

Continuous Fixed Bed Column Adsorption of Copper (II) Ions from Aqueous Solution by Calcium Carbonate

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Abstract—The fixed bed column adsorption study was conducted in a column of 35 cm height, 2 cm inner diameter in which aqueous solution of copper (II) ions of concentration 20 mg/L at a constant flow rate of 10 mL/minute passed upwards through calcium carbonate bed of depth 10 cm. The break through time and exhaust time were found to be 153 and 344 minutes respectively. The time required for the formation of adsorbent zone was estimated as 85.95 minutes. The adsorption zone height was found to be 5.63 cm and the degree of saturation of the adsorbent bed was estimated as 69%. The rate at which the adsorption zone was moving through the bed was 1.77 cm/hour. The adsorption rate constant (K) was found out as 0.072 L/mg hour and adsorption capacity coefficient (N) as 1555.63 mg/L. The concentrations of heavy metal ions before and after adsorption process were measured by Atomic absorption spectroscopy. Almost 100 % removal of copper (II) ions was achieved during the experimental study. The adsorptive removal of copper (II) ions by CaCO_3 was found effective and economic and can be applied for industrial waste water treatment.

Key words—Fixed bed column, Break through curve, Adsorption zone.

I. INTRODUCTION

The effluents discharged from various industries are responsible for numerous deteriorations on ecosystems and threaten human health and environment. The contamination of waste water by heavy metals and their effective removal is one of the most important issues worldwide. Heavy metals have been used for thousands of years in many different areas. Heavy metals are metals and metal compounds harmful to human and environment when absorbed or inhaled. Industries such as Chemical, Leather, Mechanical and Electrical are the significant sources of heavy metal pollution [1]. Although heavy metals support life when consumed in very small amounts, they can become toxic when taken in large amounts. Examples of heavy metals include arsenic, cadmium, chromium, copper,

lead, mercury and zinc. Generally, heavy metals have densities above 5 g/cm^3 . As the heavy metals cannot be degraded or destroyed, they are persistent in all parts of the environment. Human activity affects the natural geological and biological redistribution of heavy metals through pollution of the air, water and soil.

Copper is an essential trace nutrient that is required in small amounts (1-1.5 mg per day in food) by humans, other mammals, fish and shell fish for the synthesis of hemoglobin, carbohydrate metabolism and the functioning of more than 30 enzymes. Although copper can be an essential trace element, it could be harmful when it exceeds the tolerance limit. Copper finds wide application in the manufacture of fungicides, anti-fouling paints and also in electrical industries. Copper fume causes irritation of the eyes, nose and throat, headaches, stomach aches, dizziness, vomiting and diarrhoea and an illness called metal fume fever. High uptakes of copper may cause liver and kidney damage and even death. Copper strongly attaches to organic matter and minerals when it ends up in soil. As a result it does not travel very far after release and it hardly ever enters groundwater. Copper does not break down in the environment and because of that it can accumulate in plants and animals when it is found in soils. On copper-rich soils, only a limited number of plants have the chance of survival and hence there is not much plant diversity near copper disposing factories [2]. Several techniques have been developed for waste water treatment such as adsorption, coagulation, electrochemical, filtration, floatation, ion-exchange and membrane processes. In particular, adsorption is an effective and economic method for removal of pollutants from waste water [3].

A wide variety of adsorbents have been investigated by the researchers. High adsorption capability, large surface area, necessary functional groups, low cost, possibility of desorption, re-usability and environment friendly are the desired characteristics of adsorbents. Activated carbon is considered as the most effective adsorbent, but the

application of activated carbon to waste water treatment is still restricted due to its high cost. Numerous studies have explored the use of renewable and cheaper adsorbents. This research study investigates the application of pure calcium carbonate (CaCO_3) for the adsorptive removal of copper (II) ions.

Calcium carbonate comprises more than 4% of the earth's crust and is found throughout the world. Its most common natural forms are chalk, limestone and marble, produced by the sedimentation of the shells of small fossilised snails, shellfish, and coral over millions of years. Although all three forms are identical in chemical terms, they differ in many other aspects, including purity, whiteness, thickness and homogeneity. Calcium carbonate is one of the most useful and versatile materials known to man. Calcium carbonate is extensively used in cement industry. It also finds wide application in paper, plastics, paints and coatings industries both as a filler – and due to its special white colour - as a coating pigment. Calcium carbonate is used widely as an effective dietary calcium supplement, antacid, phosphate binder or base material for medicinal tablets. Calcium carbonate is used in industrial settings to neutralise acidic conditions in both soil and water due to its antacid properties. Calcium carbonate also benefits the environment through water and waste water treatment [4]. According to literature survey, limited number of references is available for the removal of heavy metals by pure calcium carbonate [5-9].

Some researchers have attempted the adsorptive removal of heavy metals by natural lime stone [10, 11]. Limestones consist essentially of calcium carbonate, with which there is generally some magnesium carbonate, and siliceous matter such as quartz grains. The average of over 300 chemical analyses of lime stones showed 92 per cent of CaCO_3 and MgCO_3 together, and 5 per cent of SiO_2 ; the proportion of magnesium carbonate is small except in dolomite and dolomitic limestones [12]. It was reported that lime stone samples containing silica, iron oxide, aluminum oxide and different kinds of clay minerals demonstrated enhanced sorption capacity [13].

Moreover, the adsorption ability of CaCO_3 has been analysed by the application of chalk, dolomite and marble [14-17]. The adsorption experiments have also been analysed by calcium carbonate rich bio-materials such as chicken egg shell [18-20] and sea shells [21]. The CaCO_3 extracted from starfish was also used as an adsorbent for the removal of heavy metal ions [22].

Due to its structural and superficial properties, CaCO_3 has been investigated intensely as an adsorbent substance that is used for the removal of metal ions from aqueous solution [23].

CaCO_3 consists of each triangular structure of CO_3^{2-} forming one layer which lies perpendicular to the central c-axis. Ca^{2+} ion is located between those layers and constructs an octahedron by sharing upper and lower oxygen ions of the triangular structure CO_3^{2-} . The structure has larger inner space compared with other compounds. The adsorption mechanism in this structure is that Ca^{2+} ions are replaced by heavy metal ions or heavy metal ions

are adsorbed at larger space, which means highly efficient in removing heavy metal ions [22].

II. MATERIALS AND METHODS

A. Materials

The AR grade of cupric sulphate penta hydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) manufactured by SD Fine Chem Limited, Mumbai, India, was used for the preparation of aqueous solution of Cu^{2+} ions. Distilled water was used to make solutions in this experimental study. The concentration of the aqueous solution was fixed as 20 ppm. Pure CaCO_3 in powdered form was procured from local market. A glass column of inner diameter 2 cm and height of 35 cm was used. A peristaltic pump (Model Miclins PP-20-EX) was used for providing constant flow of aqueous solution through the packed column. Atomic absorption spectrophotometer (Model Elico SL 194) was used to analyse the concentration of the samples. Calcium carbonate bed of height 10 cm and bulk density of about 0.239 g/cm^3 was packed in the column. 2 cm thick of glass wool was placed at the bottom of the packing to support and to increase the distribution of the solution onto the adsorbent surface and also the same at the top to prevent the leaching of the adsorbent media through the outlet.

B. Methods

1) Studies of adsorption

Both batch and continuous treatment processes are adopted for the adsorptive removal of heavy metals from solutions. Batch experiments can yield fundamental information about the effectiveness of adsorption system. In spite of that, the data may not be applicable to most treatment systems where contact times are not sufficient for the attainment of equilibrium. In order to improve the adsorption processes with conditions closer to real life water treatment system, continuous processes are adopted. A packed bed column is considered as an effective process for continuous waste water treatment for a number of reasons: it makes the best use of the concentration difference known to be a driving force for heavy metal adsorption; it allows more effective utilisation of adsorption capacity, and results in better quality of effluent. Hence it is necessary to perform equilibrium studies for heavy metals removal by packed column [24].

This research study analyses the behaviour and mechanism of adsorptive removal of copper (II) ions through a fixed bed of CaCO_3 .

2) Rate of adsorption in fixed beds [25]

The design of fixed bed adsorber requires knowledge of percentage approach to saturation at the breakpoint. This in turn requires the designer to predict the time of break point and shape of break point curve. The shape and time of appearance of break through curve greatly influences the method of operating a fixed bed adsorber. The curves generally have S shape, but they may be steep or relatively

flat. The actual rate and mechanism of the adsorption process, the nature of the adsorption equilibrium, the fluid velocity, the concentration of solute in the feed and the length of the adsorber bed (particularly if the solute concentration in the feed is high) all contribute to the shape of the curve produced for any system. In planning new processes, it is best to determine the break point and break through curve for a particular system experimentally under conditions resembling as much as possible those expected in the process.

The theory to demonstrate the break through phenomena in fixed beds has been developed by Michaels which is the simplified treatment for the design of fixed bed adsorbers [26]. The concepts of the adsorption zone height, the time required for the formation of adsorption zone, the time required for the adsorption zone to move its own height through the column and the time required for the adsorption zone to establish itself and move out of the bed have been given by Michaels. He has defined the adsorption zone height as the part of the bed, when the solute concentration changes from a low value (break point concentration) to a high value (bed exhaust concentration). The assumptions made in the Michaels theory are:

- (a) Isothermal adsorption
- (b) The equilibrium adsorption isotherm is concave to the solute-concentration axis
- (c) The adsorption zone is constant in height as it travels through the adsorption zone
- (d) The height of adsorbent bed is large relative to the height of adsorption zone

Many industrial applications fall within these limitations. The idealised break through curve is given below.

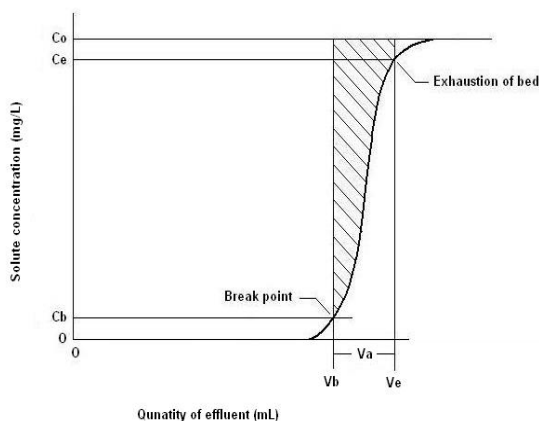


Fig.1. Idealised break through curve

The break through phenomena has been explained by Robert E. Treybal as follows: The solute concentration increases steeply with respect to time and reaches the initial concentration of feed when the adsorbent bed is saturated with adsorbate. The cumulative quantity of effluent (mL) is plotted on the x-axis and on the y - axis solute concentration in the effluent (mg/L) is shown.

Let L_s be the volumetric flow rate (mL/minute) of aqueous solution entering the bed, with initial solute concentration of C_0 (mg/L). We are mainly interested with the quantity of

effluent at V_b at the breakpoint and the nature of the curve between V_b and V_e . The total effluent accumulated during the appearance of the breakthrough curve is $V_a = V_e - V_b$. The adsorption zone of constant height Z_a cm, is defined as that part of the bed in which the concentration changes from C_b to C_e at any time.

Let θ_a be the time required for the adsorption zone to move its own height through the column, after the zone has been established. Then,

$$\theta_a = \frac{V_a}{L_s} \rightarrow (1)$$

Let θ_e be the time required for the adsorption zone to establish itself and move out of the bed. Then,

$$\theta_e = \frac{V_e}{L_s} \rightarrow (2)$$

If the height of the adsorbent bed is Z , and if θ_f is the time required for the formation of the adsorption zone, the height of adsorption zone Z_a is,

$$Z_a = Z \frac{\theta_e}{\theta_e - \theta_f} \rightarrow (3)$$

The quantity of solute removed from the solution in the adsorption zone from the breakpoint to saturation is U gram of solute. This is given by the shaded area of Fig.1, which is,

$$U = \int_{V_b}^{V_e} (C_0 - C) dV \rightarrow (4)$$

If, however, all the adsorbent in the zone were saturated with solute, it would contain $C_0 V_a$ mass of solute. Consequently at the breakpoint, when the zone is still within the column, the fractional ability of the adsorbent in the zone still to adsorb solute,

$$f = \frac{U}{C_0 V_a} = \frac{\int_{V_b}^{V_e} (C_0 - C) dV}{C_0 V_a} \rightarrow (5)$$

If $f = 0$, so that the adsorbent in the zone is essentially saturated, the time of formation of the zone at the top of the bed θ_f should be substantially the same as the time θ_a required for the zone to travel a distance equal to its own height. On the other hand, if $f = 1$, so that the solid in the zone contains essentially no adsorbate, the zone-formation time should be very short, essentially zero. These limiting conditions are described by,

$$\theta_f = (1 - f) \theta_a \rightarrow (6)$$

Equations (3) and (6) provide the adsorption zone height Z_a

$$\begin{aligned} Z_a &= Z \frac{\theta_a}{\theta_e - (1 - f)\theta_a} \\ &= Z \frac{V_a}{V_e - (1 - f)V_a} \rightarrow (7) \end{aligned}$$

The fractional approach to saturation of the column at the break point is given by,

$$\text{Degree of saturation} = \frac{z-fz_a}{z} \rightarrow (8)$$

3) Experimental procedure

The inconvenience and relatively high cost of continuously transporting solid particles as required in steady state operations frequently make it more economical to pass the solution to be treated through a stationary bed of adsorbent. As increasing amounts of solution are passed through such a bed, the solid adsorbs increasing amount of solute, and an unsteady state prevails [25].

Fixed bed column study for the adsorptive removal of copper (II) ions from aqueous solution by calcium carbonate was conducted at room temperature (30 ± 2 °C). An up flow of aqueous solution of copper (II) ions was continuously fed from the bottom of the column. The schematic representation of experimental set up is given below.

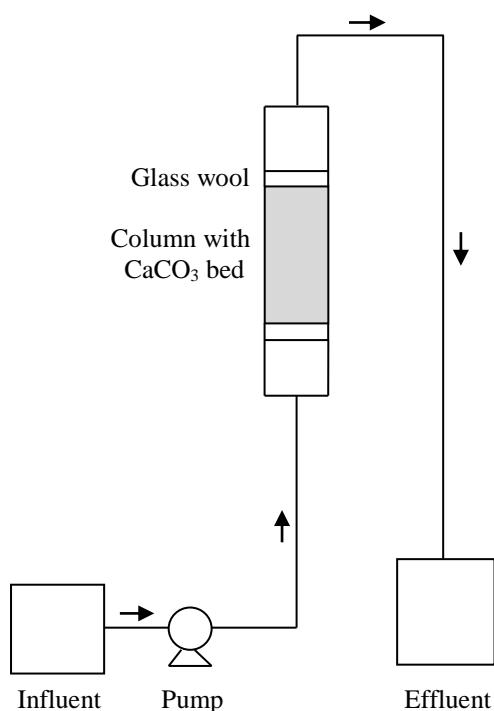


Fig. 2. Schematic representation of experimental set up

III. RESULTS AND DISCUSSION

A. Behaviour of adsorption column

A constant flow rate of 10 ml/minute of aqueous solution of copper (II) ions was passed upwards through CaCO_3 bed. The solution started to wet the bed from the bottom and slowly moved upwards. After the first drop of effluent came out, the concentrations of copper (II) ions were measured at every 15 minutes. The S-shaped breakthrough curve was obtained as shown in figure 3. The break

through time (which corresponds to $C/C_o = 0.1$) and the exhaust time (which corresponds to $C/C_o = 0.9$) were found to be 153 minutes and 344 minutes respectively.

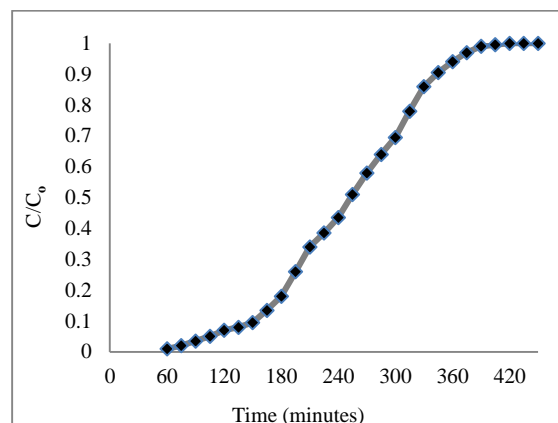


Fig. 3. Break through curve [C/C_o versus Time]

B. Evaluation of design parameters

The cumulative quantity of effluent was plotted on the x-axis and the solute concentration in the effluent was on the y-axis and shown in Figure 4.

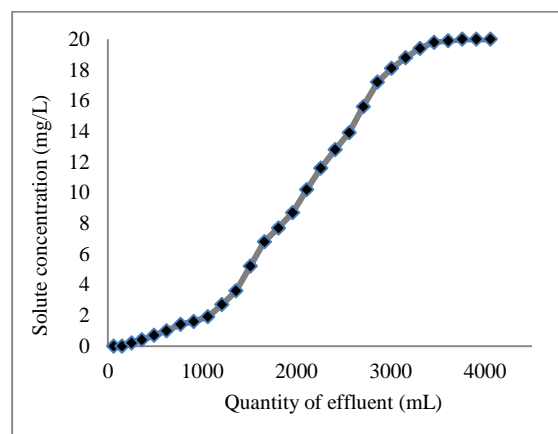


Fig. 4. Break through curve [Solute conc. in effluent versus cumulative quantity of effluent]

From the above plot, the values of V_e and V_b , are calculated to be, $V_e = 3150$ mL and $V_b = 1240$ mL. Here, V_e and V_b are the quantity of effluent came out of the bed at exhaust and break point respectively.

Time required for the adsorption zone to move its own height through the column, $\theta_a = 191$ minutes.

Time required for the adsorption zone to establish itself and move out of the bed, $\theta_e = 315$ minutes.

The fractional ability of the adsorbent in the zone still to adsorb solute, f , was calculated from the area of the shaded portion of the graph as 0.55

Time required for the formation of the adsorption zone, θ_f , was estimated as 85.95 minutes.

The adsorption zone height, Z_a , was determined as 5.63 cm.

The degree of saturation of bed was estimated as 69% and the rate at which the adsorption zone was moving through the bed was 1.77 cm/hour.

In our case, when the bed height (Z) was 10 cm, the adsorption zone height (Z_a) was estimated as 5.63 cm and the percentage utilisation of bed was estimated as 69%. The breakthrough time was 153 minutes and the time of formation of adsorbent bed was 85.95 minutes. According to Michael's theory, better utilisation of bed can be obtained if the height of bed is large relative to the height of adsorption zone. Hence we can expect better adsorption if the bed depth is increased. According to M.S. Patil et al., [26] when the bed depth is at least 2.5 times the adsorption zone height, the percentage utilisation of bed will be greater than 75 %.

A higher bed is an indication of the availability of larger amount of binding sites. When the bed depth increased, the surface area of the adsorbent increased and also the contact time extended. Hence the volume of waste water treated and the removal of heavy metal ions increased respectively. Therefore adsorption capacity increases with bed height. It has been confirmed by various researchers [27- 29].

In this adsorption study, a constant flow rate of 10 mL/minute of aqueous solution of copper (II) ions was passed upwards. The effect of flow rates on adsorption have been analysed by various researchers. The adsorption capacity decreases with increased flow rate. It is due to the lack of retention time for solute to interact with the sorbent and the limited diffusivity of solute in to the sorptive sites or pores [30-32].

The adsorption rate constant (K) and adsorption capacity coefficient (N) were calculated by logit method [33]. The logit equation is given by,

$$\ln\left(\frac{C/C_0}{1-C/C_0}\right) = -\frac{KNX}{V} + KC_0t \rightarrow (9)$$

Where, C_0 = initial copper (II) ion concentration (20 mg/L), C = concentration at any time, V = approach velocity (~190 cm/hour), X = bed depth (10 cm), K = adsorption rate constant (l/mg hour) and N = adsorption capacity coefficient (mg/L).

Rearranging equation (9), we get,

$$\ln\left(\frac{C}{C_0 - C}\right) = -\frac{KNX}{V} + KC_0t \rightarrow (10)$$

Plot of $\ln\left(\frac{C}{C_0 - C}\right)$ versus Time is shown in figure 5. The Plot gave a straight line ($R^2 = 0.971$) with slope KC_0 and intercept $-\frac{KNX}{V}$ from which adsorption rate constant (K) and adsorption capacity coefficient (N) were calculated.

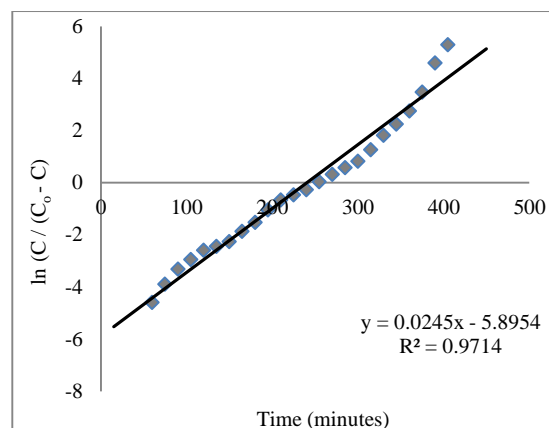


Fig. 5 Linearised logit model plot

The adsorption rate constant (K) was found out from the logit model as 0.072 L/mg hour and adsorption capacity coefficient (N) as 1555.63 mg/L.

From this study, it has been found that CaCO_3 can be effectually used as an adsorbent for the removal of copper (II) ions from aqueous solution. When performed a continuous fixed bed column adsorption of copper (II) ions from an aqueous solution of concentration of 20 mg/L by CaCO_3 , we have witnessed almost 100% removal of heavy metal ions. The application of calcium carbonate, for the adsorptive removal of copper (II) ions is effective. The data obtained from this study can be used for the designing of fixed bed column in full-scale waste water treatment plants.

IV. CONCLUSION

Experiments were conducted to investigate the potentiality of calcium carbonate as an adsorbent in a fixed bed column for the removal of copper (II) ions from aqueous medium. The break through time and exhaust time were found to be 153 and 344 minutes respectively. The time required for the formation of adsorbent zone was found out as 85.95 minutes. The adsorption zone height was estimated as 5.63 cm and the degree of saturation of the adsorbent bed was determined as 69%. The rate at which the adsorption zone was moving through the bed was 1.77 cm/hour. The adsorption rate constant (K) was found out as 0.072 L/mg hour and adsorption capacity coefficient (N) as 1555.63 mg/L. The packed bed column of CaCO_3 with continuous up flow method was found very effective and economic in the adsorptive removal of copper (II) ions from the aqueous media. The data obtained from this research study would be useful for the application of industrial waste water treatment.

Future extension of this work will be towards the adsorptive removal of copper (II) ions from industrial effluents and also to explore the possibilities of sorption-desorption cycles for the regeneration and reuse of adsorbent.

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