25 ⁰ C.

In the initial stages of the adsorption studies, experiments were conducted alone with the metal solution without adding the adsorbent and metal-ions were analyzed with the AAS. Kinetic curves have been plotted with the amount of metal ions adsorbed in mg per gram of the adsorbent version time using equation (1).

$$q = (C_0 - C) \, V/m \qquad (1)$$

Where, q = Amount of metal-ion adsorbed or the sorption capacity, mg/g, V= Volume of solution in liter, m= Mass of adsorbent in gram, C_0= Initial metal-ion concentration in mg/1, C= Metal-ion concentration in mg/ 1

Percentage adsorption

or

Percentage of metal-ion removal = [(C_0- C) / C_0] X 100

RESULTS AND DISCUSSIONS

Effect of contact time

The effect of contact time on the adsorption pro-

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cess is discussed here.

Let us consider the result of 5 mg/ 1 of initial metal ion concentration. It was observed that

➢ About 25% of removal occurs within one minute.

➢ Equilibrium time is achieved within 30 minutes.

It was also observed that uptake of metal-ion occurred in two stages i.e. an initial rapid uptake within 20 to 30 minutes followed by a subsequent slow uptake from 30 to 180 minutes. However, to ensure complete attainment of equilibrium all the experiments were continued up to 180 minutes.

The adsorption process appeared to proceed rapidly when the number of available sites was much larger than the number of metal species to be adsorbed. The required contact time increased with increased loading. The contact time required to reach equilibrium appeared to be proportional to the ratio of number of adsorption sites and number of metal species.[4]

Wide range of data has been reported for adsorption rates of heavy metal-ions by number of adsorbents. Karabulut et al., (2001)[1] studied the shaking time for adsorption of cu(II) and Zn(II) with low rank Turkish coal and found that adsorption equilibrium was achieved within 20 minutes. A similar initial rapid uptake was also observed by Jha et al., (1998)[5] in case of sorption of cadmium with chitosan.

There are several parameters, which determine adsorption rate such as stirring rate in the aqueous phase, physical nature of sorbent (e.g. porosity, surface area), dose of sorbent, ionic properties (e.g. ionic radius), initial concentration of metal-ions, sterric effects, rate of chelate formation and coexistence of other metal-ions, which might compete with metal-ions of interest[1]. The adsorption rates obtained with waste sludge seem to be satisfactory and were in good agreement with many previous researches.

Effect of initial metal-ion concentration

The kinetics of adsorption with waste sludge at different initial concentrations was studied as per the procedure discussed earlier and plotted in the figure 1. The values of equilibrium time at different initial concentrations are found to be 5,10,15 and 20 minutes for initial zinc concentration of 20,60,90 and 90 mg/l respectively..

It was observed that the time to reach equilibrium increased with increase in initial metal-ion concentra-

tion in agreement with Namasivayam et al., (1998)[6] who reported that the equilibrium time increased from 3 to 4 times by increasing the initial concentration from 10 to 40 mg/1.
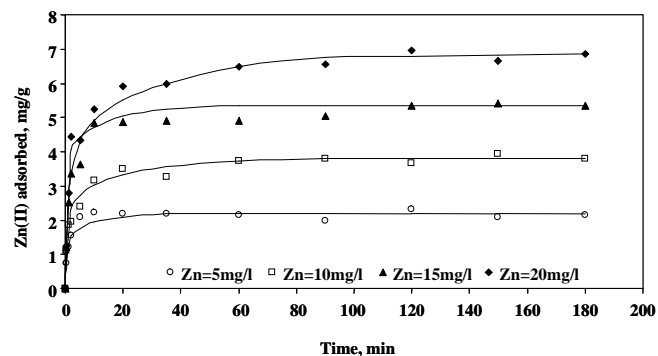
The amount of metal-ions adsorbed per gram of

Figure 1 : Plot of sorbed amount versus time for Zn(II) adsorption. Effect of initial concentration at pH=5.0, m=2g/l, Size=W

adsorbent increased with increase in initial metal-ion concentration Similar results were obtained by many researchers for these metal-ions with different adsorbents[1,7,8].

These results showed that metal removal was highly concentration dependent. The ratio of initial number of moles of metal-ions to the available adsorptions sites of adsorbent became higher with the increasing concentration and hence the sorption capacity increased.[8]

Above figure shows that percentage removal of metal-ions decreased with increase of metal-ion concentration from 5 to 20 mg/1. Chen et al. (1997)[9] reported that percentage copper removal with activated carbon was lower for higher initial concentration and it might be due to the higher surface coverage resulting from the increase in metal-ion concentration and subsequent rise of the activation energy for the reaction, therefore making it more difficult for the surface to bind the metal-ions[10,11]. Similar case might have occurred for the adsorption of Zinc.

Results of 10 mg/1 of initial concentration showed 76% adsorption of Zn(II). This was commensurate with the results reported earlier[12]. He could absorb 44% of metal by chitosan from 10 mg/l Zn (II) solution

It is concluded that by increasing metal-ion concentration the values of equilibrium time and sorption capacity were increased whereas the percentage of metal removal was reduced.

Effect of particle size of adsorbent

The kinetics of sorption of waste sludge for Zn(II) at different particle sizes (W_1 W_2 W_3 and W_4) were studied by following the procedure given earlier and are shown in figure 2. The experiments were conducted at pH = 5.0 with an initial concentration of 20mg/1 and absorbent dose of 2g/1. Time required for achieving equilibrium are 90, 90, 120 and 120 minutes with particle sizes W_1, W_2, W_3 and respectively.

It is evident that the equilibrium time is increased with increasing size of adsorbent from W_1 to W_3 and became constant with next particle size. Further Erosa et al., (2001)[13] studied the influence of particle size on Cd (II) adsorption with chitosan and observed that equilibrium time was increased by increasing the size of the sorbent. Jha et at. (1998)[5] made similar observations.

The amount of metal-ions adsorbed in mg per gram of adsorbent decreased with increasing size of waste sludge. Ho et al., (2000)[7] reported that the sorption capacity of dye decreased from 157 to 110 mg/g as the clay size increased from 0-38 to 75- 106 µm which implied that smaller size particles might have more surface area for a given mass of the clay and as a consequence the greater number of binding sites might be available in smaller size particles, Jha et al., (1998)[5] reported that sorption capacity of Cd(II) also concluded that metal-ion removal occurred by a surface mechanism. According to McKay (1983)[14], separation factor was independent of size for Hg but varied slightly with the particle size for Zn (II).

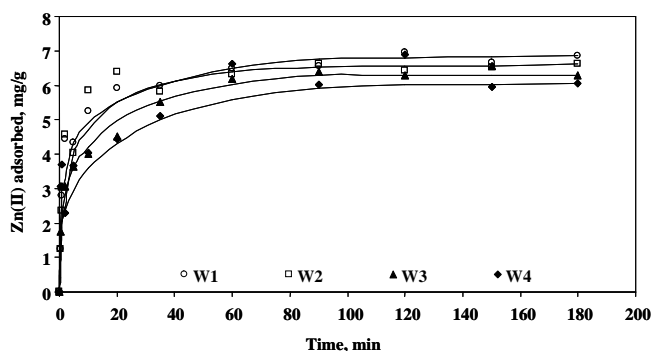The percentage removal of Zn (II) versus geometric mean diameters of waste sludge as plotted in figure 2 does not show any change. Therefore, all the experiments were carried out with the particle size W_1. It is concluded that equilibrium time, sorption capacity and the percentage of metal-ion removal decreased with increasing the particle size of waste sludge. More numbers of binding sites are available due to the availability of more surface area per gram of adsorbent. It is also in agreement with the observations reported by Jha et al. (1998)[5].

Effect of sorbent dose

The kinetics of adsorption with waste sludge at different doses of sorbent were studied and plotted in figure 3. Experiments were conducted by varying the dose from 0.25 to 5 g/1.

The equilibrium time was found to be 90 minutes for 0.25-2g/l, became 60 minutes for the dose up to 3 g/1and. further decreased to 30 minutes by increasing the dose to 4 and 5 g/1. It revealed that the equilibrium time decreases with the increase in the concentration of waste sludge.

It was observed that the sorption capacity 'q' decreased from 25.4 to 6.85 mg/g by increasing the sorbent dose from 0.25 to 2.0 g/1. Further, these values of 'q' decreased to 3.26 mg/g when the dose of sorbent was increased up to 5.0 g/1.

The metal removal efficiencies were found to be 31.7%. These values increased sharply to 68.5% when the dose was increased to 2.0 g/1. However, beyond the sorbent dose 2.0 g/1 up to 5.0 g/1 the increase in the percentage removal was marginal. Corapcioglu et al. (1987)[15] studied the removal of Zn (II) by activated carbon and reported that the percentage metal removal increased with decreasing surface loading.
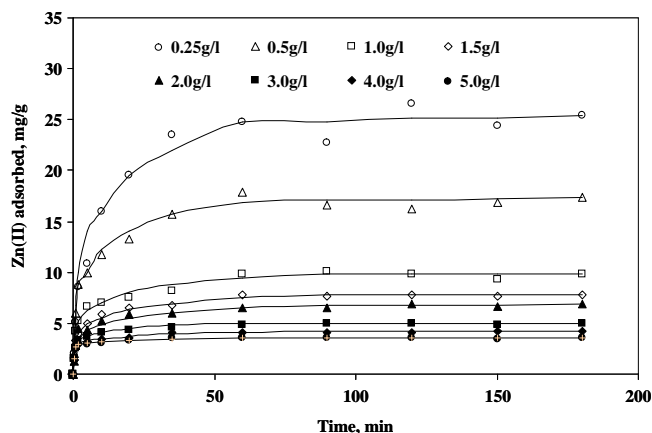

Figure 2 : Plot of sorbed amount versus time for Zn(II) adsorption. Effect of particle size at pH=5.0, m=2g /l, C_0=20mg/l

Figure 3 : Plot of sorbed amount versus time for Zn(II) adsorption. Effect of sorbent dose at pH=5.0, m=2g/l, C_0=20mg/l

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Esposito et al., (2001)[16] reported that an increase in bio sorbent concentration generally increase the adsorbed metal-ion concentration because of increasing surface area, whereas the adsorbed metal-ion quantity 'q' per unit weight of adsorbent decreased by increasing the bio sorbent quality.

It was concluded from the above discussion that by increasing the waste sludge concentration in the metal-ion solutions, the equilibrium time and the amount of metal-ions adsorbed per gram of sorbent 'q' were decreased where as, the metal removal efficiency of waste sludge was improved.

The increase in metal removal efficiency was found to be marginal with the increase of the sorbent dose from 2g/1 to 5g/1 whereas, the sorption capacity reduced to a slow value. Therefore, the dose of adsorbent was fixed at 2g/1 for all the experiments.

Effect of rate of agitation

The kinetics of adsorption with different rates of agitation were studied and plotted in figure 4. Experiments were conducted with $C_0 = 20$ mg/1, at pH = 5.0, with size W1 at agitation speed 200, 400 and 800 rpm respectively. The values of equilibrium time obtained were 90, 90, 60 minutes for Zn (II) at agitation speeds 200,400 and 800 rpm respectively, which was found to reduce with the increase of agitation speed.

It was indicated that the external adsorption of metal-ions on to adsorbent was controlled by the degree of agitation. Increase in the speed of agitation decreased the boundary layer resistance to mass transfer in the bulk at lesser time, thereby it increased the driving force of metal-ions towards adsorption. The process was influenced by the concentration gradient and the thickness of the diffusion layer, which was a function of agitation process.[8]

The values of sorption capacities 'q' (figure 4) were found to be 6.6, 6.8 and 7.1 mg/g at agitation speeds 200, 400 and 800 rpm respectively. These results showed that the increase in sorption capacity was about 6.1%, which was marginal or insignificant with respect to the increase in agitation speeds from 200 to 800 rpm.

Ho et al., (2000)[7] reported that the influence of agitation speed on sorption capacity 'q' was small in their experiments for sorption of Pb (II) with peat in the speed range from 280 to 510 rpm.
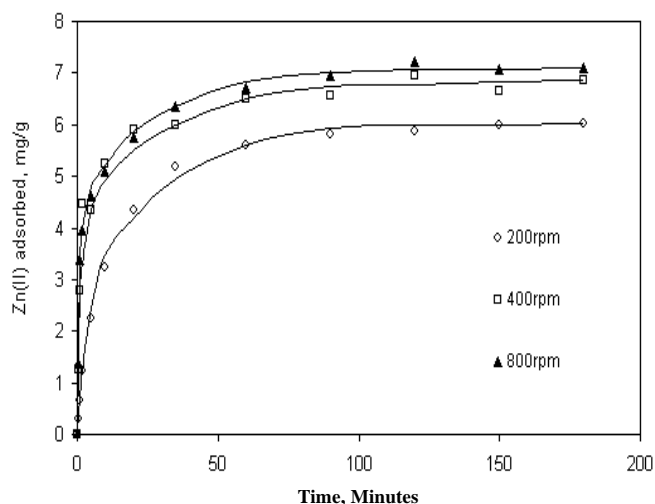

Figure 4 : Plot of sorbed amount vs. Time for Zn (II) adsorption. Effect of rate of agitation at pH= 5.0, m=2g/l, C_o=20mg/l, size=W_1

The percentage of metal removal was found to be 66,69 and 70% at 200, 400 and 800 rpm respectively. The increase in the removal of metal-ions was found to be marginal.

Unninathan, M et al., (2001)[8] observed that the percentage removal of Cr (VI) with an initial concentration of 100 mg/1 by the adsorbent (Iron complex of a polyacrylamide grafted sawdust) increased from 71% to 82% by increasing the rate of agitation from 100 to 400 rpm. They reported the increase in removal of Cr)VI) to be due to kinetic energy gained by the sorbate species during agitation and with increasing the rate of agitation Cr (VI) ions might became activated through a gain in kinetic energy and easily crossed the potential barrier. The increase of metal removal was marginal with the increase of agitation speed, but whatever the increase in metal-ion removal observed might be due to the gain of kinetic energy by the metal-ions to cross the potential barrier.

It was concluded that the equilibrium time was achieved earlier for higher shaking speed where as the sorption capacity and metal-ion removal efficiency increased marginally with the increase in the speed of agitation.

Effect of pH

It is well known that pH plays a vital role in the adsorption process. Metal-ions undergo adsorption at a different pH condition depending on the type and the form, of the adsorbent. Davis et al., (1978)[17] observed

Figure 6 : Plot of sorbed amount versus time for Zn(II) adsorption. Effect of ionic strength at pH=5.0 m=2g/l, C_0=20mg/l, size=W_1

that adsorption of metal-ions on hydroxide surfaces are highly pH dependent. The pH was chosen as the master variable in the experimental studies of Benjamin et al., (1981)[18] and Balistrieri et al., (1982)[19]

In the present investigation the effect of pH was studied in the range 2.0 – 7.0. Amount of metal-ions adsorbed versus time are plotted in the figure 5. It was observed that the time to approach equilibrium increased marginally with the increase of pH from 2.0 to 4.0 and thereafter remained constant up to pH 7.0. Therefore, the effect of pH on removal kinetics seemed to be insignificant which is in agreement with the observations made by Chen et al., (1997)[9].

The removal of metal-ions has been found to be 9.0, 20.0, 53.0 and 68.0% it was seen that by increasing the pH by another two units i.e. up to pH 7.0 could achieve only 6.7 % increase, which is quite marginal. Increasing the pH beyond 7.0 precipitated the metal-ions from the solutions.
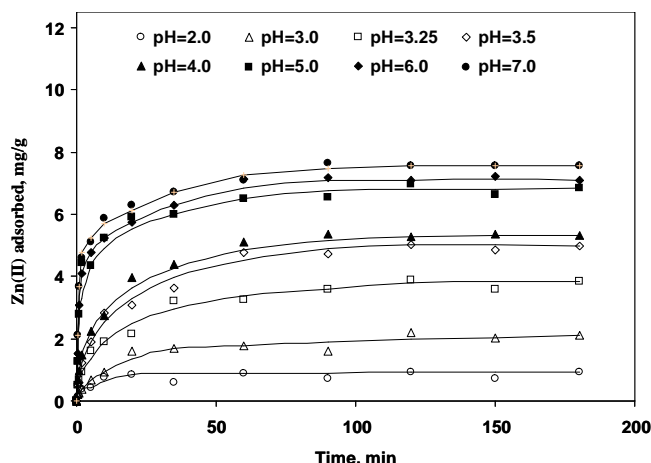

Figure 5 : Plot of sorbed amount versus time for Zn(II) adsorption. Effect of pH m=2g/l, C_0=20mg/l, size=W1

Effect of ionic strength

Adsorption of metal ions is always dependent on the ionic strength and pH of the solute. The effect of ionic strength on the sorption kinetics of waste sludge was studied by increasing the $NaNO_3$ molarities from 0.001 to 0.1m, which is shown in figure 6. Equilibrium time was observed to be 90 minutes for adsorption in presence of ionic strength of 0.1 M of Na NO_3. This kind of results indicated that there was shifting of equilibrium time.

Influence of ionic strength of 0. 1M showed that there was a reduction in metal removal to the tune of
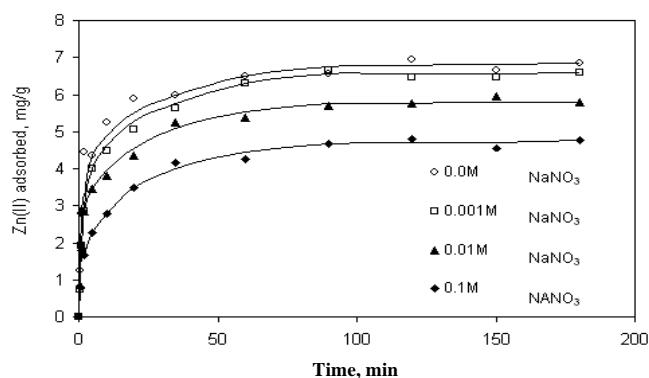
about 21, where as this value was 2.6 % at ionic strength of 0.001 M. But the extent of reduction was significant when the ionic strength was increased to 0.1M.

Chen et al., (1997)[9] in their adsorption studies reported that metal removal decreased with increase in ionic strength. They observed that the functional groups become available at lower ionic strength at pH= 5.0. However the increased ionic strength deactivate the functional groups of the adsorbent and hence% metal-ion removal is reduced. The decrease in adsorption at the higher ionic strength in the present work might be due to the above-mentioned reasons as these studies were conducted at a pH 5.0

Khaodhiar et al., (2000)[20] reported that the change in background electrolyte concentration from 0.01 to 0.1M $NaNO_3$ has minimal effect on metal adsorption by iron oxide coated sand

Effect of anionic ligands

Heavy metals are generally associated with anionic ligands in industrial effluents and wastewater. The anionic ligands form a large number of species with metals and the resultant species may be (a) highly adsorbable (b) weakly adsorbable (c) non-adsorbable depending upon the nature of the anionic ligand and the adsorbent. The stability constants of soluble ligands and the adsorbent with the metal dictate the distribution of metal between these two phases.

To investigate the effect of a broad-spectrum ligand concentration which generally occur in metal processing effluents[21], a set of experiments with 0.1, 1.0 and 10.0 and 10.0 mM of anionic ligand concentration were conducted. To minimize cationic effect sodium based

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anionic ligands were studied. These anionic ligands considered were EDTA, citrate, phosphate, acetate, fluoride and phosphate, which were studied with the above concentrations.

To study the selective sequence of anionic ligands as 3D stack bar diagrams (figure 7) for different concentration of anionic ligands. Percentage reduction in metal removal was calculated by subtracting the values obtained in presence of anionic ligands from the results of the percentage of adsorption in the absence of anionic ligands and shown in the z-axis of the above plots. The selectivity sequence of anionic ligands from highest to lowest reduction in the percentage of metal removal is as follows.

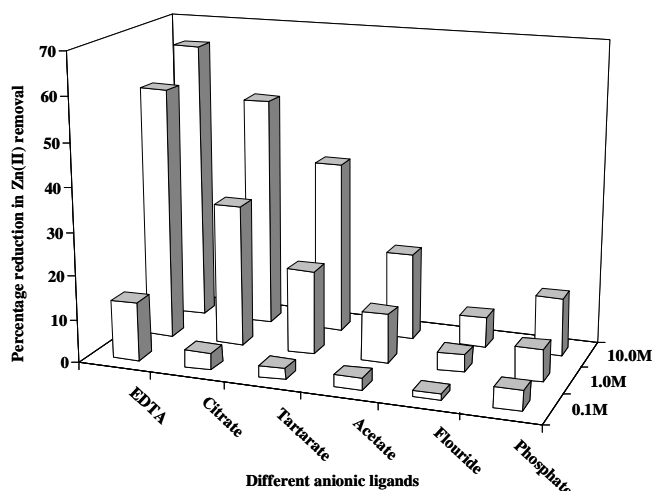EDTA>.Citrate>Tartarate>Phosphate>Fluoride>Acetate

Figure 7 : Reduction in percentage of Zn(II) removal due to the presence of different anionic ligands

It was observed that EDTA, is the strongest chelating agent among all the anionic ligands, which inhibited the uptake of metals even with a concentration of 0.1mM. Next to EDTA, higher concentration of citrate and tartarate also reduced the metal removal substantially. These anionic ligands are multidentate ligands or ligand with more numbers of binding sites. The resulting metals complexes formed with these multidentate ligands (when react with metal-ions) are extremely stable because of higher stability constants for the corresponding metal-ions. These metal complexes cannot be adsorbed with the adsorbent[22]

Rao, (1995)[23] reported from their study, selectivity sequence of anionic ligands as: EDTA> citrate> phosphate> fluoride> acetate for sorption of Pb (II) with

Kimberlite tailings. The variable selectivity for different metal-ions might be due to the different stability constants of different soluble ligands[22]

CONCLUSION

Following conclusions can be drawn.

1. Waste sludge can be used as an expensive and highly effective adsorbent for the recovery of Zinc.
2. Percentage metal removal increased with increase of adsorbent concentration and decreased with the increase of initial concentration. This was because the ratio of initial number of moles of metal ions to the available adsorption sites of adsorbent became higher with increasing concentration. Reverse was the case with increase of adsorbent concentration.
3. The sorption capacity and the percentage of metal ion removal decreased with increasing particle size due to decrease of available surface area per gram of adsorbent.
4. The equilibrium contact time depended on the ratio of the number of adsorption sites to the number of metal species that can be adsorbed.
5. Adsorption edge was in the range of pH 3.0 to 5.0.
6. Higher concentration of ionic strength reduced metal adsorption.
7. Presence of EDTA and citrate significantly affected adsorption among the anionic ligands.

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