

Kinetic Study of Copper Adsorption from Wastewater by Sodium Dodecyl Sulfate (SDS)

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Abstract: The discharge of industrial wastewater without treatment, especially those containing heavy metals into water recourses causes damage to the aquatic environment. Copper is considered toxic heavy metals found in industrial wastewater. The presence of high amounts of copper causes various physiological and health effects for human and other organisms. Flotation kinetics was studied for the flotation of copper using sodium dodecyl sulfate as an anionic collector. Chemical kinetics was studied through the influence of the parameters: pH of wastewater and collector concentration. Time-recovery plots were fit using first-order equation for flotation kinetics, namely, $R_t = R_\infty (1 - e^{-kt})$, flotation rate constant and the cumulative recovery at the infinite (R_∞) were computed. The experimental data fitted very well the first-order kinetic model.

Keywords: Copper, Sodium Dodecyl Sulfate, Flotation kinetics, First-order kinetics model, Metals

1. Introduction

The discharge of industrial wastewater to water sources without treatment, especially those containing heavy metals causes damage to the aquatic environment. Copper is considered a toxic metal found in industrial wastewater [1]. Copper that is exist in industrial wastewater is the result of some industries, such as plating baths, metal cleaning, refineries, fertilizer, paper board, pigments and paints and wood preservatives, etc [2,3]. Copper is highly toxic because it is non biodegradable and carcinogenic [4]. When copper exceed the emitted aquatic environment it can causes various physiological and health effects of human and other organisms such as hepatic and renal damages, mucosal irritation, and central nervous system damages [5]. Various maximum permitted levels of copper in the water are shown in Figure 1

Table 1: Various maximum permitted levels for copper metal composition [4].

Heavy Metal	W.H.O. [For drinking] (mg/l)	U.S.E.P.A. [For wastewater] (mg/l)	C.P.C.B. [For wastewater] (mg/l)
Copper	0.05	1.3	1.5

Many of the techniques used to remove metal ions from industrial wastewater. These techniques contain ion exchange, reverse osmosis, solvent extraction, precipitation, filtration, chemical oxidation and reduction, electrochemical treatment, flotation and adsorption [6]. However, most of these methods have some advantages such as complicated treatments process, high cost, low efficiency for heavy metal at low concentration, generation of sludge and huge amount of energy consumption. Among these methods, ion flotation technique is simple, effective and widespread in the removal of heavy metals from industrial wastewater [1]. The quantification of kinetic parameters is of increasing importance in industrial flotation to shed light on the speed of the process. Numerous researchers have studied the kinetic aspects of froth flotation paying special attention to particle

size, bubbles and their complex interactions [7]. The kinetic of the reaction varies widely depending on the metal and the conditioning parameters during the ion flotation process. The rate of collector adsorption can be influenced by many factors, such as the pH of wastewater, and collector concentration. These are key factors that determine the kinetics of the conditioning stage.

In this study theoretical estimations and experimental tests were performed in order to study the flotation rate constant of copper ions with sodium dodecyl sulphate (SDS) and cumulative recovery.

2. Experimental work

2.1 Type of Metal used

Prepared appropriate amounts of Copper chloride dehydrates ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) with double distilled water to make up of the solution were used in this study.

2.2 Flotation Agents

2.2.1. Collector agent

Sodium dodecyl sulphate provided by TCI Chemicals (India) Pvt. Ltd with 99% purity. The solutions were dissolved in water. The solute was then weighed and the desired solution obtained by successive dilutions as the agent concentrations used were very small.

2.2.2. Foaming agent

Phenol was used with different concentration of 0.0, 1.0, 2.0%, sufficient to stabilise the foam.

2.2.3. Modifying agents

HCl and NaOH were used as pH modifiers in the flotation column, and control was affected by means of a digital pH meter.

2.3 Flotation Column

Flotation column is designed and fabricated in the laboratory-scale. The schematic diagram of the experimental set up is given in figure (2.1). Flotation column was made of Pyrex glass with an internal diameter 8 mm, 0.12 mm external diameter and 120 cm in height.

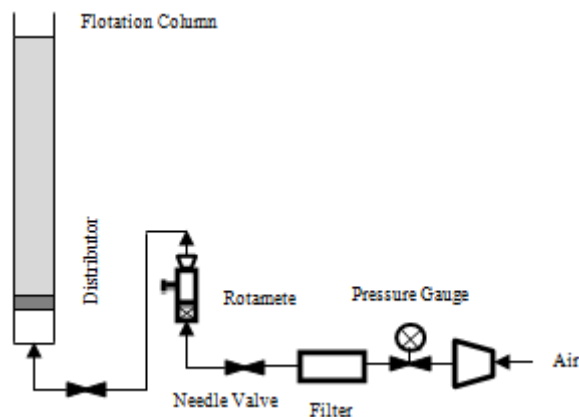


Figure 2.1: Schematic diagram of experiment system.

2.4 Working Procedure

Flotation column is designed and fabricated in the laboratory-scale. Flotation column was made of Pyrex glass with an internal diameter 8 mm, 0.12 mm external diameter and 120 cm in height. Air supplied by the compressor was fed to the flotation column through pre-calibrated rotameter. Air entered the column at the bottom was dispersed as fine bubbles in to liquid. Feed entering the flotation column was poured gently at the top. At the same time, the flotation was pressurized so as not to weep the liquid through the holes. The perforated of the air distributed was used. It is has 20 holes with 0.1 cm diameter, the holes are arranges in the equilateral triangular pitch through the whole area which are located at the bottom of column. The column was operated at batch mode as far as the liquid phase and continuous flow with respect to air. All experiments were carried out at constant temperature (Laboratory temperature, $27 \pm 1^\circ\text{C}$).

3. Flotation Kinetics

Different methods are used to calculate the order and the rate constant of the flotation metals. These methods include computational and graphical methods. Basically most of the chemical kinetic methods are dependent on the law of mass action which states that the rate of a chemical reaction proportional to the active masses of the reacting substances at any given time. Application of this law to the flotation of metals would involve the adaptation of the terms flotation for chemical reaction and floatable amount of the metals for the active masses of the chemical reactants. Many physical processes variables dominate the floatation rate. If variables such as the volume of the flotation liquid and the rate of aeration are kept at constant levels, the floatation rate will be given by the following relationship ^[1]:

$$\text{rate} = \frac{dC}{dt} = -k C^n \quad \rightarrow (1)$$

$$-\frac{dC}{dt} = k C^n \quad \rightarrow (2)$$

Where:

C: is the concentration of the floatable metal at any given time t.

k: is the rate constant.

n: is the order of reaction.

Since the flotation follows the first order kinetics, therefore the order of reaction is equal to unity or $n = 1$, so the equation 2 becomes ^[2]:

$$-\frac{dC}{dt} = k C \quad \rightarrow (3)$$

By integration of the equation 3 over the limits:

$$-\int_{C_0}^t dC = k \int_0^t dt \quad \rightarrow (4)$$

Taking the log of the integrated rate law for a first order process:

$$\ln \frac{C_0}{C_t} = kt \quad \rightarrow (5)$$

Or:

$$\ln C_t = \ln C_0 - k \times t \quad \rightarrow (6)$$

Equation 4 may be rewritten as follows:

$$\frac{C_0}{C_t} = e^{kt} \quad \rightarrow (7)$$

Or rearrangement equation 7 to:

$$C_0 - C_t = C_0(1 - e^{-kt}) \quad \rightarrow (8)$$

Where:

C_0 : is the initial concentration of the metal at time zero (at $t = 0$, $C = C_0$), this is called maximum theoretically Floatable amount or theoretically maximum possible recovery of the metal. Since the complete recovery of the metal found in the liquid is never done because some metal particles will not float such as a very coarse particles. Therefore, the initial concentration in the equation 8 replaces by the term R_∞ , where R_∞ represents the maximum recovery achievable or cumulative recovery at time infinite. Left hand side of the equation 8, $(C_0 - C_t)$ is equal to cumulative recovery at time t. So it can rewrite the equation 6 as follows:

$$R_t = R_\infty(1 - e^{-kt}) \quad \rightarrow (9)$$

4. Results

In order to find the reaction rate constant k, we used the equation (4) and we plotted $(\ln C_t)$ as a function of time (t) is a straight line with slope $(-k)$, were calculated from the straight lines slopes by statistic program and use the equation 9 to calculate the cumulative recovery. The reaction rate constants, correlation coefficients and cumulative recovery were shown in tables 2, 3. The reaction rate constant k was calculated for all the points plotted were shown through all the figures from 4.1 to 4.8 and for each initial concentration and other operational conditions. The correlation coefficients (R^2), in the tables demonstrate good linear relationship with a negative slope for each group of points. For the first of the three figures, the adsorption rate increases by increasing the initial concentration from 75 to 100 mg/L after that it is

become decreases to 125 ml/L. As can be seen in table 4.1, the reaction rate is the highest in the experiment with initial copper concentration of 100 mg/L.

Further experiments were carried out at different pH: 4, 6, 8, 10 and 12 with solutions of sodium dodecyl sulfate having the same initial 75 mg/L concentration. The experimental data are presented in table 4.2.

The influence of pH on the sodium dodecyl sulfate adsorption on copper is shown through figures 4.4, 4.5, 4.6, 4.7 and 4.8. Adsorption increases with increasing pH until it reached the highest value at pH = 10, after that the adsorption began to decline.

Results from all experiments concluded that the adsorption mechanism of sodium dodecyl sulfate on copper surface is affect with the initial concentration of copper and pH.

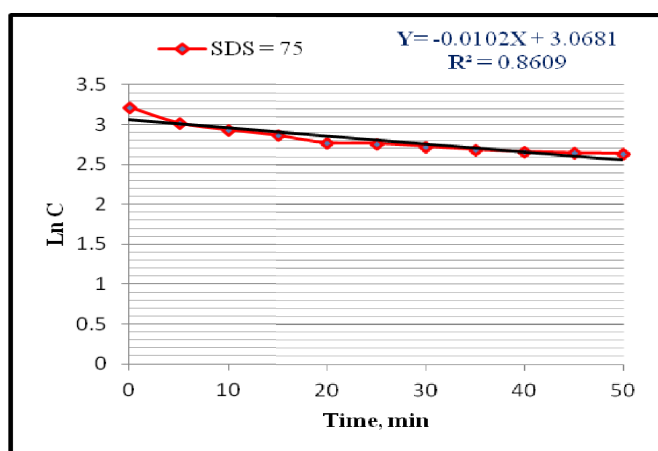


Figure 4.1: First order reaction curve for the adsorption kinetics of sodium dodecyl Sulfate on copper surface for initial concentration is 75 mg/L.

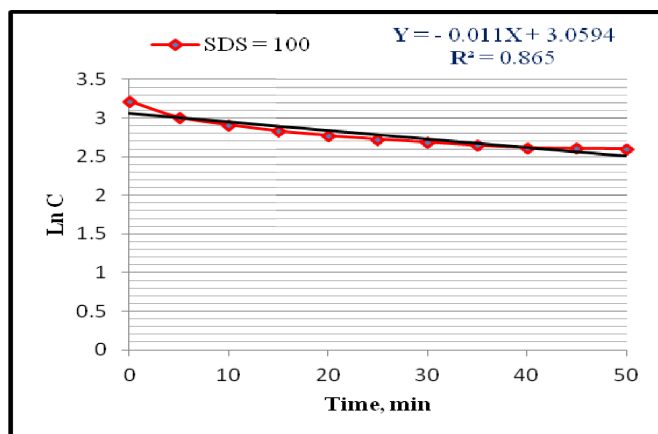


Figure 4.2: First order reaction curve for the adsorption kinetics of sodium dodecyl Sulfate on copper surface for initial concentration is 100 mg/L.

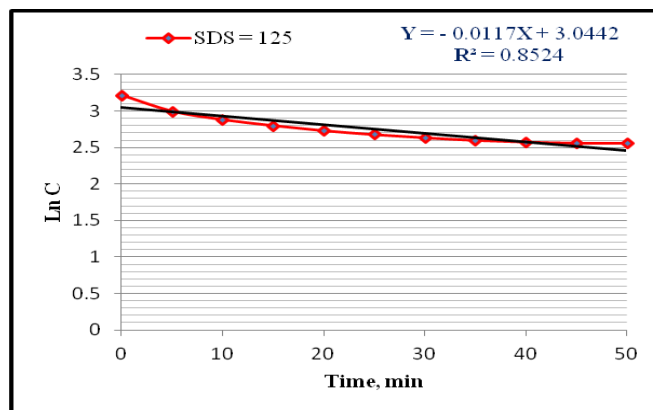


Figure 4.3: First order reaction curve for the adsorption kinetics of sodium dodecyl Sulfate on copper surface for initial concentration is 125 mg/L.

Table 4.1: Reaction rate constant and correlation coefficients for sodium dodecyl sulfate adsorption on copper surface for several initial concentration at pH = 10.0

SDS mg/L	K, min ⁻¹	R ²	R _t
25	0.04480	0.8609	89.4
100	0.06099	0.8650	95.3
200	0.04432	0.8524	89.1

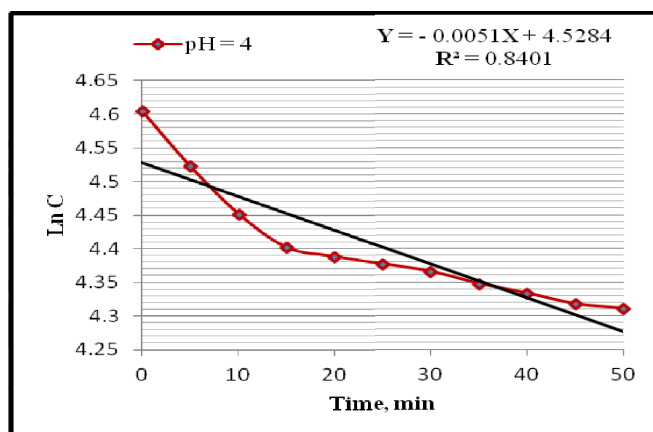


Figure 4.4: First order reaction curve for the adsorption kinetics of sodium dodecyl Sulfate on copper surface for initial concentration is 75 mg/L and pH = 4

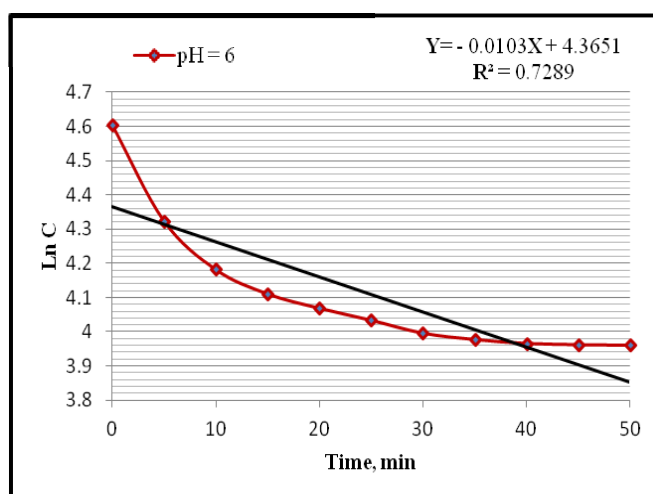


Figure 4.5: First order reaction curve for the adsorption kinetics of sodium dodecyl Sulfate on copper surface for initial concentration is 75 mg/L and pH = 6.

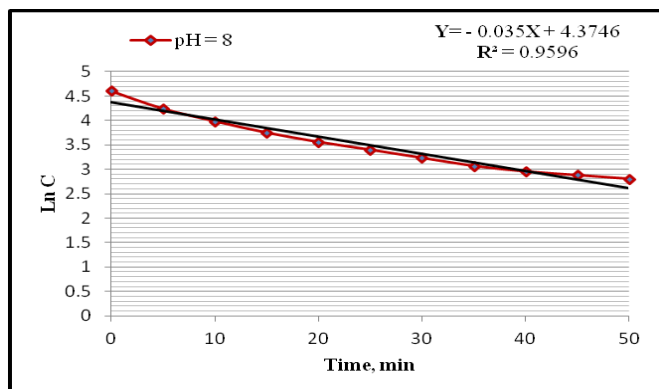


Figure 4.6: First order reaction curve for the adsorption kinetics of sodium dodecyl Sulfate on copper surface for initial concentration is 75 mg/L and pH = 8.

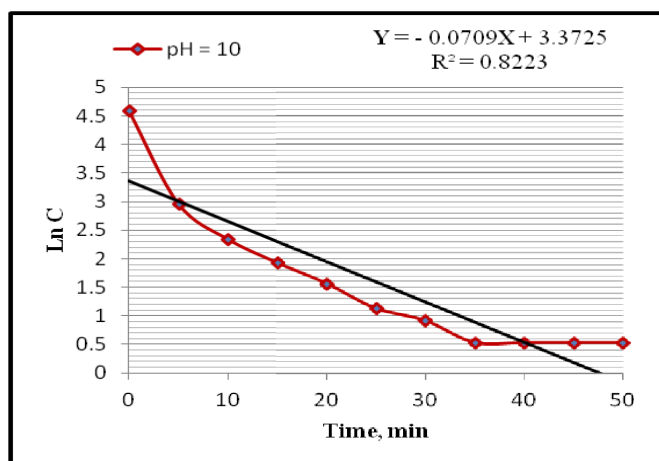


Figure 4.7: First order reaction curve for the adsorption kinetics of sodium dodecyl Sulfate on copper surface for initial concentration is 75 mg/L and pH = 10.

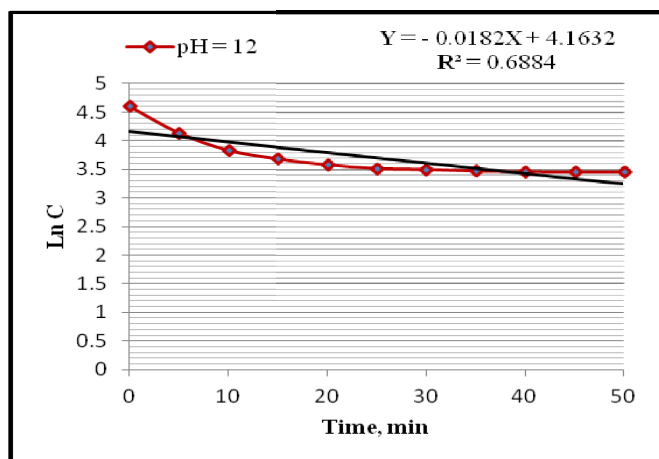


Figure 4.8: First order reaction curve for the adsorption kinetics of sodium dodecyl Sulfate on copper surface for initial concentration is 75 mg/L and pH = 12.

pH	k (min ⁻¹)	R ²	Cumulative Recovery (%)
4	5.1346×10^{-3}	0.8401	22.64
6	9.0354×10^{-3}	0.7289	36.34
8	0.03413	0.9596	81.85
10	0.06099	0.8223	95.30
12	0.01686	0.6884	57.00

5. Conclusion

The kinetics adsorption experiments were conducted in order to evaluate the adsorption characteristics of a anionic agent, namely sodium dodecyl sulfate on copper.

The rate of sodium dodecyl sulfate consumption can be expected to measure the amount of adsorbed sodium dodecyl sulfate or of the degree of conditioning.

The reaction rate constant is independent of the collector concentration; the k values are close to each other for the different experimental concentrations. The effect of pH on the reaction rate is very significant.

The experimental kinetics data could predict the floatability of copper; furthermore some connections shall be made between the parameters and performances during the conditioning stage in ion flotation and the adsorption kinetics in order to optimize the selectivity and the recovery of the desired mineral.

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