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Flotation of Cadmium Ions from Wastewater Using Air Micro-Bubbles

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ABSTRACT

In this work were carried out to verify the efficiency of micro-bubbles in flotation the heavy metals (Cadmium ions) from wastewater. Its unique attributes of being affordable, having a straightforward design, being highly efficient, and not causing any secondary contamination are the reasons for this. The flotation process (removal efficiency) was analyzed under different reaction conditions. Including PH of initial solution, initial pollutant concentration, gas (air) flow rate, type (anionic or cationic) and concentration of surfactant used, sampling port location and contact time. It was found from the experiments that the removal of Cd(II) by micro-bubbles was higher at pH 7.2, flow rate of 0.50 L/min, SDS surfactant concentration of 15 mg/L, pollutant concentration of 30 mg/L, and at a high 30 cm port, with a removal efficiency of 98.44%. In addition, normal bubbles were used in experiments alongside micro-bubbles, revealing a 56.5% increase in removal efficiency. Furthermore, the study identified the kinetic flotation order of Cd(II) ions to be approximately first order.

Keywords: heavy metals, cadmium ions, micro-bubbles, flotation process, surfactant.

INTRODUCTION

Pollutants, both organic and inorganic, endanger the environment. Heavy metal ions pose a high risk due to their toxicity and carcinogenic properties. Human activities mainly cause heavy metal pollution, with serious impacts on the food chain and ecosystem, heavy metals come from sources such as chemical industries, textile mills, tanneries, plastic manufacturers, mining operations, battery factories, paint and pigment production and more [1]. As well the release of toxic metals into waterways can affect the quality of water available for use [2]. Heavy metal ions, such as arsenic, cadmium, chromium, lead, and mercury are toxic, persistent and accumulate in living organisms, posing a significant threat to human health and the environment. As they are non-recyclable, these metals are particularly hazardous [3]. Excessive levels of heavy metal ions in water systems, which can lead to numerous health issues, are a cause for concern [4]. The permissible limits of cadmium ions according to (WHO) was (0.003 mg/L) [5]. Various methods such as, chemical precipitation, ion exchange, and filtration such as ultrafiltration, reverse osmosis and nanofiltration are available to treat heavy metal-contaminated wastewater. However. these methods have drawbacks such as limited efficacy, high operational expenses [6]. Exposure to cadmium, a highly toxic element, can result in various health problems. Inhaling its particles, for instance, can cause "cadmium blues" with respiratory damage, while higher levels can cause severe conditions like pneumonitis, bone fractures, and reproductive failure. Safe drinking water is crucial [7]. the permissible limit of cadmium ions Cd(II), according to United States Environmental Protection Agency (EPA), is 0.005 mg/L [8]. Exceeding the recommended level can lead to serious infection, so treatment method for waste depends on various factors, like waste characteristics, contaminant concentration, cleanup needed and treatment costs [9]. Flotation is a separation method that is extensively utilized in various industries due to its high efficiency. When it comes to water treatment, micro-bubbles of air and oxygen are favored over conventional methods because they have proven to be more effective than the traditional approaches [10, 11, 12]. Flotation effectively removes low-density particulate matter from water using micro-bubbles [13]. Microbubbles (30–100 μ m) are used to recover fine mineral particles (<13 µm), which has shown to improve separation efficiency compared to larger bubbles. Injecting smaller bubbles further enhances the capture of ultrafine particles (<5 µm) by increasing the bubble surface flux and reducing the bubble size distribution through the injection of smaller bubbles [16]. Due to its small bubble scale, substantial interfacial area, lengthy stagnation period, high interior pressure, and high mass transfer rates, micro-bubble wastewater treatment is quite interesting [17]. The rate of MBs is controlled by the hydrodynamic cavitation of pneumatically saturated water passing through surface tension [18]. The flotation process is extremely important to the global industrial economy [19]. In this technique, surfactants are added and compressed air is sparged in the solution, to generate a mobile gas/liquid interface (bubbles) [20]. The flotation works based on the density differences between the bubble-particle aggregate and water influent [21]. Dissolved and induced gas flotation systems are the two most widely utilized flotation technologies [22].

The higher the ratio of surface area to the volume of micro-bubbles, the more effective the processes involving transition phenomena [23]. MBs slowly rise as they get smaller, generally with a square their diameter [24]. In flotation processes. MBs collect on the larger particles, forming a floc that is less than the surrounding fluid and separating it from solutions [25]. MBs have three main components: the gas phase component, the shell material, and the aqueous or liquid phase [26]. The liquid phase surrounding the bubble's shell can be either the same material as the shell or a foaming agent, depending on the operation [27]. The balance of these forces determines the bubble's shape. The bubble is often subject to buoyancy, gravity, viscous resistance, and extra mass forces [28]. When the surface charge of the loaded substance was positive, an anionic surfactant was chosen [29]. Many different organic and inorganic substances, metal ions, reagents, oils, powders, and chemicals were floated using micro-bubble technologies [30]. and color removals [31].

In this research, we looked at cadmium Cd(II) ion removal. The study recommends injecting air microbubbles into the flotation column, which contains a mixture of the contaminant and surfactant solution, as it is a major pollutant prevalent in wastewater. The work also investigates the effect of different operational parameters on Cd(II) removal efficiency such as flotation time, feed pollutant concentration, gas flow rate, initial pH solution, location of the sampling port, the kind and amount of surfactants used, as well as the comparison between using the micro-bubbles technique and the traditional one, Predict the kinetic flotation order. The paper's contents outline the information and procedures used in this research. The removal experiment findings and analysis, taking into account the impact of the aforementioned operating circumstances The findings of this research.

METHODOLOGY

Materials

The salt Cadmium nitrate tetrahydrate $(Cd(NO_3)_2.4H_2O, BDH England)$ was used as a source of cadmium ion Cd(II) as a simulation of a contaminated solution. Were obtained in powder form. From the local markets. The permissible limit for Cd(II) ions in drinking water is 0.003 mg/L, above which serious infections may occur [32]. By dissolving 1 gram of the contaminants in 1000 ml of deionized distilled water, a stock solution with a 1000 PPM concentration was created. According to the equation below, further concentrations in the range of 10, 20, 30, and 40 mg/L were made from stock solution on a daily basis:

$$V_1 * C_1 = V_2 * C_2 \tag{1}$$

where: C_1 – the (mg/L) concentration of the stock solution;

 C_2 – the required concentration of the pollutant (mg/L);

 V_1 – an unknown volume in (ml) from the stock solution;

 V_2 – the desired in (ml) volume of the pollutant solution.

In this study, SDS (Thomas Baker, Based in Mumbai, India) was used in all experiments as an anionic ((non ionic detergent with SDS) surfactant, and another was tested, which is (non ionic detergent with SDS) surfactant (Triton X-100, Avonchem Limited, UK) has the same effect. Was compared with a different type of cationic (positively charged) surfactant (CTAB, Sigma-Aldrich, USA). and it was supplied by local markets. Sodium hydroxide (NaOH, 0.4 N) and hydrochloric acid (HCL, 0.1 N) were used to change the solution's original PH.

Experimental work

A schematic representation of the experimental system is shown in Figure 1. Before entering the flotation column made of acrylic material with dimensions (12 cm I.D., 13 cm O.D and 200 cm in height) the air is compressed by an air compressor (50 liters, INGCO, China) at a pressure of approximately 2.38 bar and then passed through a flow meter (0-1 L/min, yyzx, Instrument Company; flow capacity recommended at 0.7 L/min or less) and a ceramic micro-bubble diffuser (Point Four TM diffuser, Canada). There are 11 apertures on the column, and tests are carried out at 15 °C room temperature. After the experiment begins, samples are obtained from the solution every 5 minutesand a flame atomic absorption spectrophotometer (AAS, Shimadzu, Model 7000, Japan) is used to detect their concentrations. The following equation was used to determine the removal % in each experiment:

Removal efficiency =
$$\frac{Ci - Cf}{Ci} * 10$$
 (2)

where: C_i and C_f – in (mg/L) are the starting and ending levels of pollutants prior to and following the flotation process.

RESULT AND DISCUSSION

Effect of pH

A range of pH values (3.1, 5, 7.2, 9.2, and 11.1) were studied to see how the removal efficiency of cadmium ions in a micro-bubble flotation system is influenced by the pH of the solution. The additional factors, including (Concentration of SDS 15 mg/L, flow of air 0.50 L/min, Cd(II) ion concentration 30 mg/L and 2nd port 30 cm) were kept constant. This effect is illustrated in Figs 2 and Figure 3. Indicate that the removal efficiency went up initially at the initial 10 minutes and then slowed down due to the decrease in SDS concentration over time. The maximum removal efficiency of 96.31% was achieved at pH 7.2, while the efficiency decreased for pH values below 7.2 due to the competition for SDS between H⁺ and Cd(II) ions, and in basic media, heavy metals can form complexes with hydroxide ions. These complexes can be less reactive or less accessible to the removal medium, reducing the efficiency of the removal process. This result agrees with the findings of [16, 33, 34, 35].



Figure 1 shows a schematic of a system for micro-bubble air flotation in a laboratory; (1) micro-bubble diffuser, (2) flotation column (3) an air compressor; (4) a feed pump; (5) a feed tank; (6) an effluent tank; (7) a valve; (8) an air rotameter; (9) a pressure gauge; and 1 (1–11) sampling taps, 2 (1–3) columns, and diffuser valves



Figure 2. Changes in removal rates over time and at various initial PH levels during flotation by MBs at fixed conditions (Flow 0.50 L/min, C_{SDS} 15 mg/L, C_{CdID} 30 mg/L, and Sp 30 cm)



Figure 3. The relationship between Cd(II) removal efficiency and various initial PH solution at fixed (Flow 0.50 L/min, C_{SDS} 15mg/L, C $_{Cd(II)}$ 30 mg/L, and Sp 30 cm)

Effect of initial concentration of Cd(II) ions

In order to learn more about how this study examined four different initial Cd(II) ion concentrations (10, 20, 30, and 40 mg/L), change the pace of removal while keeping all other variables constant (Flow 0.50 L/min, PH 7.2, C_{SDS} 15 mg/L, and S_p 30 cm). Based on the findings illustrated in the Figure 4 and Figure 5. This suggests that as the concentration of Cd(II) ions increased from



Figure 4. Changes in removal rates over time and at various initial Cd (II) values during flotation by MBs at fixed (Flow 0.50 L/min, C_{SDS} 15 mg/L, PH 7.2 and S_p 30 cm)



Figure 5. The relationship between Cd (II) removal efficiency and various initial concentrations Cd(II) values at fixed (Flow rate 0.50 L/min, C_{SDS}15 mg/L, PH 7.2, and S_p 30 cm)

30 mg/L to 40 mg/L, the removal rate decreased from 95.44% to 80.69%, respectively, at the end of flotation time.

This is consistent with the discovery of [34, 36]. The increase in the concentration of cadmium ions in the solution can decrease the percentage of its removal when using the flotation method by means of micro air bubbles due to saturation of air bubbles, competition for attachment sites, complexation with other ions, and reduction in bubble size [37].

Effect of surfactant concentration

Different SDS (sodium dodecyl sulfate) surfactant concentrations (5, 10, 15, and 20 mg/L) were used, while other parameters were kept fixed (Flow rate 0.50 L/min, C_{cd} 30 mg/L, PH 7.2 and S_p 30 cm). Figure 6. demonstrates that the Cd (II) ion was removed to 90.56% at 20 min for SDS 15mg/L and 96.01% as the highest value at

the end of the float time, and by increasing C_{SDS} to 20 mg/L the removal efficiency of Cd(II) ion was stopped at 65.39%, the competition between the metal-collector complex and free collector ions for bubble surface locations, as well as the abundance of collector, Micelles can form, which might result in potential toxicity from leftover collector in the effluent and also raise costs [16].

In the case of an increase in the concentration of surfactant this leads to exceeding the critical micelle concentration, flotation may be impaired because the ions adsorb on the micelles which are themselves unable to float due to their hydrophilic surfaces [38, 39]. Figure 7 shows the removal as a function of various C_{SDS} .

Effect of flow rate

Different gas flow rate values ranging from 0 to 0.50 L/min were used to study the effect of this parameter, while other parameters were kept



Figure 6. Changes in removal rates over time and at various C_{SDS} during flotation by MBs at fixed (Flow rate 0.50 L/min, $C_{Cd(II)}$ 30 mg/L, PH 7.2, and S_p 30 cm)



Figure 7. The relationship between Cd(II) removal efficiency and various initial concentrations C_{SDS} at fixed (Flow rate 0.50 L/min, C_{Cd(II)} 30 mg/L, PH 7.2, and S_p 30 cm)

fixed (C_{Cd} 30 mg/L, C_{SDS} 15 mg/L, PH 7.2 and S_p 30 cm). To investigate their impact on the Cd(II) ion's removal efficiency in the micro-bubble flotation column. Figure 8.

It can be noticed when the gas flow rate is 0.50 L/min after 20 min removal reached 84.59%.

It slowly increases to up to 98.44% as the highest value, and by decreasing the flow to a value of 0.3 L/min, removal starts to decrease to a value of 80.43%. ncreased fluid activity (stress) at the bottom part, early bubble detachment, bubble coalescence, and (mainly) bubble breakup are all caused



Figure 8. Changes in removal rates over time and at various flow rate during flotation by MBs at fixed (C_{CdIII} 30 mg/L, C_{SDS} 15mg/L, PH 7.2, and S_p 30 cm)



Figuer 9. The relationship between Cd(II) removal efficiency and various flow rate at fixed (C_{Cd(II)} 30 mg/L, C_{SDS} 15 mg/L, PH 7.2, and Sp 30 cm)

by increased gas flow rate, With the low gas flow rate, higher retention times were needed [39]. The efficiency of removal at the optimum flow rate of 0.50 L/min was 98.44% compared with free gravity removal (less than 6.5), as shown in Figure 9. The size of the bubbles grows in direct proportion to the flow rate.

Effect of sampling port location

Figure 10 shows the impact of the sample port's placement on the efficiency of Cd(II) ion removal. Ports were mounted overall at a distance of 15 cm all over the air flotation column (see Figure 1), from the diffuser far away and three ports were selected to test the removal efficiency (Sp1 30 cm, Sp2 60 cm, and Sp3 90 cm), while other parameters were kept fixed ($C_{Cd(II)}$ 30 mg/L, C_{SDS} 15 mg/L, PH 7.2, and Flow rate 0.50 L/min). The removal efficiency decreased axially with the height of the flotation column after 20 minutes. It was

as follows: Sp1 93.0%, Sp2 75%, and Sp3 50.0%. After that, the rates of removal began to increase slowly until they reached the end of the flotation time, when the percentages stabilized as follows: Sp1 94.38%, Sp2 84.63%, and Sp3 63.73%, as seen in Figure 10. This indicates that the first port with a height of 30 cm is the optimal port for collecting samples. The shift in the bubble's internal pressure and density (size) is one of the causes of this outcome, which decreases away from the diffuser from the bottom of the column to the top, reducing the surface area of the available bubble and lowering separation efficiency [40].

Effect of surfactant type

Figure 11 presents a comparison between three types of surfactants, including sodium dodecyl sulfate surfactant (SDS). Octylphenol ethylene oxide (Triton X-100), both negatively charged as anionic surfactants, and cetyltrimethyl



Figure 10. Changes in removal rates over time and at various sampling port during flotation by MBs at fixed (Flow rate 0.50 L/min, C_{cd(II)} 30 mg/L, C_{SDS} 15 mg/L, and PH 7.2)



Figure 11. Change of removal rates with time at different type of surfactant at same C_{sur} 15 mg/L with fixed (Flow 0. 50 L/min, $C_{cd(II)}$ 30 mg/L, PH 7.2 and Sp 30 cm)

ammonium bromides (CTAB), positively charged as cationic surfactants.

All at the same concentrations 15 mg/L, with kept fixed other parameters ($C_{cd(II)}$ 30 mg/L, PH 7.2, Flow rate 0.50 L/min and Sp 30 cm). Figure 12. indicate removal of Cd(II) ions reached 96.23% and 55.35% by using SDS and CTAB respectively. This indicates that the negatively charged surfactant (SDS) is more efficient than the positively charged surfactant (CTAB) [34, 38].

Effect of of micro-bubbles

To understand the full range of the addition's benefits of micro-bubbles technology in the flotation column liquid containing the contaminated substance, several tests were carried out to remove Cd(II) with and without the MB diffuser (i.e., with conventional bubbles) and "no bubble" (gravitational separation) and their effect on the efficiency of flotation of the liquid containing the



Figure 12. Change of removal rates with time at different MBs and without its, with fixed (flow rate 0.50 L/min, C_{Cd(II)} 30 mg/L, C_{SDS} 15 mg/L, and PH 7.2)



Figure 13. Time dependency of the estimated and experimental values of C_{cd(0)}, (a) first order, and (b) second order

Cadmium ion			
N	Units	k _n	R^2
1	1/min	0.1466	0.952
2	l/mg.min	0.0652	0.8256

Table 1. The individual orders of reaction's rate constant and correlation coefficient values

pollutant, while other parameters were kept fixed ($C_{Cd(II)}$ 30 mg/L, PH 7.2, Flow rate 0.50 L/min, and Sp 30 cm), as Figure 12.

After 30 minutes, the removal efficiency of flotation by air microbubbles was 96.23%, which is significantly higher than the removal efficiency of flotation by fine bubble, which was 61.49%, and gravitational separation, which was 6.25%. At the same operating conditions, the removal efficiency percentage increase was 56.5% higher with micro-bubbles than with fine bubbles. Our findings closely match those of [10, 11].

Flotation kinetics

Flotation kinetics will be employed to examine how the concentration of the floated material changes over time. This method is beneficial for understanding the process's mechanism and may be applied as a predictive tool for implementing flotation technology [34]. The rate of flotation is equivalent to the pace at which the concentration of floatable material in the cell alters.

$$C_t/C_o = \exp(-k_t t)$$
 (1) for first order (3)

 $C_t/C_0 = 1/(1 + C_0 k_2 t)$ (2) for second order (4)

where: $C_0 \text{ [mg/L]}$ – the pollutant's starting concentration recorded at time 0;

 C_t [mg/L] – the contaminant concentration study at time t, and the rate constants for the kinetics of the first and second orders, respectively, are k₁ [1/min] and k₂ [l/mg/min].

To determine the values of the rate constants for each order of reactions, the optimal conditions for the Cd (II) removal experiments (pH 7.2, $C_{Cd(II)}$ 30 mg/L, flow rate 0.5 L/min, C_{SDS} 15 mg/L, and Sp 30 cm) were applied to the above two equations, yielding the data shown in figures 13 (a and b), respectively. Table 1 contains the data for the rate constants and correlation coefficients.

The data presented in Table 1 suggests that the reactions studied in this experiment were most accurately described by a first-order kinetics model. The higher correlation coefficient suggests this (R^2) obtained under ideal experimental conditions, from the first-order equation as compared to the second-order equation.

CONCLUSIONS

In this study, pollutant particles were removed from water using the micro-bubble flotation technique, with a removal rate for the contaminants examined surpassing 90%. It was discovered that the pH level had an effect on the removal rate, with the ideal pH range being between 7–8 because hydrogen and hydroxyl ions were abundantly formed at both ends of this range. The behavior of metal ions and surfactants is altered, which lowers the clearance rate. The study also showed that anionic surfactants are superior to cationic ones. The removal rate constant (k) is shown to grow as the starting metal concentration lowers and flow rate rises, indicating that the kinetic flotation order for Cd(II) ions is almost first order.

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