Removal of copper and cadmium using industrial effluents in continuous column studies by mixed adsorbent

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Abstract- Continuous column study experiments were conducted for both copper and cadmium in packed bed column and the parameters such as effect of bed height (12, 24, 36cm) at fixed volumetric flow rate of 10 ml/min, and effect of volumetric flow rate (10, 20,30 ml/min) at fixed bed height of 36 cm were carried out and the breakthrough curves were plotted in terms of C_e/C_o vs time. The break through time at 12, 24, 36 cm and 10 ml/min for Cu (II) were 50, 90, and 150 min respectively. The saturation time for Cu (II) at 12, 24, 36cm and 10 ml/min were 420, 480, and 600 min respectively. Similarly the break through time for Cd (II) at 12, 24, 36 cm and 10 ml/min were 50, 60, and 90 min respectively. The saturation time for Cd (II) at 12, 24, 36 cm and 10 ml/min were 210-240, 330-360, and 390-420 min, respectively. The optimized breakthrough curves were obtained at 36 cm bed height and 10 ml/min for both the metals copper and cadmium.

Key words: Column study, copper, cadmium, packed bed column, Effect of bed height, Volumetric flow rate, breakthrough curves, saturation time.

1. Introduction

The contamination of water from various industries has become a serious problem to human and aquatic life and further failure to treat wastewaters has become a challenging task to avoid the environmental pollution. Producing clean drinking water to the next generation is a great concern and many industrial techniques such as electrochemical methods, reverse osmosis, adsorption, co-precipitation, evaporation, chemical coagulation/floatation, flocculation, cementation, heavy metal removal from biosurfacants, biosorption, ion exchange, chemical precipitation, chemical oxidation and reduction, ion exchange, filtration, electrochemical treatment, reverse osmosis (membrane technologies), evaporative recovery and solvent extraction have been adopted for the wastewater treatment [1-3].

In the environment, the heavy metals are generally more persistent and toxic than organic contaminants such as chemicals released from pesticides, fertilizers and petroleum by products, etc. Heavy metal harm was because of drinking water through tainting (ex. lead channels, mechanical and industrial waste) and passes through the way of life through food chain or high ambient air conditions near emission sources. Heavy metals are of special concern because they are non-degradable and thus persistent. Heavy metals have harmful effect on the human body, physiological and other biological systems when they exceed the tolerance levels [4]. Exposure to these metals can cause liver diseases, brain damage, and kidneys failure and even to death ultimately. Besides chronic exposure to these contaminants present even at low concentrations in the environment also proved to be harmful to the human health and due to the above reasons the heavy metals must be removed from industrial effluents [5].

These classical or conventional techniques give rise to several problems such as unpredictable metal ions removal and generation of toxic sludge which are often difficult to de-water (remove the contaminants) and require extreme caution in their disposal. Besides that, most of these methods also have some limitations whereby they are economically viable at high or moderate concentrations of metals but not at low concentrations (1 to 100 mg/l) of dissolved metals. Heavy metals removed by classical techniques involve expensive methodologies. These are due to high energy and frequent reagent requirements. Comparing with conventional methodologies, generally the adsorption and bio sorption of heavy metals is a very cheap, eco-friendly and efficient methodology for the removal of heavy metals from industrial waste water [5-7].

Adsorption refers to the selective collection and concentration of a particular type of molecules contained in a fluid phase onto a solid surface. The molecules of the adsorbate come from the fluid phase into the interface, where they remain for a period of time. In a reversible process, the molecules go back to the phase from which they came or reversibly pass into another phase while other molecules replace them at the interface. On reaching the solid surface the adsorbed molecules exchange energy with structural atoms of the surface and if sufficient time was there for adsorption, the adsorbed molecules and the surface atoms reach thermal equilibrium and at equilibrium, the number of molecules arriving at the interface in a given time is equal to the number of molecules leaving the interface to go into the fluid phase [8-9].

2. Materials and Methodology

The methods of adsorbent preparation, physical characterization and continuous column study procedure along with the design have been explained in this section.

2.1 Mixed adsorbent preparation

The mixed adsorbent was prepared by mixing activated charcoal (AC) and bone charcoal (BC), in 1:1 ratio and particle size analysis (Malvern, Malvern Instruments Ltd, United Kingdom) was carried out in particle size analyzer to determine the particle size of the mixed adsorbent. The average particle size of the mixed adsorbent was reported to be as 572.2 nm. The surface area of the mixed adsorbent was found to be 951 m^2/g.

2.2 Continuous column flow studies

Persistent column flow operation analyses were conducted in a cylindrical round and hollow plastic cylinder (4 cm internal diameter and 100 cm height) as shown in the **Fig 1.** A 20 mesh size stainless sieve was attached to the bottom of the column. A known quantity of the mixed adsorbent in 1:1 ratio was added in the column from top to yield the desired bed weight of 50 g, 100 g, and 150 g, respectively. Cu (II) & Cd (II) effluent solutions of known concentration (100 mg/l) were pumped into the column from the bottom using a 40 W submersible pump at the desired flow rates of (10, 20, 30 ml/min) respectively. Samples were collected from the exit of the column at different bed heights at different intervals of time until the equilibrium was attained and the residual metal ion concentration (MIC) were analyzed using AAS (Atomic Absorption Spectrophotometer) (Make –Thermo Scientific). The parameters that were studied in the continuous flow operations involve the study of breakthrough curves with respect to weight of the adsorbent, volumetric flow rates, initial metal ion concentration. The parameters that were involved in the column design are

- Weight of the mixed adsorbent added into the column from the top 50 g, 100 g, and 150 g
- Inner Diameter of the column 4 cm
- Total height of the column = 100 cm
- Mixed adsorbent ratio = 1:1 (AC+ BC)
- Submersible pump for sending effluent from bottom to top (into the column) = 40 Watt.
- Initial concentration of the metal ions Cu and Cd (C_o = 100 ppm)
- Effect of volumetric flow rates (10, 20, 30 ml/min)

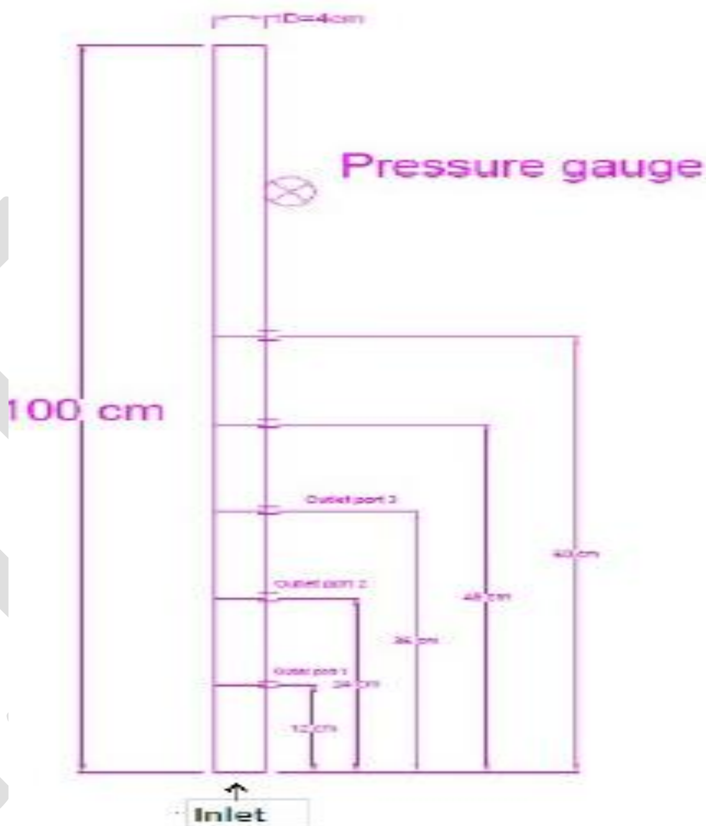

Fig 1: Experimental set up of the packed bed column

3. Results & Discussion

3.1 Continuous column studies for the removal of copper and cadmium using industrial effluents

Continuous column study experiments were conducted for both copper and cadmium in packed bed column and the parameters such as effect of bed height (12, 24, 36 cm) at fixed volumetric flow rate of 10 ml/min, and effect of volumetric flow rate (10, 20, 30 ml/min) at fixed bed height of 36cm are carried out and the breakthrough curves were plotted in terms of C_e/C_o vs time.

3.1.1 Effect of bed height / adsorbent dosage for Cu (II) and Cd (II) removal from industrial effluent

It is observed that the adsorption of metal ion in the packed bed column is directly proportionally to the quantity of adsorbent in the column. The blended adsorbent (1:1 ratio) of 50 g, 100 g, and 150 g are taken in a column and experiments were carried out to investigate the parameters required to evaluate the efficiencies of column in adsorption process. The adsorption breakthrough curves are obtained by changing the bed height from 12, 24 and 36 cm at fixed volumetric flow rate of 10 ml/min. Faster breakthrough curves were obtained for a bed height of 12 cm, while the slowest breakthrough curve was observed at a bed height of 36 cm. Higher the absorbent packed in the column, more the active sites that are accessible for the metal particles to attach and diffuse deep on to the pores as well as on to the surface of the mixed adsorbent [10] which leads to the achievement of higher bed capacity. Further, when the flow rate is less, the metal ion solution has more contact time to run in the column and the increment of bed height brought more active sites that were being in contact with the metal ions to interact and bind with the adsorbent [11]. This phenomenon has permitted the metal particles to diffuse deeper into the active sites of the mixed adsorbent. Subsequently, the percentage of metal ion removal increased when the bed height was increased. Both the breakthrough time and saturation time increased for Cu (II) with the increase of bed height from 12 cm to 36 cm. The break through time at 12, 24, 36 cm and 10 ml/min for Cu (II) were 50, 90, and 150 min respectively. The saturation time for Cu (II) at 12, 24, 36cm and 10 ml/min were 420, 480, and 600 min respectively. It can be observed from **Figs. 2 and 3** that the optimized break through curve were obtained at 36 cm bed height and 10 ml/min and further predicts that 36 cm bed height was taken as an optimized value and further experiments were carried out at 20 ml/min, 30 ml/min with the same bed height of 36cm to study the effect of volumetric flow rate on Cu (II) and Cd (II) metal ions removal using packed bed column. Similarly the break through time for Cd (II) at 12, 24, 36 cm and 10 ml/min were 50, 60, and 90 min respectively. The saturation time for Cd (II) at 12, 24, 36 cm and 10 ml/min were 210-240, 330-360, and 390-420 min, respectively.

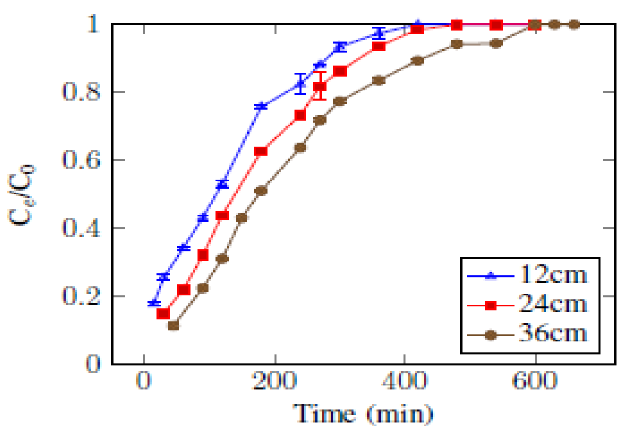

Figure 2 Breakthrough curves for copper at 10 ml/min flow rate, IMC of 100 ppm at different bed heights of 12, 24 and 36 cm

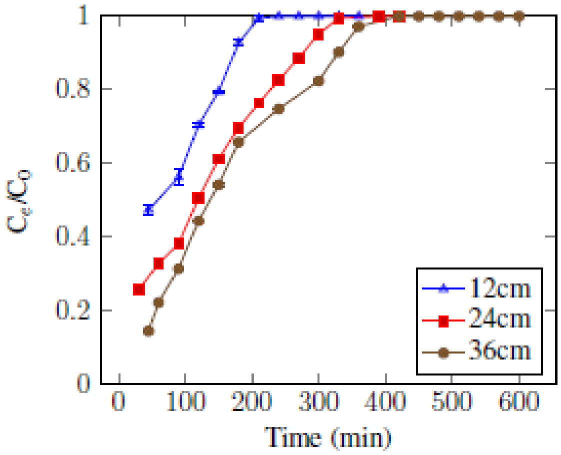

Fig 3 Breakthrough curves for cadmium at 10ml/min flow rate, IMC of 100 ppm at different bed heights of 12, 24 and 36 cm

3.1.2 Effect of volumetric flow rate on removal of Cu (II) and Cd (II) from industrial effluent

The effect of flow rate on Cu (II) and Cd (II) ions from industrial effluent by using the mixed adsorbent was investigated by varying the flow rate of the metal ion solution from 10, 20 and 30 ml/min while maintaining the fixed initial metal ion concentration of 100 mg/l and bed height at 36 cm (150 g) respectively. A graph of metal ion concentration ratio on y-axis vs effluent outlet time / sampling time on x-axis at different flow rates was plotted. The quicker breakthrough was observed for the highest flow rate of 30 ml/min, with a bed height of 36 cm due to less contact time between the metal ion particle and the mixed adsorbent. When the volumetric flow rate increased, there was less contact time between the metal ion and the adsorbent which leads to the decrease of bed capacity. But at lower flow rates of metal ion solution, the contact time between the metal ions and the adsorbent were more [11] which results in a slower breakthrough curve. Conversely at the higher flow rates the metal ion solution will leave the bed before its attainment of equilibrium. This will result in reduced amount of metal ion concentration being adsorbed from the industrial effluent. The break through time and saturation time for Cu (II) at 36 cm (150 g) with different flow rates of 10, 20, 30 were 45 and 600 min; 30 and 480 min; 15 and 360 min, respectively were observed in this experimental study. Similarly the break through time and saturation time for Cd (II) at 36 cm (150 g) with different flow rates of 10, 20, 30 ml/min were 90 and 390-420 min; 60 and 240-270 min; 30 and 210-240 min, respectively were observed. In the continuous column experiments, the breakthrough point shifted towards the right side for both Cu (II) and Cd (II) when the adsorbent dosage was increased from 50 to 150 g at a fixed initial metal ion concentration of 100 ppm. It was observed from the **Figs. 4 and 5** that the optimized break through curve were obtained at 36 cm and 10 ml/min for both Cu (II) and Cd (II). A longer breakthrough time implies better adsorption capacity which means that it would take a longer time for the adsorbent material to completely get saturated with the adsorbate solution.

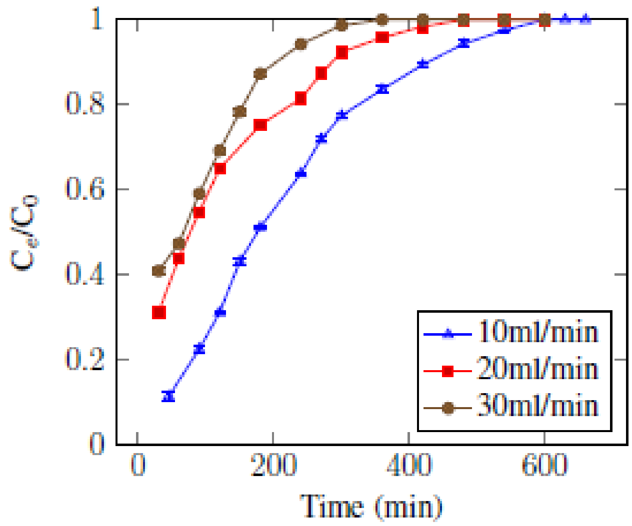

Fig 4 Breakthrough curves of copper at 36cm BH, IMC of 100 ppm at different flow rates of 10ml/min, 20ml/min, and 30 ml/min

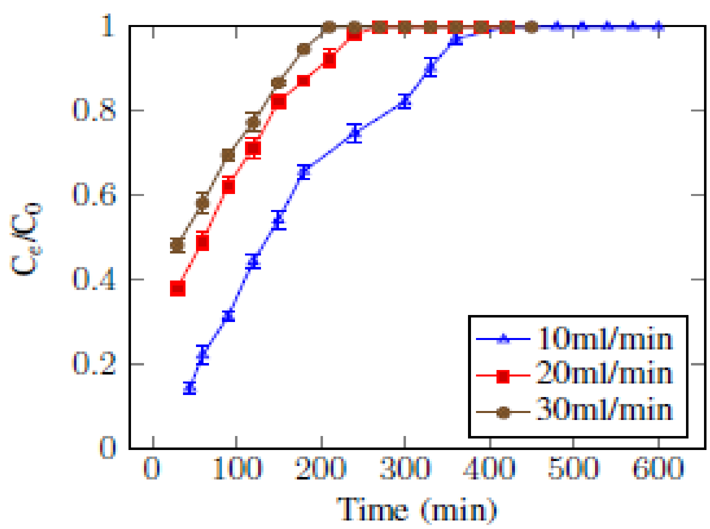

Fig 5 Breakthrough curves of cadmium at 36cm BH, IMC of 100 ppm at different flow rates of 10ml/min, 20ml/min, and 30 ml/min

4. Conclusions

Continuous column study experiments were conducted for both copper and cadmium in packed bed column and the parameters such as effect of bed height (12, 24, 36cm) at fixed volumetric flow rate of 10 ml/min, and effect of volumetric flow rate (10, 20, 30 ml/min) at fixed bed height of 36cm are carried out and the breakthrough curves were plotted in terms of C_e/C_o vs time. The break through time for Cd (II) at 12, 24, 36 cm and 10 ml/min were 50, 60, and 90 min respectively. The saturation time for Cd (II) at 12, 24, 36 cm and 10 ml/min were 210-240, 330-360, and 390-420 min, respectively. The break through time and saturation time for Cu (II) at 36 cm (150 g) with different flow rates of 10, 20, 30 were 45 and 600 min; 30 and 480 min; 15 and 360 min, respectively were observed in this experimental study. Similarly the break through time and saturation time for Cd (II) at 36 cm (150 g) with different flow rates of 10, 20, 30 ml/min were 90 and 390-420 min; 60 and 240-270 min; 30 and 210-240 min, respectively were observed. The optimized breakthrough curves were obtained at 36 cm bed height and 10 ml/min for both the metals copper and cadmium.

Conflict of Interests The authors declare that they have no conflict of interests.

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