REMOVAL OF COPPER ION FROM WASTEWATER BY FLOTATION

Ahmed A. Mohammed and Farah I. Abed

Environmental Engineering Department

University of Baghdad Iraq

ABSTRACT

Several industrial wastewater streams may contain heavy metal ions, which must be effectively removal before the discharge or reuse of treated waters could take place. In this paper, the removal of copper(II) by foam flotation from dilute aqueous solutions was investigated at laboratory scale. The effects of various parameters such as pH, collector and frother concentrations, initial copper concentration, air flow rate, hole diameter of the gas distributor, and NaCl addition were tested in a bubble column of 6 cm inside diameter and 120 cm height. Sodium dodecylsulfate (SDS) and Hexadecyl trimethyl ammonium bromide (HTAB) were used as anionic and cationic surfactant, respectively. Ethanol was used as frothers and the optimal removal conditions have been established. Successful removals about (98%) and (76%) could be achieved for copper ions with SDS and HTAB, respectively. Copper removal reached about 80% under the optimum conditions at low pH; at high pH it became as high as 98% probably due to the contribution from the flotation of precipitated copper. It was found that the presence of NaCl in the solution reduced the recoveries. Adding ethanol at 1% concentration increased the removal efficiency. From the results the rate of flotation was found to be first order.

Key words: bubble column, copper ions, flotation.

1. Introduction:

Water pollution is nowadays a matter of deep apprehension. Many industrial wastewaters contain numerous toxic metals, such as chromium, mercury, cadmium, lead, copper, which must be removed before reuse of the water or its discharge to the environment. According to environmental regulations, there is an increasing concern about the removal of metal in the effluent streams. Therefore, the scientific research is being directed towards the implementation of novel approaches dealing with the efficient removal of toxic metals from wastewater (Zhang et al., 2009).

The wastewater treatments used for removal of toxic metals include the convention a physicochemical treatment of addition of inorganic coagulants and polymers, subsequent precipitation, aeration, and final neutralization. However, the final step, which should involve the treatment and safe disposal of toxic sludge, has been largely ignored (Matis et al., 2001).

In the treated industrial wastewaters, depending on reuse/recycling options; some of the values often exceed legal limits. Therefore, the necessity of innovative, simple, and economical treatment methods for the final polishing step or tertiary treatment are needed (Matis et al., 2001).

Copper has received considerable attention owing to its uses in metallurgy, chemical industries and is necessary for other many biological important functions (Ghazy et al., 2008). The primary sources of copper in industrial wastewaters are metal process pickling baths and plating baths (Eckenfelder et al. 2009).Copper may also be present in wastewaters from a variety of chemical manufacturing processes employing copper salts or a copper catalyst in different range from 0.12 mg/l to 183 mg/l such as mining acid, mine drainage, paint and pigment manufacturing and motor vehicle (Metcalf and Eddy, 2003).

There are various methods for removing metals from water and wastewater, e.g., chemical precipitation, ion exchange, reverses osmosis. These methods are relatively expensive, involving either costly equipment or elaborate procedures, and with some techniques, large volumes of secondary wastes are generated (Sabti et al., 2002).Flotation is one of the adsorptive bubble separation techniques which have many advantage such as high selectivity to remove contaminants, high overflow ,low detention periods and low operating costs(Sulaymon and Mohammed,2010).

Several researches have been done on the copper removal from wastewater using foam separation techniques. A thermodynamic approach was investigated to model the removal of cupric ion using different surfactant types and ion flotation systems by liu et al., 2001.

Doyle et al., 2003 reported that the effect of a neutral chelating ligands, triethylenetetraamine (Trien) on the ability to separate copper (II) and calcium (II) ions.

A study concerning the kinetics of Cu^{+2} ion separating by precipitate flotation using alkyl amine type and alkylammonium salt as cationic collectors and alkylsulphate and alkylcarboxilic type as anionic collectors was presented by Stoica et al., 2003.

Lazaridis et al., 2004 was investigated the recovery of copper ions from wastewater. They used three different mechanisms: ion flotation using xanthates, precipitate flotation generating copper hydroxide and sorptive flotation using zeolites as a sorbent material.

Ghazy et al., 2008 developed a simple, rapid and economic procedure for copper (II) and lead (II) removal under the optimum conditions. It was based on the complex formation between Cu^{+2} and Pb^{+2} ions and diphenylcarbazone (HDPC) followed by flotation with oleic acid (HOL) surfactant.

Liu et al.,2009 Investigated the Ion Flotation of Co^{+2}, Ni+2, and Cu^{+2} using Dodecyldiethylenetriamine(Ddien),They obtained that a chelating surfactant, dodecyldi-ethylenetriamine (Ddien), could selectively remove one metal ion over others at different pH values.

A system for removal of Cu^{+2} from aqueous solution by foam fractionation using Dodecyl Benzenesulfonic acid (the anionic surfactant) was proposed by Zhang et al., 2009.

Abryutin et al., 2010 investigated the regularities of the ion flotation of copper by using sodium diethyldithiocarbamate (DEDTK) as the collector.

2. Experimental Apparatus and Procedure:

The foam flotation tests were carried out in a bubble column (acrylic) of 6 cm inside diameter and 120 cm in height. **Fig. (1)** Show a schematic diagram of experimental apparatus. Air supplied by the compressor was fed to the column through a pre-calibrated rotameter. Air entered the column was dispersed as bubbles in to liquid. Feed inter with different metal concentration (25 up to 200 ppm) was poured gently at the top of the column. At the same time, the column was pressurized so as not to weep the liquid through the holes. Two perforated plates of the air distributor were used. The first one has 20 holes with 0.1 cm diameter, and the second one has 25 holes with 0.05 cm diameter. The holes are arranges in the equilatered triangular pitch through the whole area which are located inside the column. The column was operated at batch mode as far as the liquid phase and continuous flow with respect to air. This column contains six taps of 0.2 cm inside diameter, these taps arranged at interval of 15cm and used to draw samples from the column. Synthetic polluted water samples containing maximum concentration of copper (200mg/l) were prepared by dissolving ($CuCl_2.2H_2O$) in distilled water. Surfactants and ethanol were added to the synthetic polluted water. Solution pH was adjusted to a desired value using H_2SO_4 or NaOH. Then the solution was placed in the flotation column. Foam samples were taken at preset time intervals as 5, 10, 15, 20, 25, 30, 35 and 40 minutes. A port 0.45 m above the base was used for periodic sampling. About 3ml of solution was drained from the port before withdrawing each sample; samples were withdrawn slowly, to minimize entrainment of air bubbles.Between experiments, the column was cleaned using HNO_3, and then rinsed three times with double distilled water.

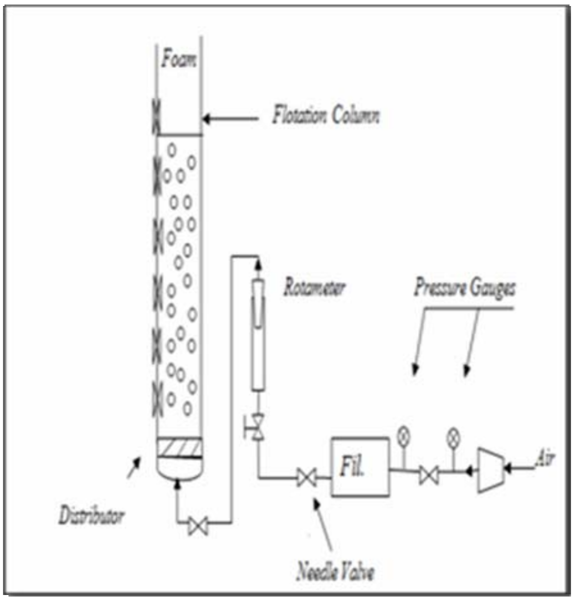

Figure (1): Schematic diagram of experiment system.

3. Results and Discussion

3.1 Effect of pH

The effect of pH on the recovery of copper by bubble column is shown in **Fig. (2)** by plotting the removal ratios versus time at various pH values .As shown in this figure the removal ratios decreases suddenly after approximately ten minute from the beginning of the run, then, these ratios began to decrease slowly with time. It was found that the highest removal achieved when the pH of the solution was 10. This results are in accordance with Polat and Erdogan (2007) that suggested that the charge of copper ion was positive Cu^{+2}, $CuOH^{+}$ at pH below 10 whereas they are negatively charged $Cu(OH)^{-3}$ and $Cu(OH)_4^{-2}$ at pH values greater than 10. At and around pH 10, precipitation of neutral $Cu(OH)_2$ takes place. The formation of the precipitation of $Cu(OH)_2$ can explain the higher recovery for pH values at and around 10.

3.2 Effect of surfactant type

The removal rate of copper from water was studied at two different types of surfactant (sodium dodecyl sulfate and Hexadecyltrimethyl ammonium bromide) in order to show the effect of adding anionic and cationic surfactant on the removal rate of copper ions. The effect is shown in **Fig. (3)** at the two surfactant types. From this figure, it can be seen that the anionic surfactant (SDS) is more efficient than the cationic surfactant (HTAB) and at pH lower than 10 no significant removal rate was obtained using (HTAB) and the removal rate increases for pH more than 10.

3.3 Effect of surfactant concentration

The effect of different sodium dodecyl sulfate (SDS) concentration in the copper removal was shown in **Fig. (4)**. It can be seen that there is no significant difference in removal rates with increasing SDS concentration from 25 mg/l to 75 mg/l. Further increasing in surfactant concentration results in decreasing in the copper removal .The decreasing in the copper removal for raised collector concentration can be due to competition between coligend-collector complex and free ion collectors for a place in the surface of the bubble (Medina et al., 2005).

3.4 Effect of initial copper concentration

The removal rate of copper at various initial copper concentrations is shown in **Fig. (5)** by plotting (C/C_0) rate versus time. From these figures, it was found that there is no significant difference in removal rate with increasing copper concentration from 100mg/l to 200mg/l. However at low copper concentration (25mg/l) the removal rate decreased because of large

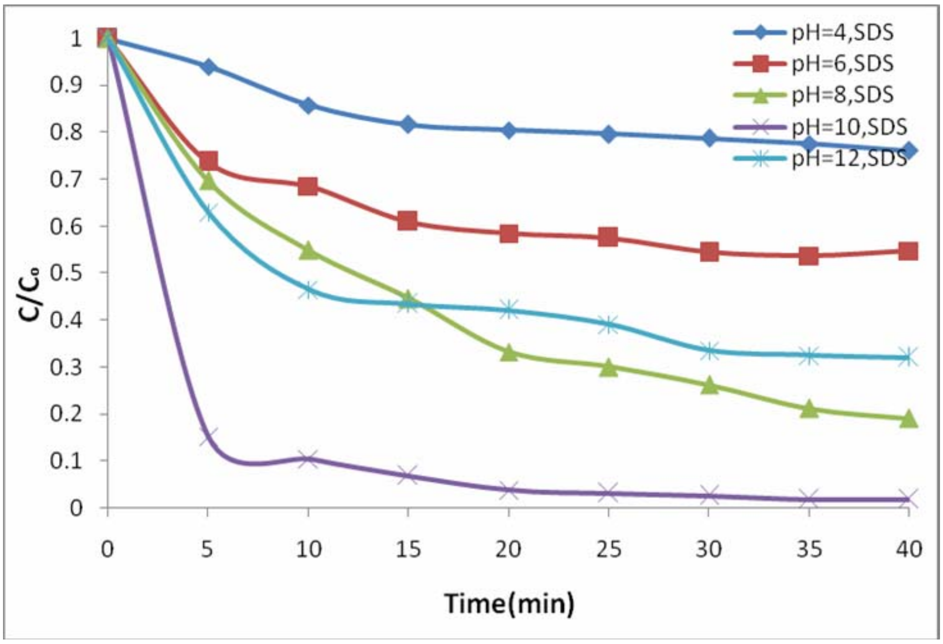

Figure 2. Effect of pH on the removal ratio of copper ions (C_o=100mg/l; SDS=75 mg/l; Q =250 ml/min; ethanol=1%, do=1mm).

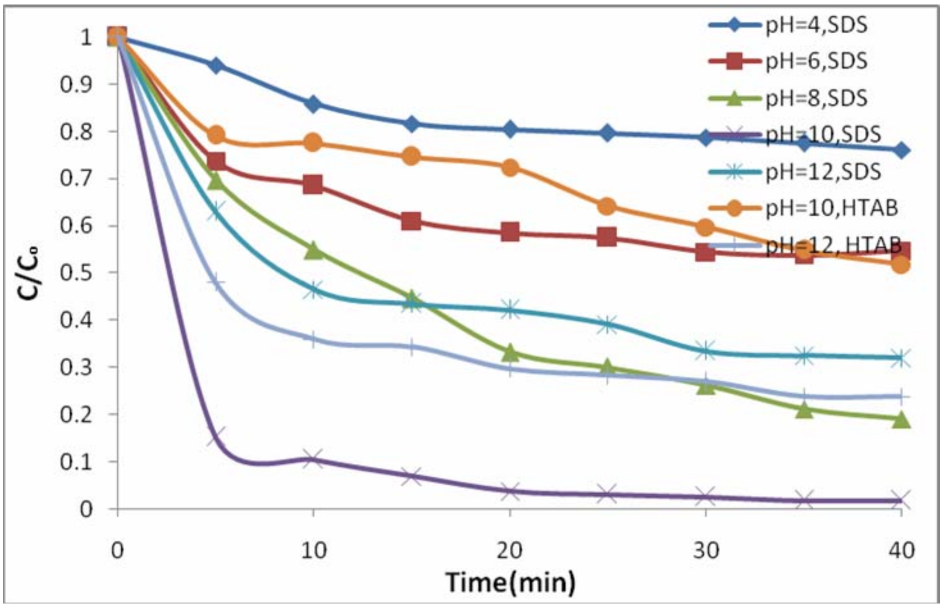

Figure 3. Effect of surfactant type on the removal ratio of copper (Co=100 mg/l; Q = 250 ml/min; SDS=75mg/l; HTAB=75mg/l; ethanol = 1 %, do =1 mm).

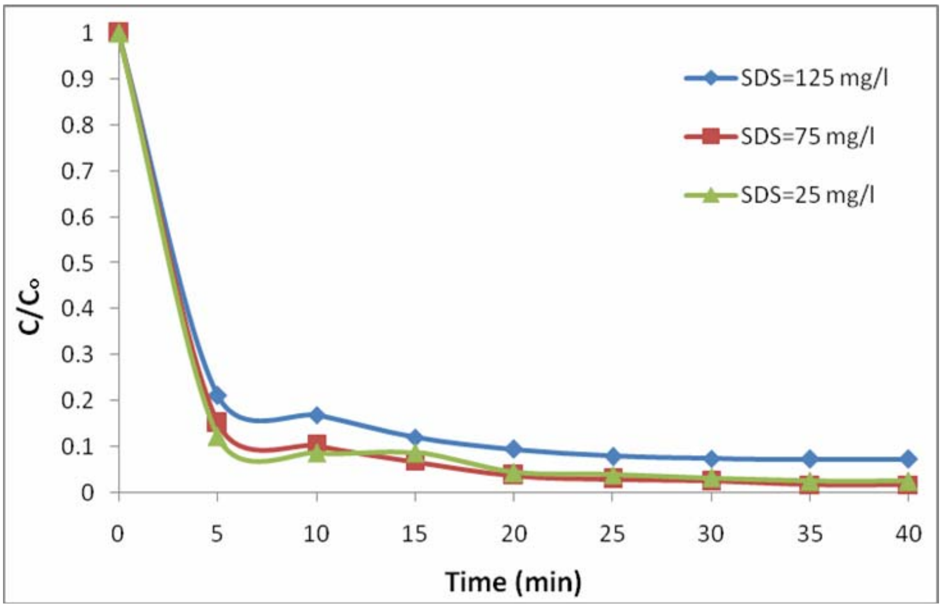

Figure 4. Effect of surfactant concentration on the removal rate of copper (pH=10; Co=100 mg/l; Q=250 ml/min; ethanol=1%; do=1mm).

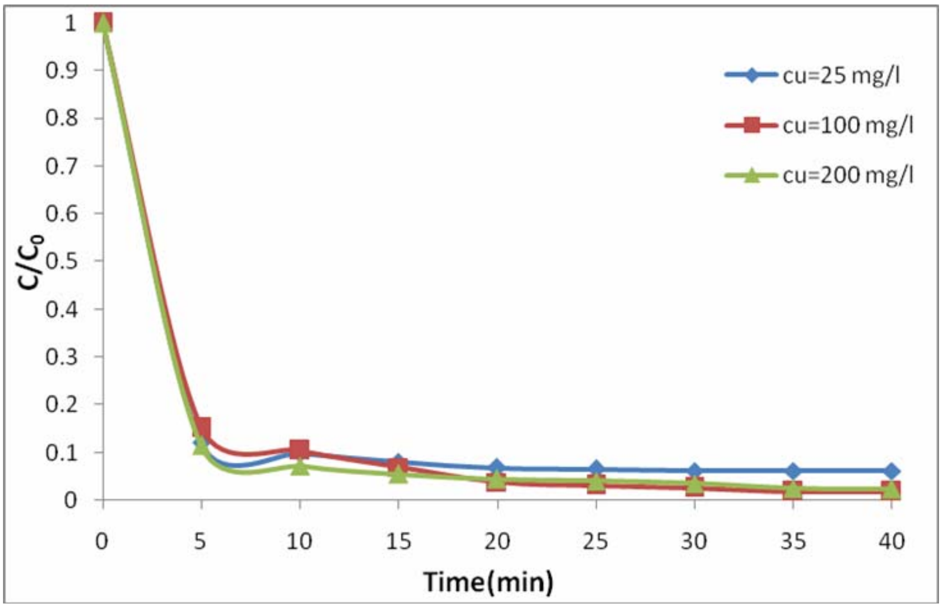

Figure 5 Effect of copper concentration on the removal rate (pH=10; SDS =75mg/l; Q =250 ml/min; Ethanol=1%, do=1mm).

Surfactant: copper ion ratio which cause competition, for bubble surface, between the metal–collector product and free collector ions (Shakir et al., 2010).

3.5 Effect of air flow rates

The effect of gas flow rate (100,250 and 500ml/min) on the removal efficiency of copper in the bubble column was investigated .The results are shown in **Fig. (6)**. The removal rate was highly affected by the gas flow rate. As gas flow rate increased, the removal ratio increased, This is because increased gas flow rate causes early bubble detachment, large fluid activities (stress)at the bottom section and bubble coalescence and (mostly) break up (Sulaymon and Mohammed, 2010).This results in a large number of small bubbles which leads to increasing surface area available for adsorption metal-collector.

3.6 Effect of frothers

The effect of adding ethanol to the copper ions removal is shown in **Fig. (7)**. The figure show that adding ethanol leads to increase removal rate of copper ions and at higher ethanol concentration the efficiency decreased. Increasing the removal efficiency with increasing in ethanol concentration in the solution is presumably attributed to decrease of degree of coalescence of gas bubbles leading to formation of more fine bubbles (Cho and Laskowski, 2002). Consequently, the surface area of the gas phase increases leading to improvement in flotation efficiency. However, an increase in ethanol concentration over a certain value results in reduction in the removal efficiency. This reduction in removal is attributed to that on elevation of frother concentration over a particular concentration (the critical coalescence concentration) the bubble size becomes no longer controlled by coalescence but will strongly depend on the sparger geometry and hydrodynamic conditions (Shakir et al.,2010). Also at the higher ethanol concentrations, the number of sites on the interface liquid-gas available for metal- collector complex adsorption will be reduced due to adsorption of alcohol molecules, which may lower metal removal (Medina et al., 2005).

3.7 Effect of ionic strength

The effect of adding NaCl to the copper ions removal was shown in **Fig. (8)** .It can be seen that the removal rate decreases with increasing NaCl concentration. The explanation of this improvement is that Na ions compete with copper ions so the metal ions cannot find enough dodecyl sulfate molecules to attach to (Choi et al., 1998).

4. Flotation kinetics

Flotation kinetics studies the variation of floated concentration according to flotation time.
Chemical kinetics principles are used in the modeling of flotation processes, particularly in the formulation of the basic rate eq.(1):

$$\frac{dc}{dt} = -kc^n \qquad (1)$$

where, (C) is the residual concentration of chromium at time t, (t) is the flotation time,(n) is the order of the flotation process, and k is the flotation rate constant, C_o is the initial concentration of copper . The results suggest that the process of copper(II) removal by precipitate flotation follows kinetics of first order being represented by equation(1): The integration of Eq. (1) gives:

$$\ln\left(\frac{C}{Co}\right) = kt \qquad (3)$$

The values for $\ln(C/C_o)$ plotted against flotation time gives a straight line with a slope equal to 0.092 and n equal to 0.944.

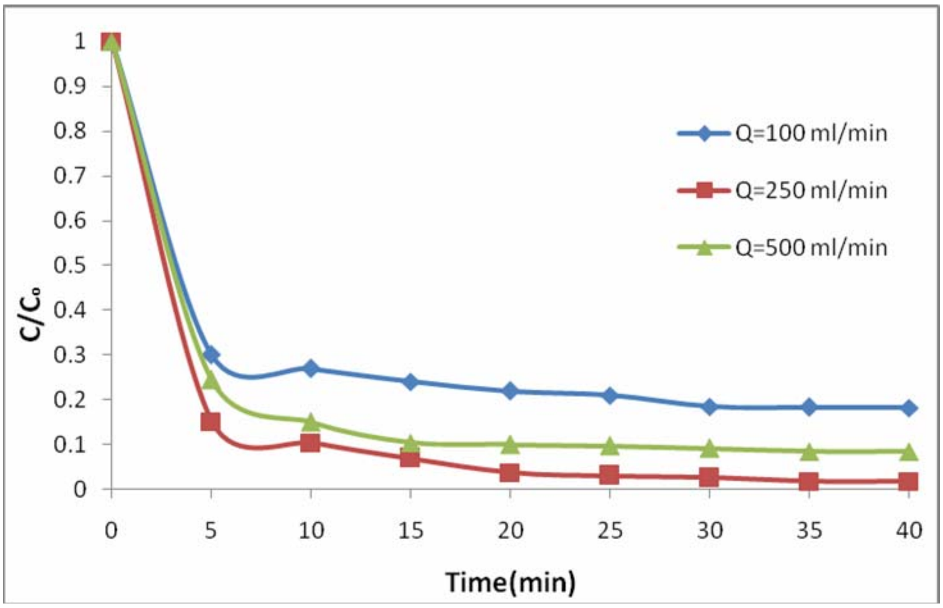

Figure 6. Effect of gas flow rate on the removal rate of copper (pH=10; Co = 100 mg / l; SDS=75 mg/l; ethanol=1%, do=1mm).

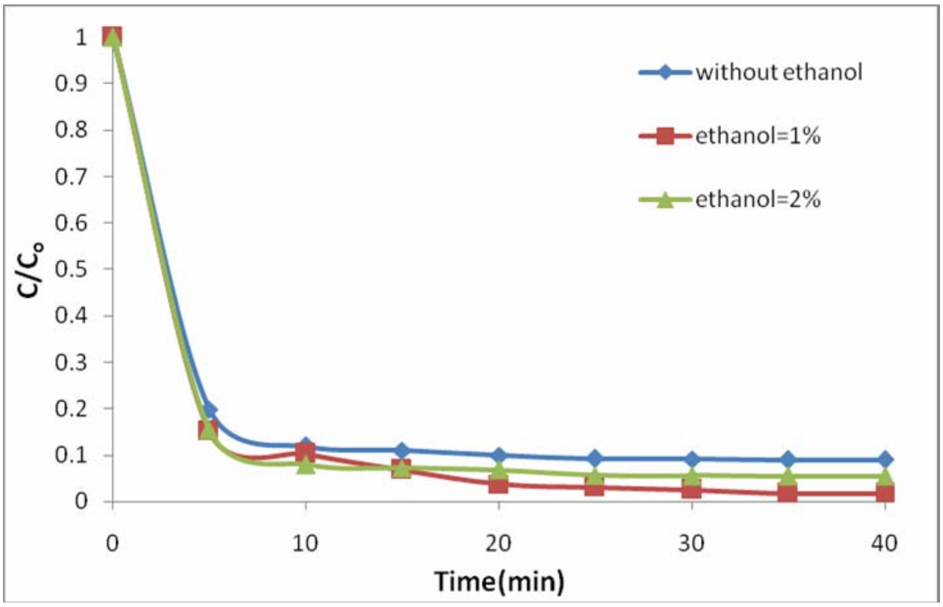

Figure 7. Effect of ethanol concentration on the removal rate of copper (pH=10; Co =100 mg/l; SDS=75 mg/l; Q =250 ml/min, d_o=1mm).

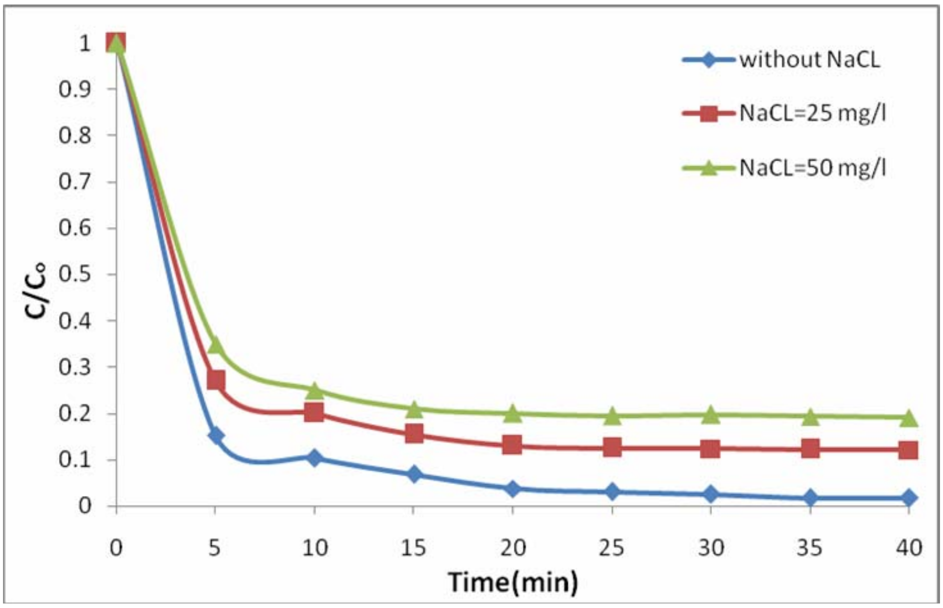

Figure 8. Effect of NaCl concentration on the removal rate of copper (pH=10; Co = 100 mg/l; SDS=75 mg/l; Q =250 ml/min; ethanol = 1 %, d_o=1mm).

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