



Comparison studies for copper and cadmium removal from industrial effluents and synthetic solutions using mixed adsorbent in batch mode

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Abstract : The results from the batch studies for copper using industrial effluent indicates that % removal was highly dependent on pH and the highest % removal of 96.5 was obtained at an equilibrium time of 120 min. The % removal of metal ions decreased for industrial effluent as it contains other heavy metals, phenols, cresols, and waste contaminants. The optimized pH was found to be 6 for both the metals having 96.5% removal of copper and 69.3% removal for cadmium respectively. The % removal of Cu varies from 83.76 to 96.2 % for industrial effluent and 87.16 to 99.74 % for synthetic sample at 5 g/L respectively. The equilibrium time was found to be 120- 150 min for both Cu (II) and Cd (II) ions. The % removal of cadmium varies from 81.32 to 89.68 % for industrial effluent and 83.9 to 91.2 % for synthetic sample at 5 g/L respectively. The results shows that for the industrial effluent with respect to increase of contact time the % removal increases and the optimized contact time for copper and cadmium with the mixed adsorbent was found to be 120 to 150 min where 80.68% removal of copper and 75.56 % removal of cadmium was reported at pH 6 and 5g/L of adsorbent dosage. The synthetic sample of copper and cadmium has the % removal of 94.83%, 77.35 % respectively at pH 6, and adsorbent dosage of 5g/L.

Key words : Batch study, pH, Industrial effluents, Synthetic sample, Equilibrium time, Contact time, Mixed adsorbent, Adsorbent dosage.

Introduction

Earth's surface comprises of 70% water is the most valuable natural resource existing on our planet. Without this invaluable compound, the life on the Earth would not exist. Although this fact is widely recognized, pollution of water resources is a common problem being faced today. Heavy metal pollution occurs directly by effluent outfalls from industries, refineries and waste treatment plants and indirectly by the contaminants that enter the water supply from soils/ground water systems and from the atmosphere via rain water. Modern industry is, to a large degree, responsible for contamination of the environment. Lakes, rivers and oceans are being overwhelmed with many toxic contaminants. Among toxic substances reaching hazardous levels are heavy metals. Commonly, heavy metals can be found in wastewater from industries. Heavy metals are one of the major classes of pollutants in industrial effluent. Among them are Cd (II), Pb(II), Fe (III), Cu (II), Ni (II), Mn (II) and Zn (II). Absorption of wastewater (containing heavy metal) by marine animals and indirectly enter the human food, present a high risk to consumer. Heavy metals can also contaminate and accumulate in the soil for a long term and it is held in the soil as a result of adsorption, chemical reaction and ion exchange of soil.

Although some heavy metals are necessary for the growth of plants, but after certain concentration, the heavy metals become poisonous for both plant and organisms. There are a lot of toxic heavy metals in metallurgical, tannery, chemical manufacturing, mining, battery manufacturing, etc. All of these will generate wastewater contaminated with hazardous heavy metals.

Metals are extensively used in several industries, including mining, metallurgical, electronic, electroplating and metal finishing. The presence of metal ions in final industrial effluents is extremely undesirable, as they are toxic to both lower and higher organisms. Under certain environmental conditions, metals may accumulate to toxic levels and cause ecological damage.

Now a day the main concern is the release of pollutants to the water bodies and which will cause adverse effect on living species. Copper and Iron are the most important and commonly used material which is associated with day to day life of human being. The major source of copper and Iron are the metal plating industries, which may release the coated water to environment without proper treatment and hence causing the potential hazards like lung cancer [1]. It is well known that there are various methods to reduce the concentration of these metal ions in the water bodies like precipitation, ion exchange, extraction operations, dialysis and electro dialysis etc [2] [3][4]. But all the above methods are not feasible in terms of economy for small and medium scale industries. But these methods are expensive or inefficient when the concentrations of metals are low (below 100ppm) and there is generation of large quantities of wastes. Development of eco-friendly, efficient and low - cost processes is the need of the hour and in this aspect, adsorption is a versatile technology with the advantages of high efficiency and selectivity for adsorbing metals in low concentrations, recycling of the adsorbent and minimization of the sludge generation. Hence the adsorption operation is the preferred and widely used technique for the removal of heavy metals because of its low cost and ease of regeneration.

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 [5-6].

2. Materials and Methodology

This section gives the details of materials and methodologies that were used in batch studies and simultaneous removal of copper and cadmium.

2.1 Chemicals used

Analytical grade salts of $\text{CuSO}_4 \cdot \text{H}_2\text{O}$, $\text{CdCl}_2 \cdot \text{H}_2\text{O}$, purchased from Sigma Aldrich were used for the preparation of synthetic effluents. Activated charcoal (AC) and Bone charcoal (BC) purchased from Sigma Aldrich with a purity of 95% were used as a mixed adsorbent by blending in (1:1 ratio) for this study.

2.2 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 as 572.2 nm.

2.3 Batch studies

Following a systematic procedure for the removal of heavy metal ions, initially the presterilizing flasks containing heavy metal ion solution of 50 mg/l of Cu (II) and Cd (II) were prepared and the mixed adsorbent of 0.5 g/L of mixed adsorbent was added after maintaining the desired pH. pH was adjusted by adding 0.1 M NaOH or 0.1 M HCl. Adsorption process was carried out in the rotary shaker/agitator until the equilibrium was

attained. The analysis was done for the filtered samples by Atomic Absorption Spectrophotometer (AAS) (Thermo Scientific) to find the residual concentrations at various time intervals from the collected samples. After the analysis equilibrium time and the residual concentration were reported. The data obtained in the present studies were used to calculate the % removal of the heavy metal ions and metal ion uptake capacity by using **Eq. 1 and Eq. 2** given as follows. Experiments were done thrice and the average values were reported for the adsorption system.

The % removal was evaluated using the mathematical relationship given by

$$\% \text{ removal} = \frac{C_o - C_e}{C_o} \times 100 \quad (1)$$

The equilibrium metal adsorptive capacity of the metal ions (q_e) was calculated by using mass balance given by

$$q_e = (C_o - C_e) \left[\frac{V}{M} \right] \quad (2)$$

Where C_o , C_e is the initial and equilibrium concentration of metal ions in mg/l. q_e is the amount of heavy metal ion adsorbed per unit weight of adsorbent in mg/g, V is the volume of the solution treated in liters. M is the mass of the adsorbent in grams.

2.4 Industrial effluents collected from BHEL, Haridwar

Confirmation experiments have been carried out for both copper and cadmium in batch and column studies using industrial effluents collected from BHEL, Haridwar plant. The initial metal ion concentration of copper and cadmium in the industrial effluent was found to be 350 ppm and 180 ppm respectively. Further studies were carried out in batch by diluting the Copper and Cadmium to 50 ppm of Initial metal ion concentration respectively. The effect of pH, adsorbent dosage, and contact time were studied for both the metals in batch studies. pH is considered to be important factor influencing not only site dissociation but also the solution chemistry of the heavy metals, hydrolysis, complexation by organic and or inorganic ligands [7]. The experiments were carried out at $T = 25^\circ\text{C}$, agitation rate of 180 rpm, adsorbent dosage of 0.5 g/L and contact time of 120 min for both copper and cadmium at pH of 2, 4, 6, 8, and IMC of 50 ppm. (diluted from 350 to 50 ppm for copper; 180 to 50 ppm for cadmium).

2.5 Binary sorption experiments for the simultaneous removal of Cu (II) and Cd (II) in batch studies using industrial effluents

The initial metal ion concentrations in the feed containing Cu (II) and Cd (II) from the industrial effluents have been found to be (Cu 350 ppm) and (Cd 180 ppm) respectively. Hence, Cu (II) metal ion concentration was diluted from 350 ppm to 50 ppm. The cadmium concentration can be found by using $C_oV_o = C_2V_2$, by substituting $C_o = 350$ ppm, $V_o = 14.3$ ml, and $V_2 = 100$ ml, C_2 and the initial concentration of cadmium were found to be 25.74 ppm. Hence the batch studies can be carried out simultaneously to find the effect of Cu (II) having initial concentration of (50 ppm) and Cd (II) having initial concentration of (25.74 ppm) and the % removal, adsorption capacity were found. Two parameters were studied namely the effect of adsorbent dosage, contact time and those results were reported. The results were shown in Figs 7 to 12 and the % removal, adsorption capacities were reported for both the metals. The batch studies has been carried out at room temperature of 25°C , agitation rate of 180 rpm, contact time of 2 hr, pH 6 by varying the adsorbent dosage from 0.5, 1, 2, 3, 5 g/L. After optimizing the maximum % removal from the adsorbent dosage, the experiments were conducted to find the effect of contact time.

3. Results and Discussion

The results obtained for both the metals copper and cadmium on various parameters such as effect of pH, adsorbent dosage and contact time with industrial effluents are reported and the results are compared with the synthetic solution data obtained in batch studies.

3.1 Effect of pH on Cu (II) and Cd (II) removal from industrial effluent

Fig 1 indicates that % removal of copper was highly dependent on pH and the highest % removal of 96.4 was obtained at an equilibrium time of 120 min. The % removal for synthetic sample and industrial effluent was found to be 97.21 and 96.4% respectively at 120 min for pH 6, 84.79 and 80.88% removal for pH 4, 77.94, 73.76 % removal for pH 2, 52.21 and 46.48 % removal at pH 8. The optimized pH was found to be at 6 with 96.4% removal of Cu (II).

Similarly for Cd (II), the % removal for synthetic solution and industrial effluent was 78.76 and 69.3% respectively for 120 min at pH 6, 63.42 and 57.92% removal at pH 4, 56.04, 50.94 % removal at pH 2, 44.16 and 38.4 % removal at pH 8. **Fig 2** shows the % removal vs time for cadmium at 25 °C, 180 rpm, 0.5 g/L of ads dosage, 50 ppm IMC and contact time of 120 min. The optimized pH was found to be 6 having 69.3% removal of Cd (II). Overall in comparison of % removal with industrial effluent and synthetic solution a significant difference of 6-10% more removal was observed in case of synthetic solutions for cadmium.

The % removal of heavy metal ion increases with the increasing order of pH as $6 > 4 > 2 > 8$ for Cu (II) and Cd (II) metals and in the base range it forms as an hydroxide precipitate at pH (≥ 8). The % removal of metal ions decreased for industrial effluent sample as it contains other heavy metals, phenols, cresols, and waste contaminants, biodegradable mass and suspended solids for both the metals copper and cadmium.

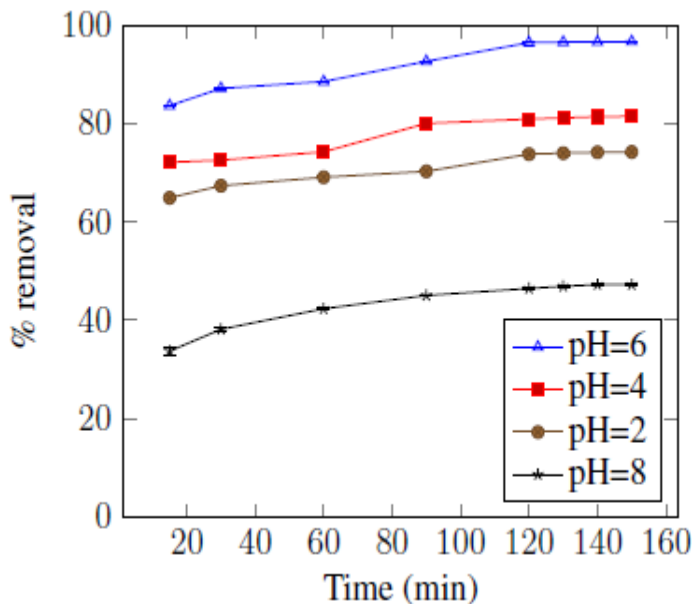


Fig1: Effect of pH on Cu (II) removal using industrial effluent at 25°C, 180 rpm, 0.5 g/L of ads dosage, 50 ppm IMC and contact time of 120 min

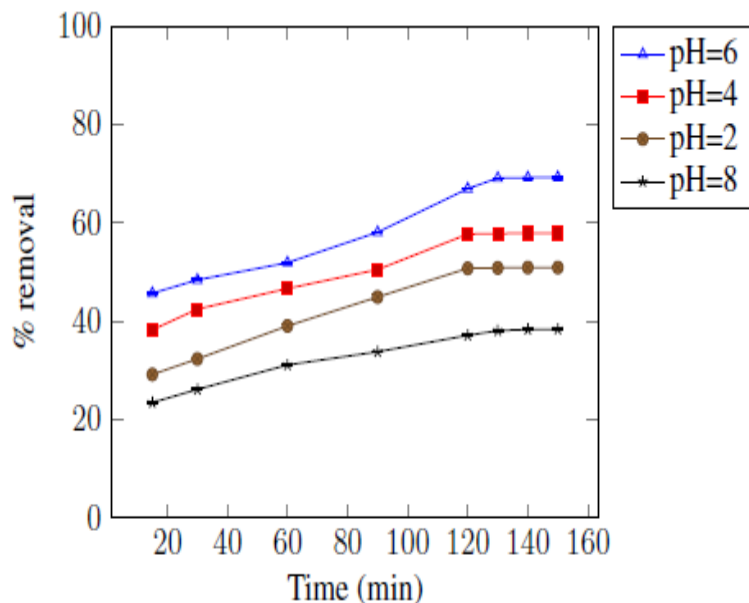


Fig 2: Effect of pH on Cu (II) removal using industrial effluent at 25°C, 180 rpm, 0.5 g/L of ads dosage, 50 ppm IMC and contact time of 120 min

3.1.1 Effect of point of zero charge on mixed adsorbent

Point of zero charge is the pH at which the mixed adsorbent has a net zero charge, above this pH it has a negative charge and is capable of attracting cations, below this pH it has a net positive charge capable of binding to anions. The value of pH used to describe PZC is only for the systems in which H^+ or OH^- ions are the potential determining factors and play an important role. When the pH is lower than the PZC value, the system is said to be below PZC. Below the PZC, the acidic water donates more protons than hydroxide groups, and so the adsorbent surface was positively charged (attracting anions). Conversely; above PZC the surface was negatively charged (attracting cations/repelling anions). The PZC for the mixed adsorbent was found to be 3 as shown in **Fig 3**, which predicts that the adsorbent surface was negatively charged that attracts cations. Hence more % removal was observed in case of pH 4 and 6. The metal ions got precipitated at pH 8 by forming copper and cadmium hydroxides. The same trend was observed for cadmium and PZC was reported to be 3. Hence lower % removal was observed at pH 2 due to formation of more protons (H^+ ions) and the surface of the adsorbent is positively charged. Hence repulsion occurs between the Cu^{2+} and Cd^{2+} ions with the mixed adsorbent which leads to lower adsorption of metal ions in the solution. The pH was controlled during the sorption process and maintained constant therefore at 2, 4, 6, 8 respectively using 0.1 M HCl and 0.1 N NaOH. Therefore a negligible change of (0.05 pH) was reported during the adsorption process and was adjusted using the acid and base treatments to maintain the respective pH.

The importance of this variable in the adsorption process was based on the fact that the signs of charge of adsorbate and adsorbent should be ideally opposed so that there was a greater electrostatic attraction between the two. If the charges are of same sign, then the adsorption process will be affected due to the electrostatic repulsion [8]. All the experiments were performed in acetate buffer of pH 3. An optimum effect was observed at pH 3, because at this pH the mixed adsorbents have negative potential which allows ion adsorption due to the attraction between the mixed adsorbent and the metal ions [9]. The experiments were carried from 1 to 6 pH for PZC analysis.

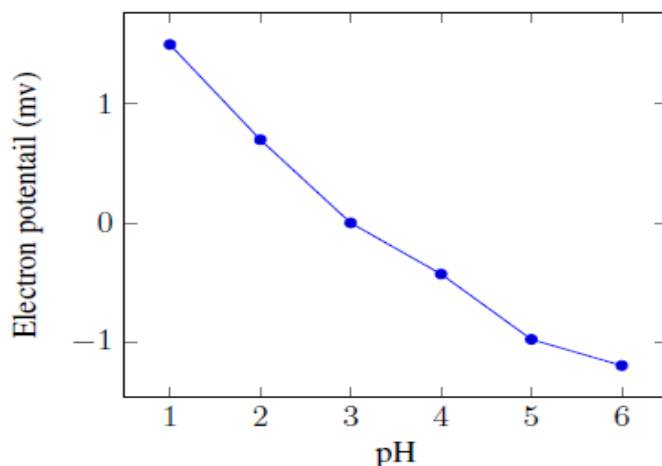


Fig 3: PZC analysis of the mixed adsorbent at different pH

3.2 Effect of adsorbent dosage on Cu (II) and Cd (II) removal from industrial effluent

The adsorption experiments were carried out at 0.5, 1, 2, 3 and 5 g/L dosage of the mixed adsorbent. The % removal was highly dependent on adsorbent dosage. Therefore the % removal increases in the order of increasing adsorbent dosage given as $5 > 3 > 2 > 1 > 0.5$ g/L as shown in **Fig 4**. The experiments are carried out at pH 6, $T = 25^{\circ}\text{C}$, 50 mg/l of initial metal ion concentration, 180 rpm, contact time of 15-120 min.

The % removal of Cu varies from 83.76 to 96.2 % for industrial effluent and 87.16 to 99.74% for synthetic sample at 5 g/L respectively. The % removal varies from 68.32 to 88.48% for industrial effluent and 77.46 to 92.35% for synthetic sample at 3 g/L respectively. The % removal varies from 55.74 to 74.8 % for industrial effluent and 58.93 to 78.88 % for synthetic sample at 2 g/L respectively. The % removal at 1 g/L of dosage varies from 49.76 to 65.96 % for industrial effluent and 52.87 to 70.13% for synthetic sample respectively. The % removal at 0.5 g/L dosage varies from 43.78 to 57% for industrial effluent and 46.9 to 60.82 % for synthetic sample respectively as shown in **Fig 4**. In comparison with synthetic sample, there was a difference of 3-4% less removal for industrial effluent of Cu (II) at 5 g/L, and 4-9% less removal at 3 g/L of dosage was observed. Similarly 3-4% less removal for industrial effluent at 2 g/L, 1 g/L, and 0.5 g/L of adsorbent dosage was observed in this study. The equilibrium time was found to be 120- 150 min for Cu (II) ion.

The % removal of Cd varies from 81.32 to 89.68 % for industrial effluent and 83.9 to 91.2 % for synthetic sample at 5 g/L respectively. The % removal varies from 64.72 to 83.18 % for industrial effluent and 77.66 to 89.2 % for synthetic sample at 3 g/L respectively. The % removal varies from 50.92 to 70.21 % for industrial effluent and 68.84 to 85.12 % for synthetic sample at 2 g/L respectively. The % removal at 1g/L of dosage varies from 44.31 to 60.23 % for industrial effluent and 63.42 to 82.74 % for synthetic sample respectively. The % removal at 0.5 g/L varies from 40.91 to 52.81 % for industrial effluent and 53.24 to 78.76 % for synthetic sample respectively as shown in **Fig 5**.

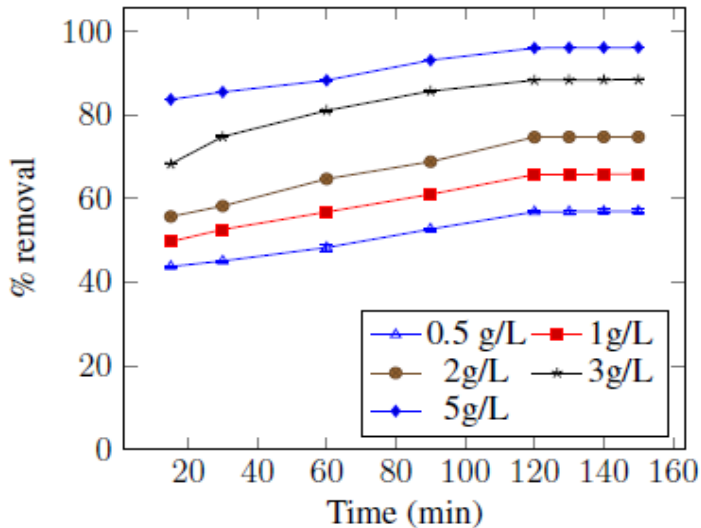


Fig 4: Effect of adsorbent dosage on Cu (II) removal for industrial effluent at pH 6 and T = 25 °C, 50 mg/l of initial metal ion concentration, 180 rpm, contact time of 120 min.

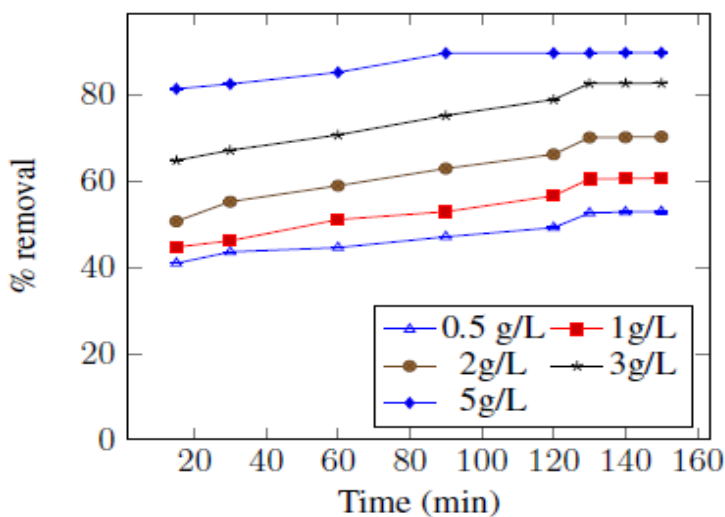


Fig 5: Effect of adsorbent dosage on Cd (II) removal for industrial effluent at pH 6 and T = 25 °C, 50 mg/l of initial metal ion concentration, 180 rpm, contact time of 120 min.

3.3 Effect of contact time on Cu (II) and Cd (II) removal using industrial effluent

The rate of adsorption increases with the increment of contact time between the adsorbent and metal ions or (adsorbate) in the solution. After the progression of time all the active sites of the adsorbent were filled either with metal ions or the solution itself was saturated, hence the increase in rate of adsorption ceases, percentage removal becomes constant and approaches a saturation point [10]. The experiments were conducted at 50 mg/L of initial metal ion concentration (IMC), 5 g/L of the mixed adsorbent dosage, agitation rate of 180 rpm, contact time of 5-120 min, pH 6, and temperature of 25°C. It can be concluded for the industrial effluent that with respect to increase of contact time the % removal increases and the optimized contact time for Cu (II) with the mixed adsorbent was found to be 120 to 150 min where 80.68% removal was observed for copper and 75.56 % was reported for cadmium at pH 6 as shown in Fig 6. Similarly for the synthetic sample the % removal for copper and cadmium are 94.83% and 77.35%. A difference of 14% was observed in case of copper and 1.8% difference in case of cadmium was observed in comparison with the industrial effluent due to the presence of other heavy metals, contaminants, suspended solids.

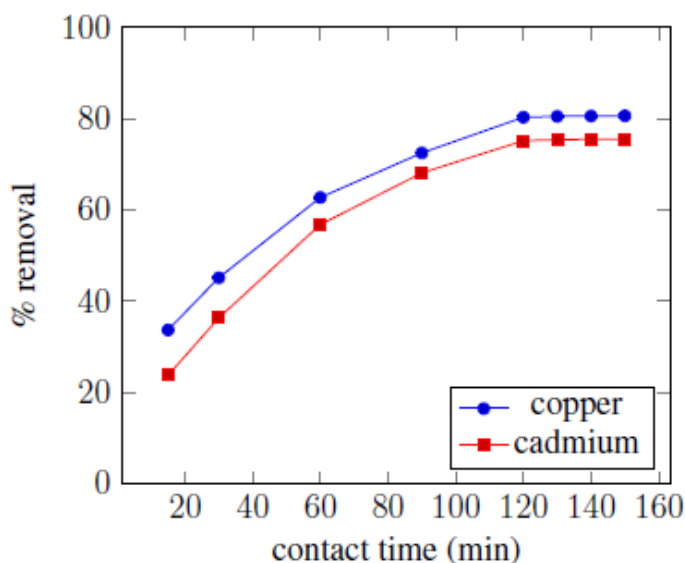


Fig 6: Effect of contact time on Cu (II) and Cd(II) %removal for industrial effluent at 50 mg/L of initial metal ion concentration (IMC), 5 g/L of the mixed adsorbent, agitation rate of 180 rpm, pH 6, and temperature of 25°C.

3.4 Simultaneous copper and cadmium metal ion removal in batch studies using industrial effluents

Simultaneous metal ion removal for copper and cadmium has been carried out in batch operation to study the effect of adsorbent dosage and effect of contact time.

3.4.1 Effect of adsorbent dosage on simultaneous Cu (II) and Cd (II) removal

The effect of adsorbent dosage on simultaneous removal of Cu (II) and Cd (II) has been studied and predicted that more % removal was obtained for Cu (II) when compared to Cd (II). The reason behind the decrease of cadmium % removal was due to more atomic weight of Cd (II) than Cu (II) (112.4 > 63.5). The maximum % removal obtained for Cu (II) and Cd (II) at 0.5 g/L are 30.46 %, 20.12 % respectively, at 1g/L are 38.96%, 28.67% respectively, at 2g/L are 44.75 %, 37.86 % respectively, at 3g/L are 54.56 %, 48.11% respectively and at 5g/L are 80.62 % and 75.95 % respectively at the saturation time of 120-150 min for both the metals as shown in **Figs 7 to 11** respectively. The maximum adsorption capacity for Cu (II) and Cd (II) at 0.5g/L were 2.1 mg/g and 1.13 mg/g respectively, at 1g/L were 1.45 mg/g and 0.97 mg/g respectively, at 2g/L were 0.88 mg/g and 0.65 mg/g respectively, at 3 g/L were 0.75 mg/g and 0.57 mg/g respectively, at 5g/L were found to be 0.7 mg/g and 0.497 mg/g respectively. The equilibrium times for both the metals were found to be 120-150 min. The % removal increases with the increase of adsorbent dosage from 0.5 to 5g/L and was due to presence of more binding sites available for adsorption. More number of active sites are available for simultaneous (copper and cadmium) ions due to the presence of synergistic effect as well as interaction of the metal ions that bind with the mixed adsorbent with the increase of adsorbent dosage. Hence % removal increases with increase in more dose.

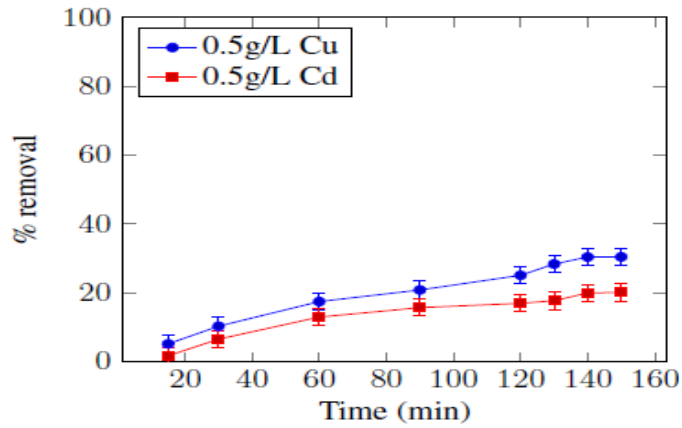


Fig 7: Effect of simultaneous metal ion removal by the mixed adsorbent at 0.5g/L of ads dosage

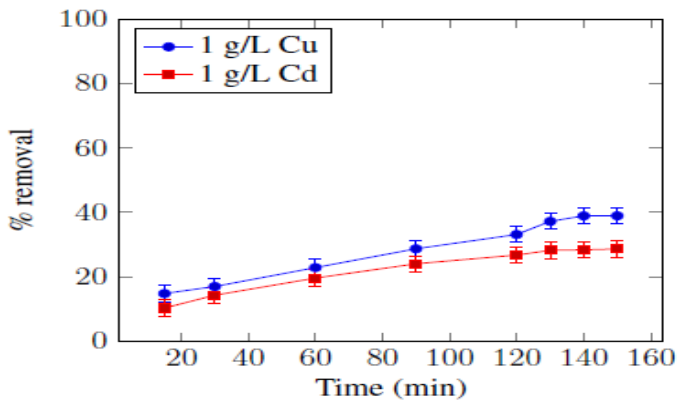


Fig 8: Effect of simultaneous metal ion removal by the mixed adsorbent at 1 g/L of ads dosage

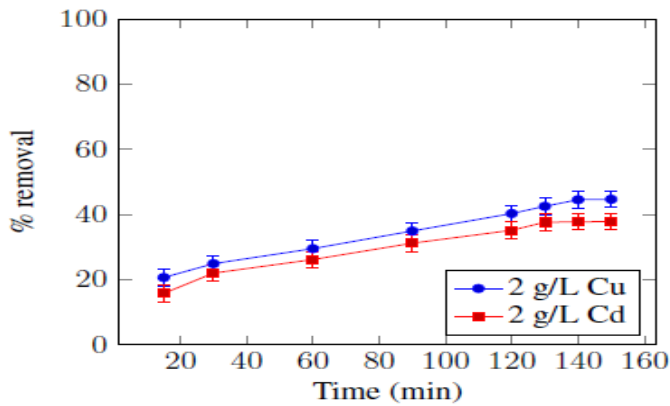


Fig 9: Effect of simultaneous metal ion removal by the mixed adsorbent at 2 g/L of ads dosage

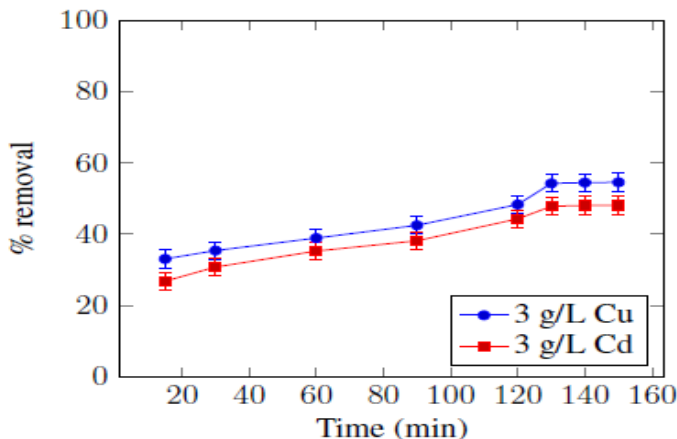


Fig 10: Effect of simultaneous metal ion removal by the mixed adsorbent at 3 g/L of ads dosage

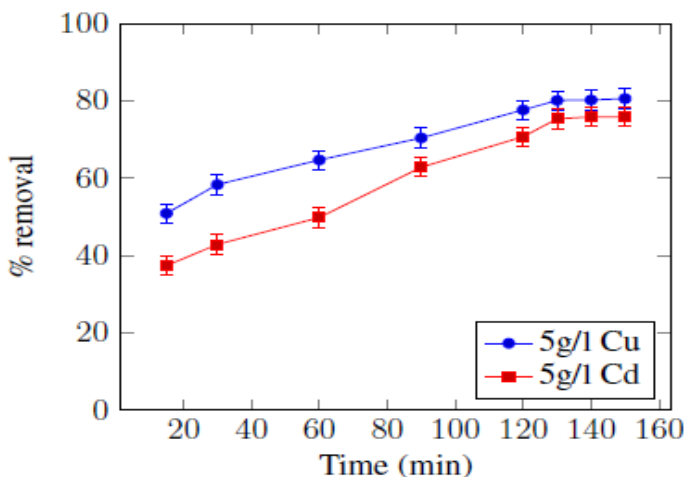


Fig 11: Effect of simultaneous metal ion removal by the mixed adsorbent at 5g/L of ads dosage.

3.4.2 Effect of contact time for simultaneous Cu (II) and Cd (II) removal

The effect of contact time on simultaneous removal of Cu (II) and Cd (II) has been studied and predicted that more % removal was obtained for Cu (II) when compared to Cd (II). The maximum % removal obtained for Cu (II) and Cd (II) were 80.62 % and 75.95 % respectively at the saturation time of 120-150 min for both the metals. The maximum adsorption capacity for Cu (II) and Cd (II) were found to be 0.7 mg/g and 0.497 mg/g respectively. The reason behind the decrease of cadmium % removal was due to more atomic weight of Cd (II) than Cu (II) ($112.4 > 63.5$). The rate of adsorption increases with the increase of contact time between the mixed adsorbent and the metal ions present in the solution. After the progression of time, all the active sites got saturated by filling with metal ions or solution itself became saturated and reaches an equilibrium state and the rate of adsorption ceases, and percentage removal becomes constant. The optimized contact time for simultaneous removal of metals ions were found to be 120-150 min as shown in Fig 12. In comparison from the graphs drawn for simultaneous removal of copper and cadmium for the adsorbent dosage and contact time the highest % removal and adsorption capacity was obtained for Cu (II) than Cd (II) due to lower atomic weight of Cu when compared to Cd.

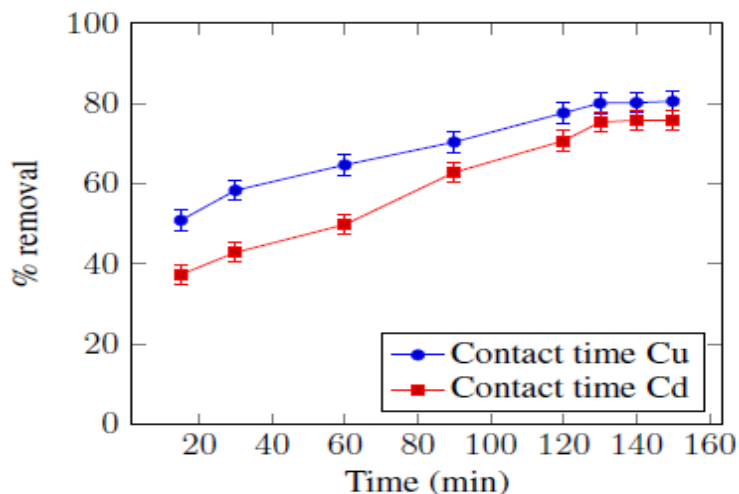


Fig 12: Effect of contact time on simultaneous metal ion removal by the mixed adsorbent at 5 g/L of ads dosage, pH 6.

4. Conclusions

The conclusions from the batch studies for copper using industrial effluent indicates that % removal was highly dependent on pH and the highest % removal of 96.5 was obtained at an equilibrium time of 120 min. In comparison of industrial effluent with synthetic sample of copper, the % removal for synthetic sample and industrial effluent was 97.21% and 96.5% respectively for 120 min at pH 6. The % removal of metal ions decreased for industrial effluent as it contains other heavy metals, phenols, cresols, and waste contaminants. The optimized pH was found to be 6 having 96.5% removal of copper. In comparison of industrial effluent with synthetic sample for cadmium, the % removal for synthetic sample and industrial effluent was 78.76% and 69.3% respectively for 120 min at pH 6. The optimized pH was found to be 6 having 69.3% removal of Cd (II). Overall in comparison of % removal with industrial effluent and synthetic samples a significant difference of 6-10% more removal was observed in case of synthetic samples. The % removal of Cu varies from 83.76 to 96.2 % for industrial effluent and 87.16 to 99.74 % for synthetic sample at 5 g/L respectively. The equilibrium time was found to be 120- 150 min for Cu (II) ion. The % removal of cadmium varies from 81.32 to 89.68 % for industrial effluent and 83.9 to 91.2 % for synthetic sample at 5 g/L respectively. The equilibrium time was approached from 120- 150 min and active sites got saturated and the % removal becomes constant. It can be concluded that for the industrial effluent with respect to increase of contact time the % removal increases and the optimized contact time for copper with the mixed adsorbent was found to be 120 to 150 min where 80.68% removal was reported at pH 6 and 5g/L of dosage. The synthetic sample has the % removal of 94.83%. A difference of 14% was reported in comparison with the industrial effluent due to the presence of other heavy metals, contaminants and suspended solids. The optimized contact time for cadmium with the mixed adsorbent was found to be 120 to 150 min where 75.56 % removal was reported at pH 6 and for the synthetic sample the % removal was 77.35 % at pH 6, adsorbent dosage of 5g/L. A minimum difference of 1.8 % removal was observed in comparison with the industrial effluent due to the presence of other heavy metals.

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

Declaration by the Authors

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