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Comparative Studies And Performance Of Cu And Cd Removal Using Industrial Effluents And Synthetic Samples In Continuous Column Reactor

Srinivas Tadepalli*

**Assistant Professor, Department of Chemical Engineering, - Imam Mohammad Bin Saud Islamic University, Riyadh-11564, Kingdom of Saudi Arabia. Email id: stadepalli@imamu.edu.sa*

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Abstract

The experimental data obtained proved that the effect of bed weight, flow rate and initial metal ion concentration plays a significant role on the removal of Cu (II) and Cd (II).The column performance calculation involves various parameters such as breakthrough time, saturation time, Volume treated at breakthrough point (ml), Volume treated at saturation point (ml), m_{ads}, m_{total}, % removal have been calculated for both the metals using synthetic and industrial effluents. The detailed comparison studies have been reported in this paper along with explanation for both copper and cadmium. The cadmium metal % removal for synthetic solutions is better than industrial effluents at different bed heights and volumetric flow rates. The inverse trend for copper % removal is observed which shows that industrial effluent is better than the synthetic sample which may be due to more adsorbent dosage and influence of synergistic effect in the column. This trend is due to presence of Phenols, cresols, other heavy metals, sludge, major concentrations of adsorbates and impurities in industrial effluent. Overall in comparison with industrial effluents for cadmium, the synthetic solutions have proved to be more superior in terms of column total % removal and better performance was observed with synthetic solutions than industrial effluents. The adsorbent can be used for longer time before it needs replacement or regeneration.

Keywords: *Bed weight; Break through time, Industrial effluents, Initial Metal ion Concentration, Percentage removal, Saturation time, Synthetic solution, Volumetric Flow rate.*

1. Introduction

The contamination of surface waters by heavy metal ions has become a serious ecological issue and health problem due to their toxic effect even in low concentrations. Heavy metals are of special concern because they are non-degradable and thus persistent. Heavy metal ions such as cobalt, copper, chromium, nickel, palladium, lead, zinc are detected in the waste streams from the mining operations [1], tanneries [2], electronics [3], electroplating, batteries [4] and petrochemicals [5] industries has major effects on the human and aquatic life [6].

Water pollution remains a major problem in the environment due to the development of urbanization and industrialization which have contributed to the large scale of pollution for both human and aquatic life. The wastewater is discharged into the streams. Wells, Rivers and other water bodies without proper treatment. The pollution depreciates the land values, increases the municipal cost, operational cost and cause adverse

biological and human health effects. Heavy metals are non-biodegradable in nature and cause and their presence in the water streams leads to bioaccumulation in living organisms causing health problems in animals, plants and human life [7]. Industrial effluents containing enormous quantities of inorganic and organic chemical wastes, which are steadily become more difficult to treat by ongoing conventional methods.
A number of conventional treatment technologies such as Chemical precipitation, ion exchange, electro dialysis, membrane separations, reverse osmosis, and solvent extraction and adsorption have been considered for treatment of wastewater contaminated with organic substances. Among them adsorption is found to be the most effective method [8]. Adsorption is found to be superior to any other treatment methods because of the simplicity of design, ease of operation, capability for adsorbing a broad range of different types of adsorbate concentrations efficiently. Commercial activated carbon is regarded the most effective material for controlling the organic load [5].
Adsorption denotes to the separation of solute particles in a confined space from a liquid phase (fluid phase) on to solid surface. The particle of the adsorbate comes from the fluid segment into the boundary, the place they persist for an interval of phase. In a rescindable method, the particles return to the segment from which they got here or reversibly cross into an alternative segment even as other particles exchange them at the boundary. On accomplishment of the solid surface, the adsorbed particles interchange energy with structural atoms of the outside surface and if enough period was once there for adsorption, the adsorbed particles and the surface atoms reach thermal stability .The quantity of molecules entering on the boundary in a assumed period is equivalent to the number of molecules parting the boundary to go into the fluid segment [9-10].

1.1Break through Curves

The performance of a fixed-bed column was described through the concept of the breakthrough curve. The time for breakthrough appearance and the shape of the breakthroughcurve are very important characteristics for determining the operation and the dynamic response of an adsorption column. The loading behaviour of metal ion to be adsorbed from solution in a fixed-bed is usually expressed in term of C_e/C_o as a function of time or volume of the effluent for a given bed weight giving a breakthrough curve.
In any case, the performance of an adsorption treatment mainly depends on the thermodynamic aspects of solute-solvent-sorbent interactions and on the transport phenomena involving the diffusive-convective transport within the porous media [11, 12]. In a fixed-bed device, the contaminated water is introduced in a clean bed of mixed adsorbent from the top of the column and pollutant removal occurs in a narrow band at the top of the column, referred to as mass transfer / exchange zone (MTZ). As operation proceeds, the upper layers of blended adsorbent get to be saturated (soaked) with solute and the adsorption zone moves downwards until bottom of the column is reached. Under these conditions, the solute concentration in the effluent begins to increase. The MTZ extent mainly depends on liquid-solid relative velocity, and on the adsorbent properties (particle diameter, micro porous structure). The higher the MTZ extent the lower the efficient use of the adsorbing bed. Experimental dynamic tests showed that an increase in initial concentration and the liquid flow rate leads to shorter breakpoint time; moreover, the breakthrough curves become steeper as a consequence of higher velocity that enhances the external mass transport. The plot between the ratio of logarithm of equilibrium outlet concentration to the initial concentration of the metal ion, gives a relation between $\ln(C_e/C_o)$ vs reaction time in terms of various linear models (by various parameters) and predicts the nature of the adsorbent-adsorbate system are called Break through curves. They depends on the effect of volumetric flow rate, weight of the adsorbent packed at different bed weights and initial metal ion concentration of the metal ion solution. The study of variation of flow rate with bed weight at a fixed initial concentration of 100 ppm gives the concentration ratio profile with respect to outlet effluent sampling time (min).
In this paper a systematic and detailed study have been carried out to for the removal of Cd (II) and Cu (II) using mixed adsorbent prepared by mixing Activated charcoal and Bone Charcoal (1:1 ratio) in Continuous flow operation and these results are presented in the form of break through curves.

2 .Materials & Methods

All the chemicals including adsorbents used for the studies were purchased from Sigma Aldrich, India and have purity above 99.5 %. All the reagents, buffer solutions used for the study were Analytical grade.

2.1Methods

Atomic Absorption Spectrophotometer (Thermo Scientific ICE 3000 series) used to analyze Cu (II) & Cd (II) before and after adsorption.

2.1.1 Preparation of the mixed adsorbent

The mixed adsorbent was prepared in 1:1 ratio and sieve analysis (SELEC XT 264, AIMIL company ltd) was carried out in a rotary sieve shaker to determine the particle size of the mixed adsorbent. The average particle diameter of the mixed adsorbent was obtained as 572.2 nm (Nano meters).

2.1.1.1 Column Studies

Continuous flow operation experiments were conducted in a transparent cylindrical plastic column (4 cm internal diameter and 100 cm height) as shown in Fig 1. A 20-mesh size stainless sieve was attached to the bottom of the column. A known quantity of the adsorbent in the ratio of 1:1 (mixed adsorbent) was added in the column to yield the desired bed height (12cm, 24cm, 36cm). Cu (II) and Cd (II) solution of known concentration (100 mg/l was pumped into the column using a 40 W submersible pump at the desired flow rate (10ml/min, 20ml/min, 30ml/min). Samples were collected from the exit of the column at different bed heights and at different intervals of time until the achievement of equilibrium and analyzed using Atomic Absorption Spectrophotometer (AAS).

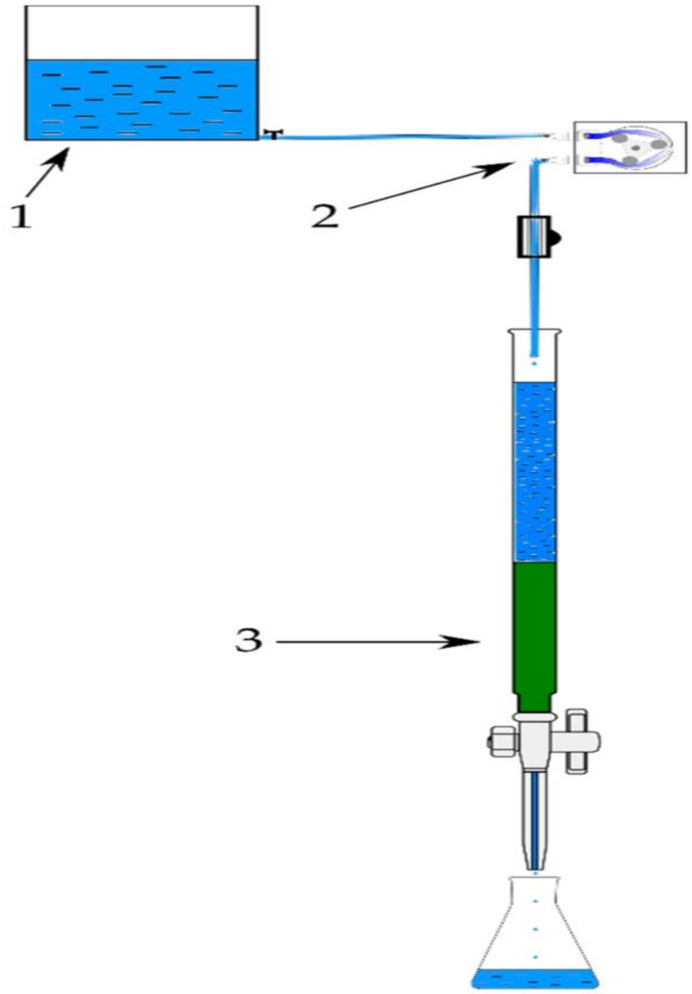

Figure 1. Schematic illustration of the fixed-bed column experiments. 1—heavy metal solution; 2—peristaltic pump; 3—adsorbent bed

2.1 .2 Parameters & Dimensions of the packed bed column

Weight of the mixed adsorbent added 50g, 100g, and 150g respectively (for 12 cm -25 g each; for 24 cm -50 g each; for 36 cm -75 g each.)

Inner Diameter of the column: 4cm

Bed height studied = 12, 24, 36cm

Total height of the column =100cm

Adsorbent ratio = 1:1(AC+ BC)

Submersible pump used for sending the effluent into the column = 40 Watts.

Initial Con of the metal ions Cu and Cd are (C_o) = 100 ppm

Effect of volumetric flow rate -10, 20, 30 ml/min
Effect of Weight of the adsorbent (bed height) -12cm, 24cm, 36cm

2.2Study of bed heights (weight of the adsorbent) and volumetric flow rate

The design of the packed bed column has been studied at a bed height of 12 cm, 24 cm, 36 cm and by flow rates varying from 10, 20, 30 ml/min with an initial concentration of 100 ppm. The main design of the column involves the study of break through curves experimentally with the effect of bed height and volumetric flow rate wrt column performance for both the metals.

3. Results and Discussion

The results obtained through column studies using industrial and synthetic solutions for copper and cadmium were compared in terms of breakthrough time, saturation time and % removal of metal ions. There was no significant time difference of breakthrough time (50, 60, 65 min) for synthetic solutions at fixed volumetric flow rates and variation of bed height in comparison with industrial sample having (50, 90, 45 min) for copper. This large difference of time in industrial effluent was due to the presence of other heavy metal ions, phenol, cresols, other sludges in the effluent so that it has taken more time to reach break through points.

Similarly, the same trend for copper was observed for saturation time (more time taken in case of industrial effluent) in comparison with synthetic solution and this may be due to the presence of other heavy metals which blocks the adsorbent pores and in turn leads to more time of saturation. But in case of different volumetric flow rates and fixed bed heights of (36 cm or 150 g dosage) a negligible time gap of (5-10 min) was observed for saturation time as shown in TABLE 1 and TABLE 2 respectively.

This was due to the increase in dosage from 50 g to 150 g in the column, as there was more number of active sites present in the column that are readily available for metal ions to occupy and further leads to late saturation. But in case of breakthrough time at fixed bed height of 36cm and varying volumetric flow rates there was a difference of 20 min, 25 min, 35 min were observed at 10, 20, 30 ml/min respectively. This was due to the change of volumetric flow rate from 10 ml/min to 30 ml/min. With the increase of flow rate, more metal ion solution was passed through the column and there was a competitive adsorption of metals ions for the same active sites and due to the presence of other heavy metals the pores got blocked quickly, which leads to the attainment of difference in breakthrough time.

In comparison with column performance in terms of total % removal at 12 and 24 cm and a fixed vol.flow rate of 10 ml/min, the more % removal was observed in case of synthetic samples having 62.13 % ,67.45 % than industrial effluents. The less % removal was observed for synthetic sample (78.24 %) at 36 cm bed height and 10 ml/min when compared to industrial sample having 82 % as shown in TABLE 1 and TABLE 2. This difference of 4% removal between the industrial effluent and synthetic sample for copper was due to more adsorbent dosage of 150 g at 36cm bed height. Similarly, at fixed bed height of 36 cm (150 g) and varying volumetric flow rates from 10, 20, 30 ml/min there were a difference of 4 %, 9 %, and 4 % between industrial effluent and synthetic samples for copper was observed and this may be due to more dosage of 150 g at 36 cm bed height. Overall in the column performance comparison between synthetic samples and industrial effluents for copper, synthetic solution performance was more superior at fixed volumetric flow rates of 10 ml/min and varying bed heights from 12 cm to 36 cm [12].

However a reverse trend was observed for copper in case of fixed bed heights of 36 cm (150 g) and variation of volumetric flow rates from 10 ml/min to 30 ml/min which indicates that industrial effluent performance was superior when compared to synthetic solution and this may be due to more adsorbent dosage and influence of synergistic effect in the column. The data for both industrial effluent and synthetic solution for copper were shown in TABLE 1 and TABLE 2. respectively. Similarly for cadmium there was a significant time difference of breakthrough time (50, 35, 60 min) for synthetic solutions and industrial effluent having (50 min, 60 min, 90 min) at fixed volumetric flow rates and variation of bed height for cadmium was observed.

The breakthrough time increases for cadmium -industrial effluent due to the presence of other heavy metals, phenols, cresols, and other sludge which affects the performance of the column and also gives a competitive adsorption effect for cadmium along with other metals in the column [13].

Similarly the same trend was observed for cadmium in-terms of saturation time in comparison with the synthetic solution and this may be due to presence of other heavy metals which blocks the adsorbent pores and in turn leads to more time of saturation at fixed volumetric flow rate of 10 ml/min and different bed heights of 12 and 24 cm. But at 36 cm and 10 ml/min, the saturation time for industrial effluent decreased (405 min) in comparison with synthetic sample having (450 min) and this may be due to the increase of bed height which leads to attainment of more adsorption capacity (due to adsorbent dose) in the column, as well as due to the presence of synergistic effect of the mixed adsorbent which leads to quick saturation [14].

In case of fixed bed height of 36 cm (150 g) and different volumetric flow rates from 10 to 30 ml/min, the break through time increased from 60 to 90 min at 10 ml/min, 40 to 60 min at 20 ml/min, and the same break through time of 30 min was observed at 30 ml/min as shown in TABLE 3 and TABLE 4. This increase in break through time for industrial effluent was due to the presence of other heavy metals and sludge that plays a role of competitive adsorption in the column along with cadmium [15-17].

Similar to copper, a reverse trend for cadmium was observed in-terms of saturation time at fixed bed height of 36 cm and different volumetric flow rates. The saturation time was more for synthetic samples (450, 320 min) when compared to industrial effluents (405, 255 min) and this may be due to the presence of synergistic effect of the mixed adsorbent as well as high amount of dose (150 g) in the column.

The reverse trend for cadmium was observed at 30 ml/min and 150 g, where the saturation time was less in case of synthetic sample (200 min) when compared to industrial effluent having (225 min) and this may be due to more volumetric flow rate of (30 ml/min) as well as due to the presence of other heavy metals that blocks the adsorbent particles and further leads to the late arrival of saturation zone as shown in the TABLE 3 and TABLE 4.

In comparison with the column performance of cadmium in terms of total % removal, at 12, 24, 36 cm and 10 ml/min (fixed volumetric flow rate), the more % removal was observed in case of synthetic samples having 32.63%, 66.47%, 70.28% in comparison with industrial sample having 28.1%, 55.35%, 52.77%, respectively. The similar type of trend for cadmium was observed at fixed bed height of 36 cm (150 g) and different volumetric flow rates of 10, 20, and 30ml/min. The more % removal was observed for synthetic samples having 70.28%, 54.38%, and 44.12% in comparison with industrial effluents having 52.77%, 38.18%, and 44.77% which was due to the presence of other heavy metals, sludges apart from competitive adsorption of cadmium present in the industrial effluent. Overall in comparison with industrial effluents for cadmium, the synthetic solutions have proved to be more superior in terms of total % removal and better performance was observed with synthetic solutions rather than industrial effluents for cadmium as shown in TABLE 3 and TABLE 4.

Table 1: Column performance calculations of industrial effluent for copper removal at different bed heights and volumetric flow rates

Ads dosage (g)	Bed heights (Cm)	Volumetric flow rates (ml/min)	IMC	Break through time (min)	saturation time(min)	Vol treated at BTP (ml)	Vol treated at saturation point (ml)	M_{ad}(g)	m_{total} (g)	Total % removal
50	12	10	100	50	420	500	4200	254	420	60.48
100	24	10	100	90	480	900	4800	264.65	480	55.14
150	36	10	100	45	600	450	6000	491.4	600	81.9
150	36	20	100	30	480	600	9600	619	960	64.48
150	36	30	100	15	360	450	10800	644.44	1080	59.67

Table 2: Column performance calculations of synthetic solutions for copper removal at different bed heights and volumetric flow rates

Ads dosage (g)	Bed heights (Cm)	Volumetric flow rates (ml/min)	IMC	Break through time (min)	saturation time(min)	Vol treated at breakthrough point (ml)	Vol treated at saturation point (ml)	M_{ad}	m_{total} (g)	Total % removal
50	12	10	100	50	400	500	4000	248.5	400	62.13
100	24	10	100	60	450	600	4500	303.51	450	67.45
150	36	10	100	65	600	650	6000	469.46	600	78.24
150	36	20	100	55	490	1100	9800	542.96	980	55.4
150	36	30	100	50	350	1500	10500	582.48	1050	55.47

Table 3: Column performance calculations of industrial effluent for cadmium removal at different bed heights and volumetric flow rates

Ads dosage (g)	Bed heights (Cm)	Volumetric flow rates (ml/min)	IMC	BTT min	saturation time min	Vol treated at breakthrough point (ml)	Vol treated at saturation point (ml)	M_{ad}	m_{total} (g)	Total % removal
50	12	10	100	50	325	500	3250	91.3	325	28.09
100	24	10	100	60	345	600	3450	190.95	345	55.35
150	36	10	100	90	405	900	4050	213.7	405	52.77
150	36	20	100	60	255	1200	5100	194.71	510	38.18
150	36	30	100	30	225	900	6750	302.21	675	44.77

Table 4: Column performance calculations of synthetic solutions for cadmium removal at different bed heights and volumetric flow rates

Ads dosage (g)	Bed height (Cm)	Volumetric flow rates (ml/min)	IMC	Break through time (min)	saturation time (min)	Vol treated at breakthrough point (ml)	Vol of sol treated at saturation point (ml)	M_{ad}	m_{total} (g)	Total % removal
50	12	10	100	50	180	500	1800	58.73	180	32.63
100	24	10	100	35	320	350	3200	212.7	320	66.47
150	36	10	100	60	450	600	4500	316.25	450	70.28
150	36	20	100	40	320	800	6400	348.04	640	54.38
150	36	30	100	30	200	900	6000	264.74	600	44.12

4. Conclusion

Based on the analysis of data obtained in continuous flow operation from breakthrough curves and kinetic models, it was concluded that the mixed adsorbent can be treated as the better adsorbent for the removal of heavy metal ions. The experimental data obtained proved that the effect of bed weight, flow rate and initial metal ion concentration plays a significant role on the removal of Cu (II) and Cd (II). Overall in comparison with industrial effluents for cadmium, the synthetic solutions have proved to be more superior in terms of column total % removal and better performance was observed with synthetic solutions than industrial effluents. In continuous column studies, 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. The adsorbent can be used for longer time before it needs replacement or regeneration.

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