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Zinc Removal from Simulated Wastewater by Flotation Method

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Abstract: ***Tests were done to achieve the best results removing zinc ions from wastewater that was simulated in the laboratory. This was investigated by implementing flotation method which was accomplished by employing sodium dodecyl sulfate; i.e. SDS as a surfactant. Experiments were carried out to study the effect of various parameters such as pH (4, 5, and 8), initial zinc ions concentration (30, 60, and 120) mg/L, flow rates (250, 500 and 1000cm^3/min), and SDS concentration (30, 60, and 120) mg/L. The results show that the maximum removal efficiency was 93%, obtained under optimum conditions; pH=6, 60mg/l SDS concentration, 500cm^3/min flow rate and at30 mg/L zinc ion concentration. The obtained results proved that the flotation process is an efficient technique for removing Zinc from aqueous solutions.***

Keywords: zinc ion; SDS surfactant; wastewater; flotation method

1. Introduction

Increased use of metals and chemicals in process industries has resulted in generation of large quantities of effluent that contain high level of toxic heavy metals and their presence poses environmental–disposal problems due to their non-degradable and persistence nature [1].Industrial effluents loaded with heavy metals are hazardous to humans and other forms of life [2]. The presence of heavy metals in the aquatic environment has been of a considerable concern because an increase in discharge causes increase of their toxic effects, in addition to other adverse effects on water and subsequently on aquatic life [3]. Heavy metals like cadmium, zinc and lead have general toxic effects on human organisms and plant metabolism even when present in low concentrations [4]. Zinc (II) is usually found in effluents discharged from industries mainly of galvanized iron, bronze, paint, electroplating, pigments, battery manufacturing units, mining, fertilizers, metallurgy and municipal wastewater treatment plants [4]. Zinc (II) is a well-known toxic metal that can threaten human life by bioaccumulation in the food chain. The World Health Organization recommended a maximum acceptable zinc concentration in drinking water of 5.0 mg/L. The removal of zinc (II) ions or decreasing its concentration to the permitted levels before discharge is necessary to prevent deleterious effects on the ecosystem and public health [5]. Zinc ions in water may occur naturally fromanthropogenic sources and from leaching of ore deposits that mainly include solid waste disposal and industrial effluents. The levels of heavy metals in water system have substantially increased over time with rapid development of industrial activities [6].Traditional methods for removing heavy metals from aqueous solutions include chemical precipitation, solvent extraction, coagulation, electrolysis, ion exchange, membrane separation and adsorption [7].Flotation as a separation process has recently received a considerable interest owing to its simplicity, rapidity, economy, good separation yields (Recovery> 95 % for small impurity agent concentrations (10.6 to 10.2 mol/l), a large prospect of applications for species that have different nature and structure, flexibility and friability of equipment and processing for the significant purpose of recovery and an additional production of more concentrated sludge, occupying smaller volumes [8]. It is well believed that this process will soon be incorporated as a clean technology to treat water and wastewater [9].Ion flotation usually involves the elimination of surface inert ions (colligend) from an aqueous solution which is done by adding surfactants that act as collectors. The subsequent passage of gas bubbles through the solution transfers the surface-active ions to the top [10].Compared to other separation methods, ion flotation has advantages in its ease of operation and low cost. It shows particular promise for treating large volumes of dilute aqueous solutions [11]. Typical surfactant molecules like those applied in this study consist of an ionic polar head along with a chain of non polar hydrocarbon. Attachment of the group of polar head to the metal ion leads to an exposure of the section that is a non polar hydrophobic of the concerned surfactant into the concerned solution. When introducing air bubbles within the flotation cell, the heavy metal ion surfactant gatherings are collected by the air bubbles because of the interactions between the bubbles and the exposed hydrocarbon chains. Therefore, sometimes the surfactant molecules are also named "collectors" by the floatation terminology. The bubbles of air enriched by the heavy metal ions tend to float towards the surface at the top and are thereafter taken out as a froth that is enriched in metal ion content. The air bubbles size in the flotation cell would be extremely small (ranging limits to few hundred micrometers) to grant an adequate surface area sufficient for collection. The reagents that control the air bubble size via reducing the interfacial tension of air to water ratio are called "frothers". Some of the widespread frothers used in flotation are (MIBC) i.e. methyl isobutyl carbinol, ethanol, methyl ethers for example, Dowfroth 250 and polypropylene glycol. A few common frothers could have both frothing and collecting properties at the same time [12].

2. Flotation Kinetic

Flotation kinetics is studying the variation of floated concentration along with flotation time. Studies of the kinetics of flotation are helpful in the clarification of the mechanism process, and work as useful predictive tools in the implementation of the flotation technology [13].

There is a direct relationship between the rate of flotation and the amount of floatable material remaining in the cell that is:

$$\text{Flotation rate} = k^* (\text{concentration in cell})^a \quad \dots (1)$$

Flotation rate can be defined as the rate of change of concentration of the floatable materials in the cell, thus Equation (1) might be rewritten as:

$$\frac{dc}{dt} = -kc^a \dots\dots\dots\dots\dots (2)$$

This equation could be considered the fundamental rate equation, where k is the flotation rate constant while the value of (a) represents the order of the equation.

Integrating Eq. (2) with (a) equals to one (i.e. first order equation) gives:

$$C = Co\, e^{-kt} \qquad (3)$$

Where C (mg/l) represents the final concentration of remaining material at time t and Co (mg/l) is the valuable material concentration at zero time, Taking Ln of Eq. (3)

$$\mathrm{Ln}\frac{C}{C_o} = -k\,t \dots\dots\dots\dots\dots\dots\dots (4)$$

When plotting values of ln(C/Co) against (t) and having a =1, the resulting graph would be a straight line with slope value of k.

The rate constant (k) in this equation shows how rapid the species float. A high rate constant gives an indication that these species float rapidly while a low rate constant means lagging in flotation [14].

The aim of this research is to investigate the zinc ions removal efficiency by floatation method using sodium dodyecyl sulfate (SDS) as surfactant. The effect of pH, different zinc ion concentrations, flow rate, SDS concentrations were considered.

3. Materials and Method

3.1 Materials

Sodium dodyecyl sulfate (SDS) was considered an ionic collector; which is a white powdery substance of a chemical structure ($C_{12}H_{25}OSO_3Na$) with a M.Wt.=288.38g/mole. Ethanol (C_2H_5OH) as a frother. Zinc ions ($ZnSO_4.7H_2O$), M.wt.= 287.54g/mole. Hydraulic acid (HCL) and caustic soda (NaOH) were used as reagents for pH adjustment. The mass of zinc material required to achieve the wanted concentration was calculated according to the following equation:

$$W = V\,.C_O\,.\frac{M.Wt}{At.Wt} \dots\dots\dots\dots (5)$$

Where W indicates total weight of zinc salt (mg), V is the solution volume (l); C_O is the initial or starting concentration of zinc ion in the solution (mg/l), M.Wt and At.Wt. are molecular weight of zinc salt and atomic weight of zinc ion respectively (g/mole).The concentration of zinc in solutions was determined by using an atomic absorption spectrophotometer device. The adsorbed amount of zinc was calculated by the following equation:

$$qe = \frac{V\,(Co-C)}{W} \quad \dots\dots\dots\dots (6)$$

Where qe is the internal concentration of solute per unit weight of activated carbon, V is volume of container, W is the weight of activated carbon, Co and C are initial and final concentration of solute.

3.2 Method

Synthetic wastewater was formulated for the research by solving $ZnSO_4.7H_2O$ in distilled water and adding surfactant and ethanol then adjusting the pH to the required value using either HCL or NaOH.

Foam floatation tests were performed in an acrylic bubble column having a 6cm inside diameter with a height of 120cm. Figure 1 shows schematic diagram of experimental work. A compressor was connected to the apparatus to supply air to the column. An air distributor plate which has 25 holes each of 0.05cm in diameter was introduced to the system to disperse air bubbles into the liquid. Samples were taken through tab from column at specific time intervals. Preparation of samples and testing were done in room temperature. Before each experiment the column was cleaned by HCL then thoroughly rinsed with distilled water.

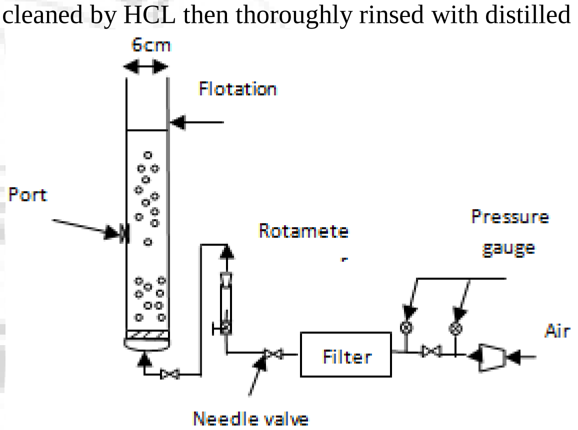

Figure 1: Experimental setup diagram

4. Results and Discussion

4.1 Effect of pH

To investigate the influence of pH of a solution on the separation efficiency of the zinc ion towards the collector used in single system, different pH values ranging from 4 to 8 were conducted at a flow rate of 500 cm3/min, SDS concentration and zinc concentration of 30and 60 mg/l respectively and plotted in Figure (2), from seeing the figure it can be noted that the efficiency of removal increases suddenly at the first 3 minutes interval from starting the experiment, afterwards the removal begins a slow increase with time because of the effective use, i.e. consumption of the surfactant with time. Whenever pH increased, removal efficiency increased. The highest removal was 89% for $Zn^{+}2$ accomplished at pH value 8 that corresponds to the metal ion precipitation while at pH less than 6, the removal decreased due to the active surface was either dissociated or charging positively causing emitting of protons that compete with zinc ion resulting in a decrease of zinc removal efficiency [15].A similar trend was noticed by [16, 17, 18, and 19]. A removal rate constant (k) at various pH was calculated by

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plotting ln (C/Co) aligned with time consistent with equation (4). The obtained rate constants were plotted in figure (3) and the estimated values are documented in table (1). It has been noted that by increasing pH, the rate constant (k) increased significantly.

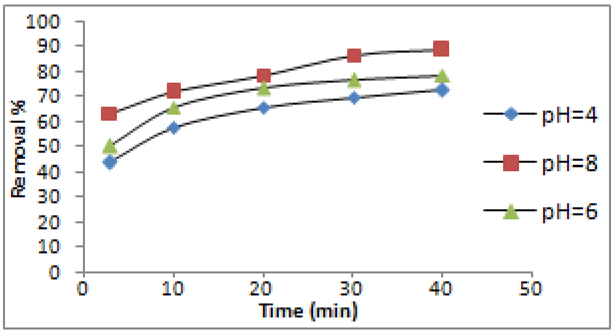

Figure 2: Effect of pH on the removal efficiency of zinc ions

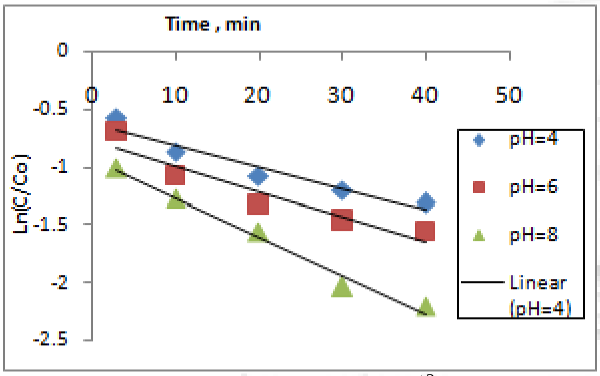

Figure 3: Ln(C/Co) versus time for Zn^{+2} at different pH

Table 1: Rate constant (k) at different pH

pH	4	6	8
$K*10^{2}$ (min^{-1})	2.879	2.204	3.354

4.2 Effect of Surfactant

In order to find a suitable concentration of SDS for removing Zn^{+2} ion from aqueous media, a series of experiments were conducted at pH 6, air flow rate 500 cm^3/min and zinc concentration 60 mg/l using different concentrations of SDS of 30, 60and 120 mg/l as can be seen in Figure 4. It can be derived from this figure that Zn^{+2} ion removal efficiency peaked when SDS concentration was 60 mg/l, high SDS concentration (120mg/l) deterred floatation process, where poor floatation occur at high surfactant concentration [20] For low SDS concentration, low removal efficiency was obtained. This can be explained by the insufficient amount of surfactant required to complete floatation process, an insufficient froth layer forming at the surface [16, 21]. The removal rate constant (k) at different SDS concentration was found by plotting ln (C/Co) aligned with time consistent using equation (4). The rate constants obtained were plotted in figure (5) and the values were tabulated in table (2). It was noticed that maximum rate constant was at surfactant concentration 60mg/l.

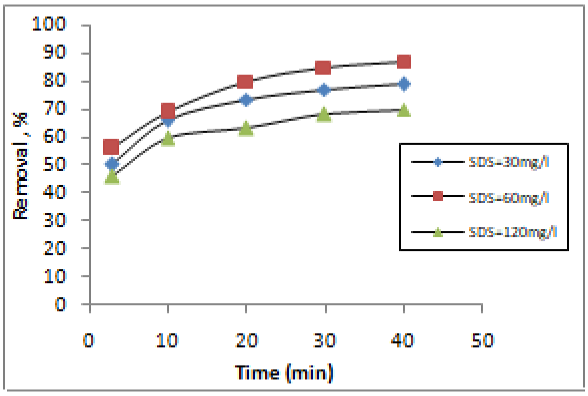

Figure 4: Effect of different surfactant concentrations on zinc removal efficiency.

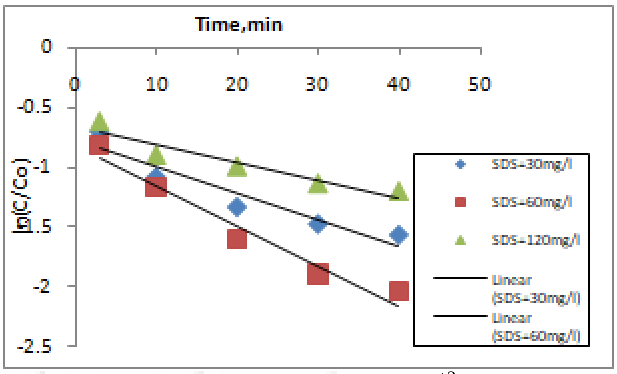

Figure 5: Ln(C/Co) versus time for Zn^{+2} at various SDS concentrations.

Table 2: Rate constant (k) at different surfactant concentrations

SDS concentration (mg/l)	30	60	120
$K*10^{2}$ (min^{-1})	2.204	3.33	1.476

4.3 Effect of Air Flow Rate

The effect of different air flow rates (250, 500 and 1000 cm^3/min)on Zn^{+2} ion removal efficiency at pH 6 , 60mg/l zinc ion concentration and SDS concentration of 60mg/l is shown in Figure 6,this figure indicates that as gas flow rate increases, the removal efficiency increased [20, 22].Nevertheless, higher air flow rate (1000 cm^3/min) ultimately causes a decrease in the removal efficiency from the maximum due to the re-dispersion of some of the metal collector product right back in to the solution [23].The rate constants attained for different air flow rate were shown in figure (7) and their constants of removal rate (k) were estimated and tabulated in table 3, which shows that a rate constant increases with an increase of air flow rate from 250 to 500 cm3/min then decreases in 1000 cm^3/min.

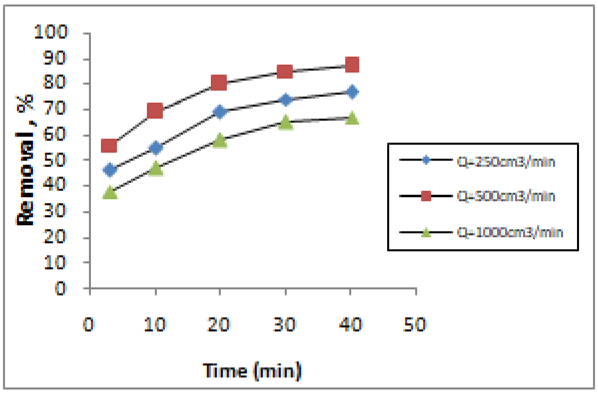

Figure 6: Effect of flow rate on zinc removal efficiency

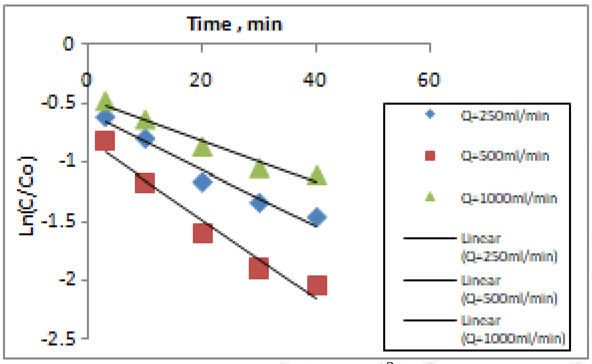

Figure 7: Ln(C/Co) versus time for Zn^{+2} at different flow rate

Table 3: Rate constant (k) at different air flow rate

Air flow rate (cm3/min)	250	500	1000
K*10^2 (min-1)	2.385	3.334	1.771

4.4 Effect of Initial Concentration

Different initial metal concentrations of (30, 60 and 120) mg/l were tested in this study keeping other parameters constant. The removal efficiency of zinc ion at various initial concentrations is shown in Figure 8. Maximum removal efficiency recorded was 93% for lowest zinc concentration of 30 mg/l. This behavior coincides with [24] which can be attributed to increase of collector and the effect of decreasing zinc concentration because competition for bubble surface between free collector ions and the metal-collector product. The resulting rate constants attained from the slope of lines were shown in figure (9) and the corresponding constants of removal rate (k) at different initial zinc ion concentration were estimated and tabulated in table 4, which noticed that as fastest metal ions removal happened at a lower initial concentration.

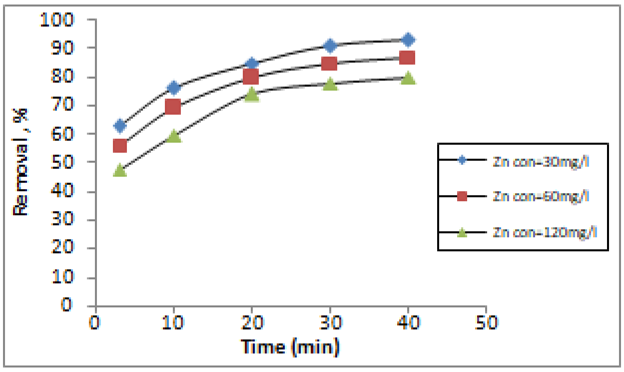

Figure 8: Effect of the initial concentration on zinc ions removal efficiency.

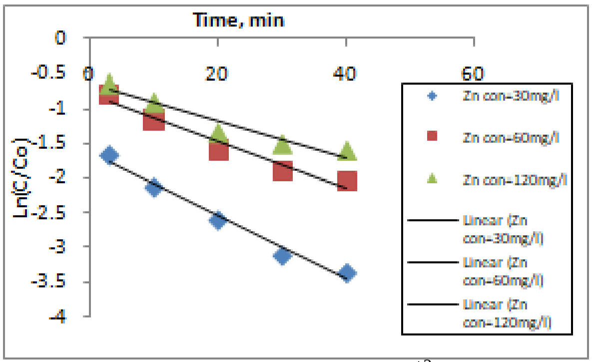

Figure 9: Ln(C/Co) versus time for Zn^{+2}at different ion concentration

Table 4: Rate constant (k) at different initial concentration

Zinc initial concentration (mg/l)	30	60	120
K*10^2 (min^{-1})	4.655	3.334	2.668

5. Conclusion

The main objective of this study was to optimize the parameters in zinc ion flotation. To achieve the aim, various parameters such as pH, the concentration and SDS surfactant concentration were investigated to compute the optimum flotation conditions. The maximum percentage removal in the batch system was 93%, obtained under optimum conditions; pH=6, 60mg/l SDS concentration, 500cm^3/min flow rate and at30 mg/l zinc ion concentration.

The results indicate that the data of flotation tests were well fitted with the kinetic equation of the first order, also the computed values of rate constant (k) increase with decreasing initial metal concentration.

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