Comparison studies of orange peel and mixed adsorbent for the removal of Cu (II) and Cd (II) from Industrial effluent and their regeneration studies

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Abstract

In this paper the adsorption and desorption studies for industrial effluents have been studied using orange peel and mixed adsorbent prepared by mixing 1:1 ratio of activated charcoal and bone charcoal. In comparison with the orange peel powder, the highest % removal was obtained for mixed adsorbent (AC+ BC) due to the high surface area of the activated charcoal as well as –ve charge from the bone charcoal which induces the synergistic effect. The reaction was allowed to takes place for 60 min at a rotational speed of 150-180 rpm in an orbital shaker followed by washing with water to remove the traces of metal ions. The pH of the metal ion solution for Cu (II) and Cd (II) was optimized to 6, and the batch studies are carried to find the effect of adsorbent dosage varying from 0.5 g/l, 1 g/l, 2 g/l, 3 g/l, 5 g/l with the same adsorbent conditions. After optimizing pH at 6, adsorbent dosage of 5 g/l, further studies were carried out to find the effect of contact time on Cu and Cd % removal varying time from 15 min to 4 hrs. The average equilibrium adsorptive capacities were found and the % removal of metal ions was reported. In these studies, the regeneration process involves the extensive washing of mixed adsorbent with 0.2 M HCl solution. These results indicate that the Cu (II) and Cd (II) adsorption on the mixed adsorbent is almost completely reversible and the bonding between the mixed adsorbent and adsorbed Cu (II) and Cd (II) ions is likely to be strong. It is relatively easy for the adsorbed Cu (II) and Cd (II) to be desorbed from the mixed adsorbent by achieving 90% and 94% desorption efficiency rate. In comparison between Cu (II) and Cd (II), cadmium achieved more desorption rate for each adsorbent dosage and further predicted that regenerations studies can be used in the waste water treatment for the recovery of metal ions from the treated adsorbent. It can be concluded that regeneration, reuse of adsorbent and the recovery of solute are few important aspects of the adsorption which can render this wastewater treatment method more economic value for the heavy metals and cost effective.

Key words: Adsorption and desorption studies, Industrial effluents, Orange peel, Mixed adsorbent, Synergistic effect, Regeneration process, Desorption efficiency, Reuse of adsorbent.

1. Introduction

Among the various bio-sorbents used in recent era the major importance is given to the citrus family fruit peels. The amount of orange and sweet lemon peels produced is very high in almost all the countries of Asia and Africa. The adsorption process of heavy metal ions on the surface of treated peel is a function of various functional groups and their chemistry with metal ions. The binding process involves numerous mechanisms like electrostatic attraction, complexion, ion exchange etc. The orange peel is having a very good affinity towards the metal ions due the presence of cellulose, pectin (galacturonic acid), hemicellulose and lignin. So, these components possess various important functional groups like carboxylic acid and phenolic acids help in binding process of metal ions. [1]

Orange is a fruit that belongs to the Rutaceae family's citrus species *Citrus sinensis*. Nagpur Santra, Coorg Santra, and Khasi orange types are significant ones grown in India. Important oranges cultivated in India are Butwal, Dancy, Shringar, Mudkhed, Kara, and Buttra (Abohar). Main countries that produce oranges are China, India, Mexico, Brazil, America, and Spain along with Egypt. The world's top producer of oranges is Brazil with a 2013 production of 36 million tons. The United States was the second-largest producer in 2013, producing about 16 million tons. The crucial states that produce the majority of the nation's citrus fruits are Punjab, Rajasthan, and Maharashtra (FAO Statistics, 2013). After juice extraction, citrus peel is the predominant waste portion, making up over 50% of the fruit mass [2]. It is important to emphasize that citrus peel, a byproduct of citrus processing plants, is regarded as a valuable functional food.

Citrus peels may therefore enhance health in addition to the usual nutrients they contain and guard against diseases linked to food, such as osteoporosis, metabolic syndrome, type II diabetes, coronary heart disease, obesity, and hypertension. Citrus by-products, if utilized fully, could be major sources of phenolic compounds. The peels, in particular, are an abundant source of natural flavonoids, and contain higher amount of phenolics compared to the edible portions [3]

The total phenolic content of lemon, orange, and grapefruit peels was 15% higher than that of the peeled fruits. Flavonoids found in Citrus metabolites are a significant class of secondary metabolites. The peel contains the most flavonoids of any food parts and the flavonoids found in citrus fruits according to their structure, to six distinct classes They are flavones, flavanones, flavonols, isoflavones, and isoflavones, flavanols and anthocyanidins [4-5].

Oranges, also known as sweet oranges, are the fruit of the citrus-sinensis family, which originated in China. Oranges are a great source of vitamin C. Vitamin 'C' is also essential for the many healthy immune systems to function properly Oranges can be used as a snack as well as a major prescription ingredient in a variety of dishes. Orange juice is an essential component of a healthy breakfast and thus promotes a healthy start to every day. Orange is well-known for its numerous health benefits and is one of the most popular fruits worldwide. (2019, Times of India) Vitamin C is the body's primary water-soluble antioxidant, destroying free radicals and preventing cell damage. Oranges are thought to be the best source of many vitamins, including thiamine and folic acid. Thiamine and folic acid promote the growth and development of the human body's muscles, bones, and red blood cells, as well as the health of the skin. Since ancient times, 70% of total orange production has been used to manufacture derivative products, but 30% of processed fruits are converted into citrus peel waste, so these wastes contain many nutrients. Fruit peels serve as a protective coating for the underlying edible parts of fruits, shielding them from environmental factors as well as microorganisms and enzymes. They are sometimes accepted as fruits depending on their thickness and taste; however, people frequently discard their peels when using fruits, despite the fact that the nutritional properties of these fruits are also found in their peels. They aid in the prevention of many diseases and the development of disease resistance. Aside from that, these nutritious peels are used to prepare a variety of dishes, cosmetics, and medicines [6].

According to the World Health Organization's (2003) report, "Dietary nutrition and chronic disease prevention." Because of the presence of folate, it protects against heart disease in citrus fruits, which is essential for heart health. Citrus fruits contain potassium, which helps lower blood pressure and prevents stroke and kidney disease, as well as vitamins, carotenoids, and flavonoids, all of which have cardiovascular protective effects.
In view of the impact and economy of waste the present research investigation was carried out to utilize the orange peel powder to check the removal of heavy metals from industrial wastewater and also comparison studies have been done wrt mixed adsorbent along with regeneration studies. and also evaluated for their overall quality characteristics.

2. Materials & Methodology

The following details gives about the methodology for the preparation of adsorbent and the analysis of concentration from the batch study

2.1 Preparation of orange peel adsorbent by chemical treatment

The orange peel was collected from the local juice shops of Saudi Arabia and then it is washed thoroughly by tap water and followed by the rinsing with deionized water. Then the peel was treated with 0.1 N HNO_3 solution for the protonation purpose for 5 hours. Then the peel was dried in sunlight for 5 days and followed by drying in oven at 105^{o}C for 3 hours to remove the moisture completely. Thus, in the last stage the peel was crushed, ground and passed through 1 mm sieve to get uniform sized adsorbent.

2.2 Preparation of mixed adsorbent

To determine the particle size of the mixed adsorbent, activated charcoal (AC) and bone charcoal (BC) were mixed in a 1:1 ratio and particle size analysis (Malvern, Malvern Instruments Ltd, United Kingdom) was performed in a particle size Analyzer. The particle sizes of the mixed adsorbent and orange peels were reported to be 572.2 nm and 634.4 nm respectively.

2.3 Heavy metal analysis by Atomic Absorption Spectrophotometer

A standard pH meter was used for the adjustment of pH of the simulated metal ion solution. After the adsorption process the final concentration of the solution was measured by standard Atomic Absorption Spectrometer (AAS) equipment.

Various batch mode studies were conducted using industrial effluents (by diluting the concentration from 350 ppm to 50 ppm by adding 14.28ml industrial effluent and 85.72ml of deionized water) in a 250 ml conical flask. The pH of the solution was adjusted by adding 0.1N NaOH and 0.1 N HCl solutions. The 50-ppm metal ion concentration was prepared and pH was varied from 2, 4, 6, 8. The rotational speed (agitation) was carried at 180 rpm. Also, the adsorbent dosage of 0.5 g/l was added at different pH. Each conical flask was rotated for about 1hour in an orbital shaker equipment. Then all the solutions were filtered at respective time intervals from 15 min to 3.5 to 4 hrs. and the supernatant clear liquid was analyzed for final residual Cu (II) concentration in Atomic Absorption Spectrometer. The removal capacity and the % removal of the adsorbent was calculated by using the formula

$$q_e = [\frac{(C_o - C_e)}{m}] * V \text{ (mg/g)} \qquad (1)$$

$$\% \text{ removal} = (\frac{C_o - C_e}{C_o}) \times 100 \qquad (2)$$

Where q_e is the amount adsorbed, C_0 is the initial metal ion concentration in ppm, C_e is the final metal ion concentration in ppm, V is the volume of the solution in ml and m is the mass of the adsorbent taken in g.

3. Results & Discussion

The following section describes the results obtained for the effect of pH, adsorbent dosage, contact time for Cu (II) and Cd (II) metals and also gives the comparison analysis for the mixed adsorbent and orange peels.

3.1 Comparison of batch mode results for the removal of copper using orange peel and mixed adsorbent

3.1.1 Effect of pH on copper removal

Accordingly, adsorption was principally dependent on the type and ion state of the functional groups (ligands) in biomass. At low pH values, the surface of adsorbent would also be surrounded by hydronium ions, which decrease the metal ion interaction with binding sites of the orange peel by greater repulsive forces and therefore lower adsorption. In contrast, as the pH was increased, the competing effect of hydrogen ions decreased and more ligands were available. Therefore, at high pH values, the overall surface on the orange peel became more negative and adsorption increased. The study at pH higher than 8 were not conducted, because insoluble copper hydroxides get precipitated and restricted the true biosorption studies. [7]. The experiment was conducted at a temperature of 25^{o}C, 50 mg/L metal ion concentration for 60 minutes agitation with an adsorbent dosage of 0.5g/l and the samples are collected for every 30 minutes until 2hrs to reach the saturation and the residual concentrations are found by using AAS. From the below graph the maximum % removal for orange peel was obtained as 75 to 85.6 % at pH6, 63.32 to 73.54 % at pH 4, 59.6 to 69.54 % at pH 2, and 24.9 to 35% at pH 8 respectively. Similarly, for the mixed adsorbent the % removal was obtained as 83.64 to 96.62 % at pH6, 72.1 to 81.42 % at pH 4, 64.88 to 74.22 % at pH 2, and 33.76 to 47.26 % at pH 8 respectively. In comparison with the orange peel powder, the highest % removal was obtained for mixed adsorbent (AC+ BC) due to the high surface area of the activated charcoal as well as –ve charge from the bone charcoal which induces the synergistic effect. The % removal vs time graphs for both the adsorbents are shown in fig 1 and fig 2. The max adsorption capacities for mixed adsorbent and orange peels at 2 pH were found to be 7.1 and 6.55mg/g, at 4 pH was 7.8 and 6.95 mg/g, at 6 pH was 9.22 and 8.15 mg/g, at 8 pH was 4.43 and 3.1 mg/g respectively.

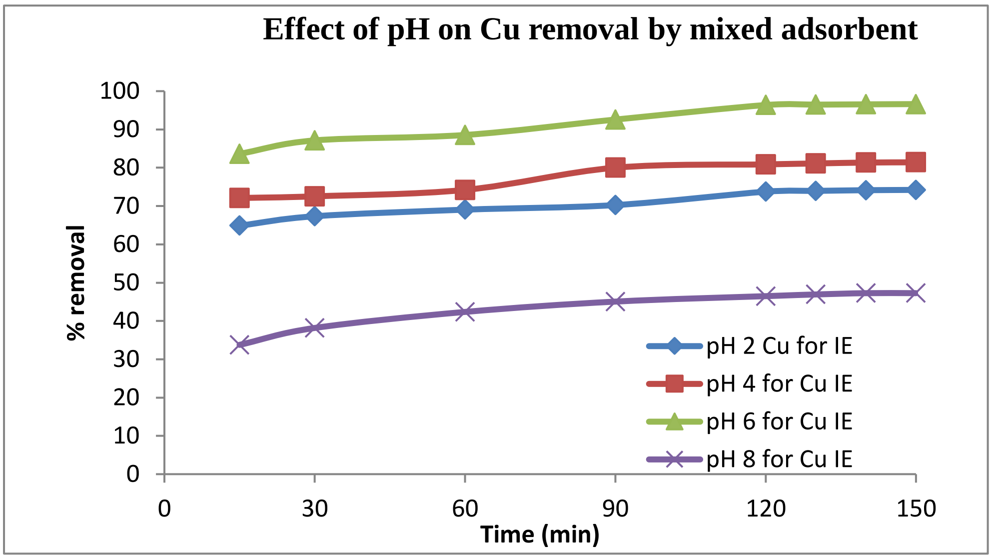

Fig 1: Effect of pH on Cu% removal by mixed adsorbent

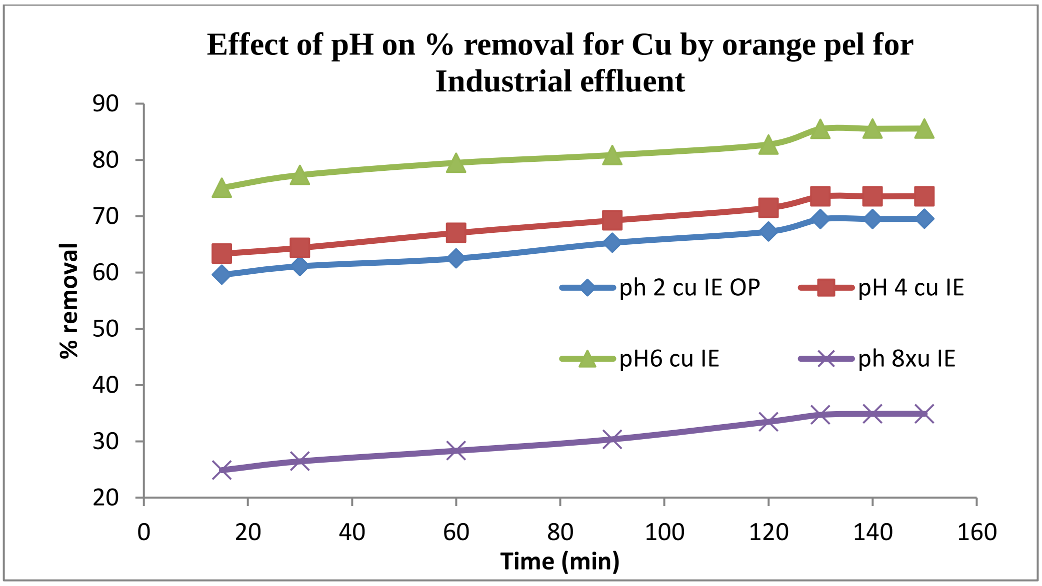

Fig 2: Effect of pH on cu% removal by orange peel

3.1.2 Effect of adsorbent dosage

The effect of adsorbent dosage was studied from 0.5g/l, 1g/l, 2g/l. 3g/l, 5g/l with the same adsorbent conditions. The experiment was conducted at a temperature of 25°C, 50 mg/L metal ion concentration for 60 minutes agitation with an adsorbent dosage varying from 0.5g/l to 1g/l, 2g/l. 3g/l, 5g/l and the samples are collected for every 30 minutes until 2hrs to reach the saturation and the residual concentrations are found by using AAS. From the below graph the maximum % removal for orange peel was obtained as 33.1 to 46.6 % at 0.5g/l, 39.1 to 51.4 % at 1g/l, 50.3 to 68.8 % at 2g/l, and 65 to 77.4 % at 3g/l, 74.9 to 85.18 % at 5g/l respectively.

Similarly, for the mixed adsorbent the % removal for mixed adsorbent was obtained as 43.78 to 57 % at 0.5g/l, 49.76 to 66 % at 1g/l, 55.74 to 74.8 % at 2g/l, 68.32 to 88.48 % at 3g/l, and 83.76 to 96.2 % at 5g/l respectively. In comparison with the orange peel powder, the highest % removal was obtained for mixed adsorbent (AC+ BC) due to the high surface area of the activated charcoal as well as –ve charge from the bone charcoal which induces the synergistic effect. The % removal vs time graphs for both the adsorbents are shown in fig 3 and fig 4.
The max adsorption capacities for mixed adsorbent and orange peels at 0.5g/l were found to be 5.22 and 4.13 mg/g, at 1 g/l was 3.02 and 2.31 mg/g, at 2g/l was 1.71 and 1.53 mg/g, at 3g/l was 1.38 and 1.21 mg/g, at 5g/l was 0.92 and 0.81 mg/g respectively.

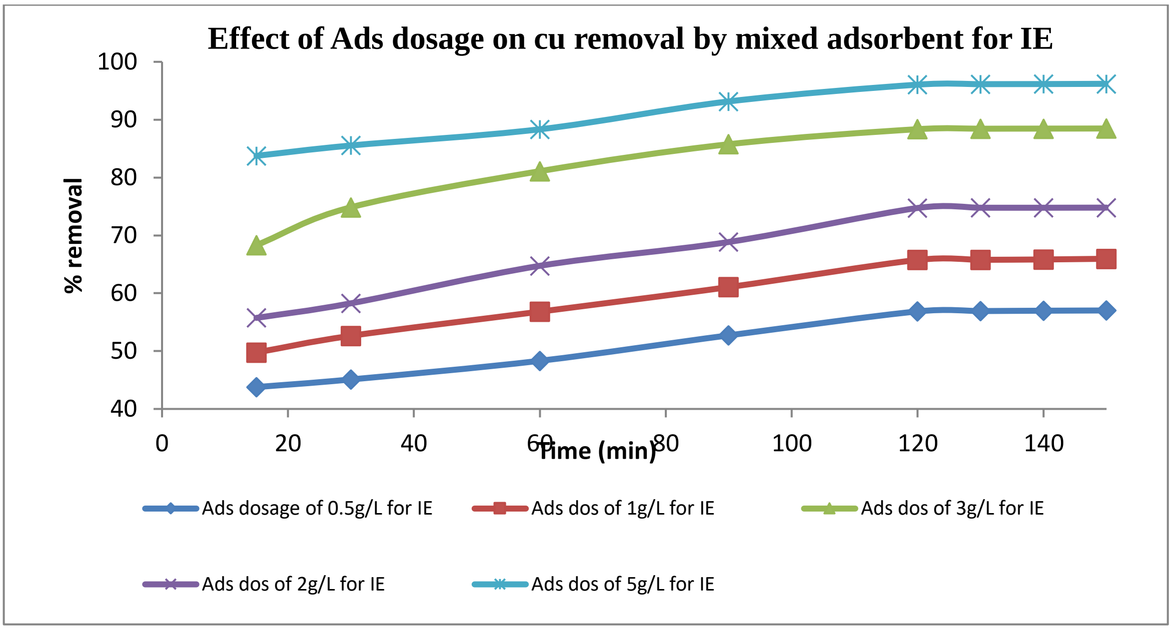

Fig 3: Effect of adsorbent dosage on Cu% removal by mixed adsorbent

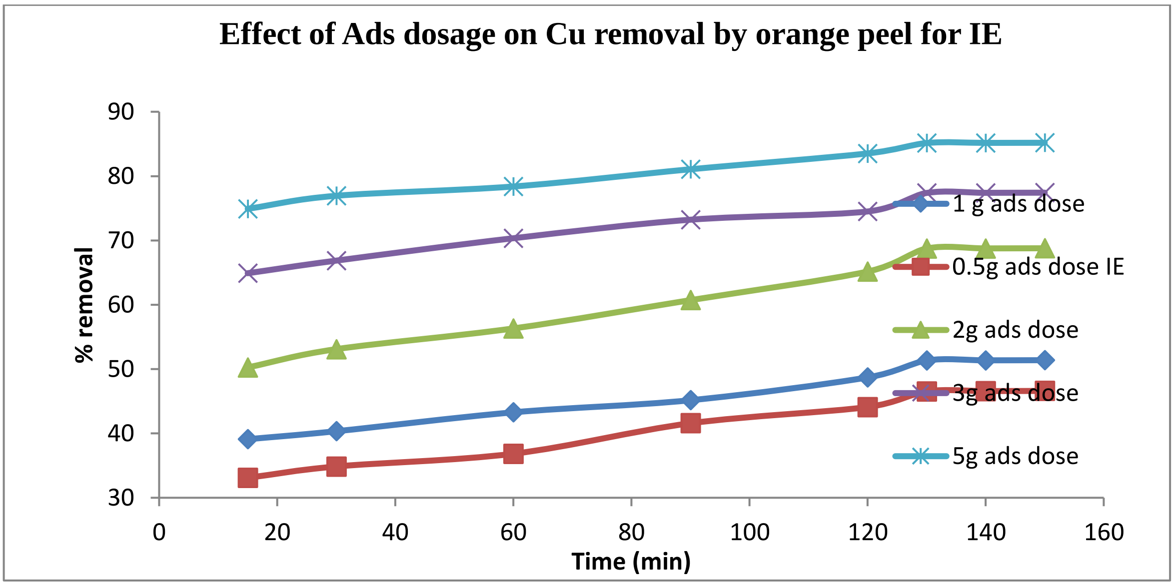

Fig 4: Effect of adsorbent dosage on cu% removal by orange peel

3.1.3 Effect of contact time

After optimizing pH and adsorbent dosage, the experiments were carried out at same adsorbent conditions to find the effect of contact time on % removal for orange peel. The experiment was conducted at a temperature of 25^{o}C, 50 mg/L metal ion concentration for 60 minutes agitation with an adsorbent dosage of 5g/l and the samples are taken at every 30 minutes interval of time and analyzed through AAS. From the below graph the maximum % removal for mixed adsorbent was obtained as 33.72 to 80.7 % at 5 g/l, and for orange peel it was 27.54 to 70.4 % at 5g/ l of adsorbent dosage. In comparison with the orange peel powder, the highest % removal was obtained for mixed adsorbent (AC+ BC) due to the high surface area of the activated charcoal as well as –ve charge from the bone charcoal which induces the synergistic effect. The % removal vs time graphs for both the adsorbents are shown in fig 5. The max adsorption capacities for mixed adsorbent and orange peels at 5 g/l were found to be 0.67 mg/g and 0.56 mg/g respectively.

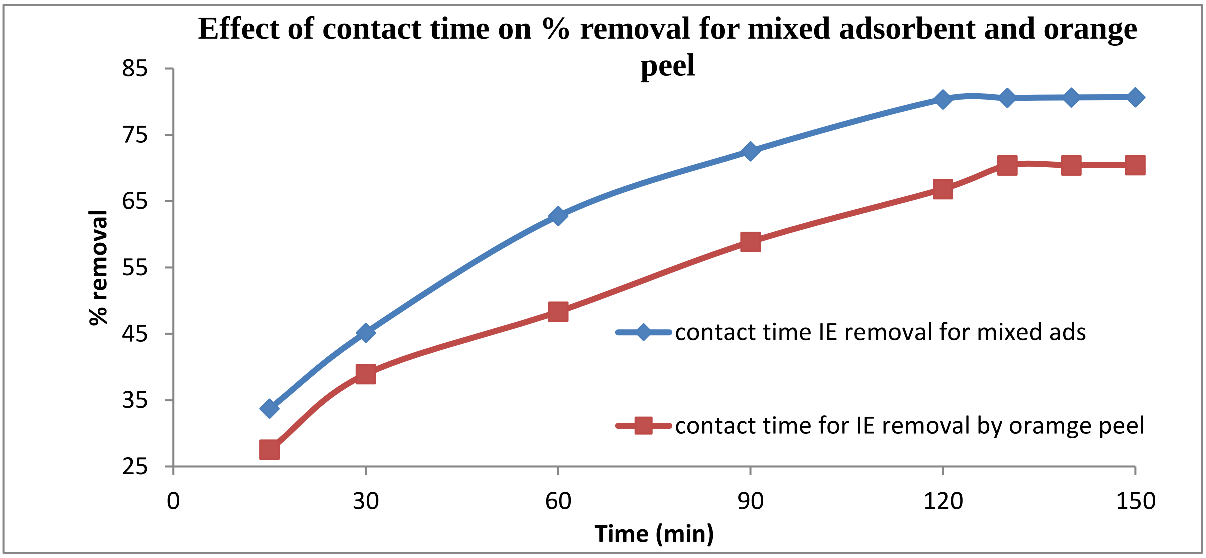

Fig 5: **Effect of contact time on % removal of copper for mixed adsorbent and orange peel**

3.2 Comparison of batch mode results for the removal of cadmium using orange peel and mixed adsorbent

3.2.1 Effect of pH on cadmium removal

The experiment was conducted at a temperature of 25^{o}C, 50 mg/L metal ion concentration for 60 minutes agitation with an adsorbent dosage of 0.5g/l and the samples are collected for every 30 minutes until 2hrs to reach the saturation and the residual concentrations are found by using AAS. From the below graph the maximum % removal for mixed adsorbent was obtained as 45.7 to 69.3 % at pH6, 38.26 to 57.92 % at pH 4, 29.18 to 50.94 % at pH 2, and 23.46 to 38.4 % at pH 8 respectively. Similarly, for the orange peel the % removal was obtained as 39.8 to 53.74 % at pH6, 31.6 to 45.62 % at pH 4, 24.88 to 40.67 % at pH 2, and 17.6 to 30.71 % at pH 8 respectively. In comparison with the orange peel powder, the highest % removal was obtained for mixed adsorbent (AC+ BC) due to the high surface area of the activated charcoal as well as –ve charge from the bone charcoal which induces the synergistic effect. The % removal vs time graphs for both the adsorbents are shown in fig 6 and fig 7. The max adsorption capacities for mixed adsorbent and orange peels at 2 pH were found to be 4.36 and 3.55 mg/g, at 4 pH was

5.11 and 4.1 mg/g, at 6 pH was 5.98 and 4.85 mg/g, at 8 pH was 3.33 and 2.61 mg/g respectively.

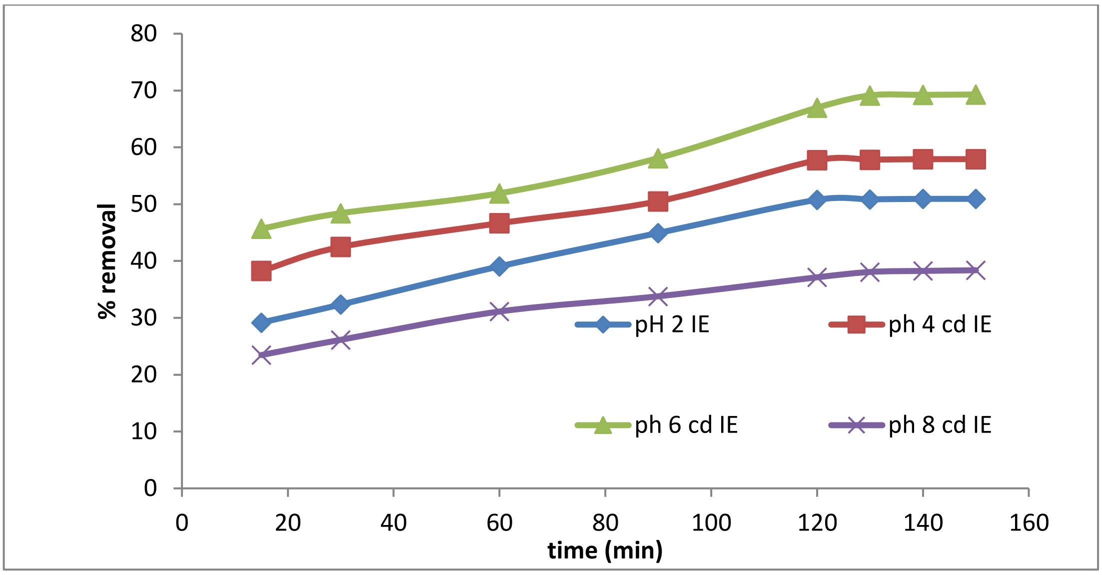

Fig 6: Effect of pH on Cd% removal by mixed adsorbent

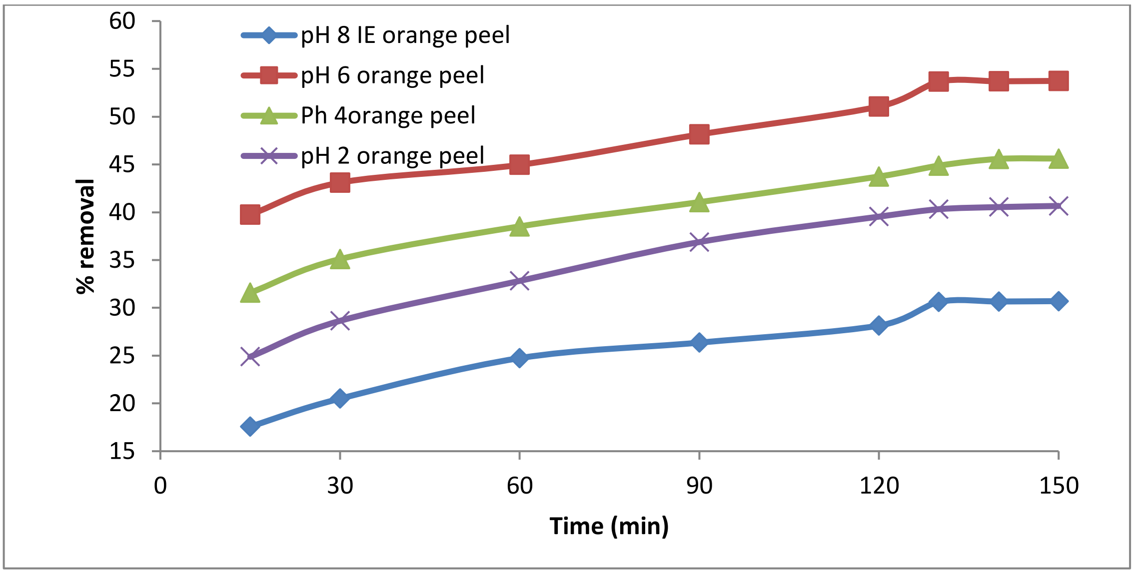

Fig 7: Effect of pH on Cd% removal by orange peel

3.2.2 Effect of adsorbent dosage on cadmium removal

The effect of adsorbent dosage was studied from 0.5g/l, 1g/l, 2g/l. 3g/l, 5g/l with the same adsorbent conditions. The experiment was conducted at a temperature of 25°C, 50 mg/L metal ion concentration for 60 minutes agitation with an adsorbent dosage varying from 0.5g/l to 1g/l, 2g/l. 3g/l, 5g/l and the samples are collected for every 30 minutes until 2 hrs. to reach the saturation and the residual concentrations are found by using AAS. From the below graph the maximum % removal for orange peel was obtained as 30.1 to 42.74 % at 0.5g/l, 35.67 to 46.8 % at 1g/l, 47.5 to 65.8 % at 2g/l, and 60.23 to 71.83 % at 3g/l, 70.18 to 80.49 % at 5g/l respectively.

Similarly, for the mixed adsorbent the % removal for mixed adsorbent was obtained as 40.91 to 52.81 % at 0.5g/l, 44.6 to 60.64 % at 1g/l, 50.62 to 70.34 % at 2g/l, 64.72 to 82.6% at 3g/l, and 81.32 to 89.68 % at 5g/l respectively. In comparison with the orange peel powder, the highest % removal was obtained for mixed adsorbent (AC+ BC) due to the high surface area of the activated charcoal as well as negative (–ve) charge from the bone charcoal which induces the synergistic effect. The % removal vs time graphs for both the adsorbents are shown in fig 8 and fig 9. The max adsorption capacities for mixed adsorbent and orange peels at 0.5g/l were found to be 4.79 and 3.82 mg/g, at 1 g/l was 2.7 and 2.12 mg/g, at 2g/l was 1.57 and 1.46 mg/g, at 3g/l was 1.25 and 1.12 mg/g, at 5g/l was 0.87 and 0.78 mg/g respectively.

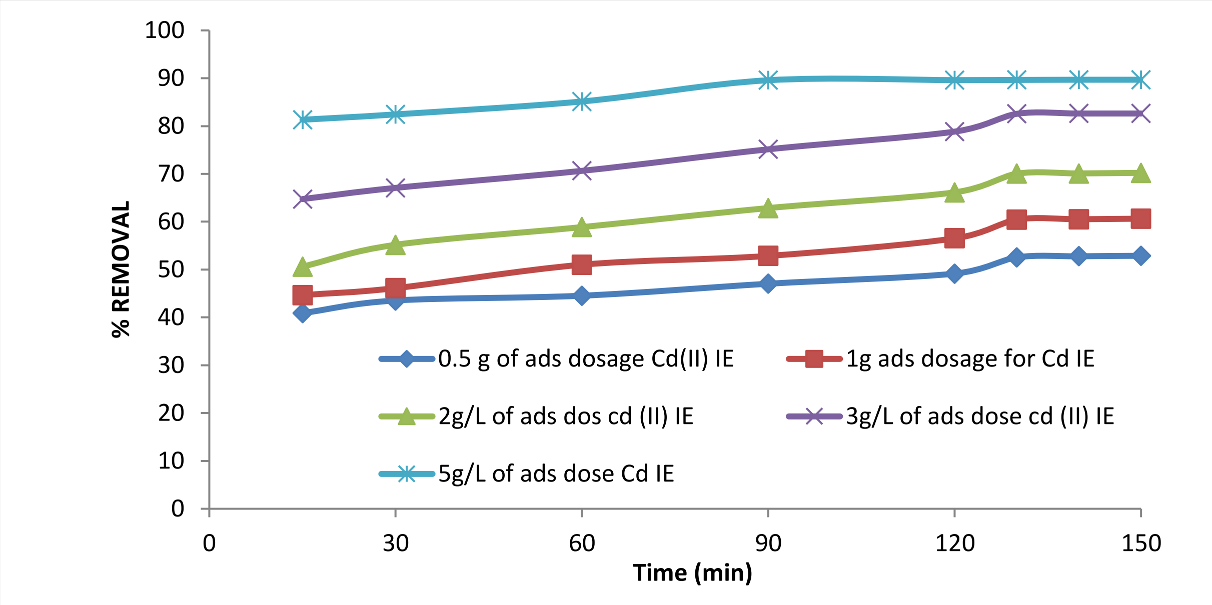

Fig 8: Effect of adsorbent dosage on Cu % removal by mixed adsorbent

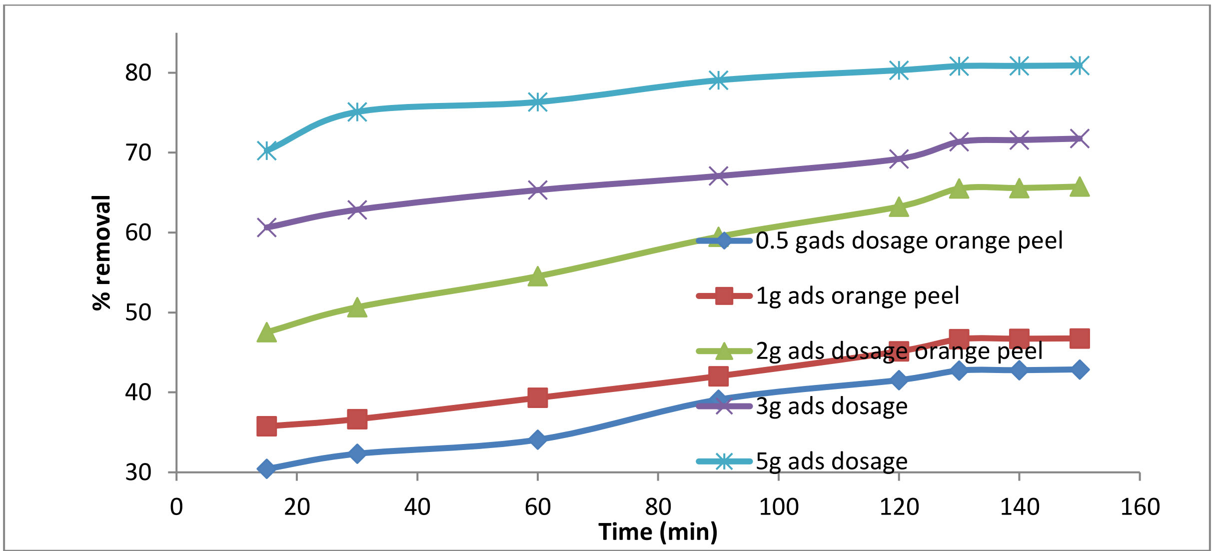

Fig 9: Effect of adsorbent dosage on Cd% removal by orange peel

Effect of contact time on cadmium removal

After optimizing pH and adsorbent dosage, the experiments were carried out at same adsorbent conditions to find the effect of contact time on % removal for orange peel. The experiment was conducted at a temperature of 25^oC, 50 mg/L metal ion concentration for 60 minutes agitation with an adsorbent dosage of 5 g/l and the samples are taken at every 30 minutes interval of time and analyzed through AAS. From the below graph the maximum % removal for mixed adsorbent was obtained as 23.78 to 75.56 % at 5 g/l, and for orange peel it was 17.54 to 50.7 % at 5g/ l of adsorbent dosage. In comparison with the orange peel powder, the highest % removal was obtained for mixed adsorbent (AC+ BC) due to the high surface area of the activated charcoal as well as –ve charge from the bone charcoal which induces the synergistic effect. The % removal vs time graphs for both the adsorbents are shown in fig 10. The maximum adsorption capacities for mixed adsorbent and orange peels at 5 g/l were found to be 0.61 mg/g and 0.45 mg/g respectively.

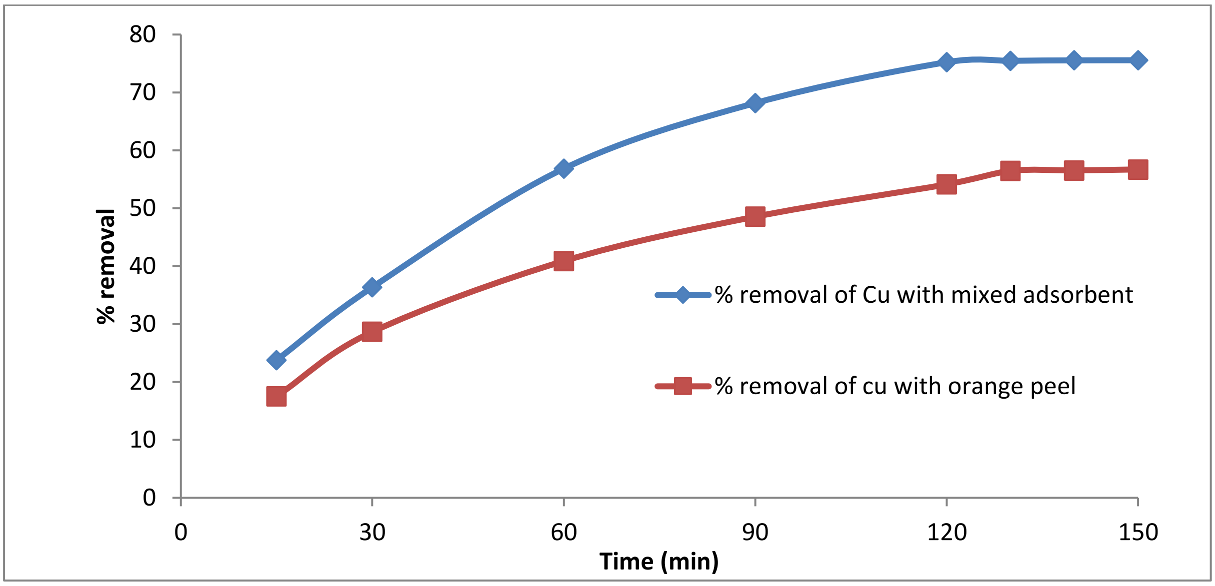

Fig 10: Effect of contact time on % removal of cadmium using mixed adsorbent and orange peel

3.3 Desorption, reusability and regeneration in batch studies for Cu (II) and Cd (II)

Regeneration is very important aspect of the adsorption from economy and environmental point of view. The disposal of adsorbent is one of the problems associated with the adsorption processes [8]. The regeneration can reduce the need of new adsorbent and also reduce the problem of disposal of used adsorbent. Various regeneration methods have been used with different degrees of success. These methods include solvent washing, thermal, chemical and electrochemical regeneration. The recovery of many solutes was possible by using solvent washing. Different eluents such as dilute HNO_3, dilute HCl, dilute H_2SO_4, mineral and organic acids are used for the desorption studies. [9- 10]

In these studies, the regeneration process involves the extensive washing of mixed adsorbent with 0.2 M HCl solution. The reaction was allowed to takes place for 60 min at a rotational speed of 150-180 rpm in an orbital shaker followed by washing with water to remove the traces of metal ions.

The tests of Cu (II) and cd (II) desorption were conducted with five adsorbent dosages of 0.5g/L, 1g/L, 2g/L, 3g/L, 5 g/L as shown in fig 11 and 12. The Cu (II) and Cd (II) desorption ability can be defined as the ratio of the desorbed cu (II) and cd (II) over the total adsorbed cu (II) and cd (II) by the adsorbent [11-12]. Therefore, the desorption ability of Cu (II) and Cd (II) can be used to indicate the degree/rate of desorbability in terms of % desorbed and time on y-axis and x-axis for Cu (II) and Cd (II) desorption from the adsorbed materials.

The graph (in fig 11) shows that the % desorbability of cu (II) (% removal of desorption) at 0.5g/L, 1g/L, 2g/L, 3g/L, 5g/L decreased drastically from 90 to 44.2 %, 75.96 to 36%, 68.17 to 17.11%, 58.84 to 12.88 %, 53.72 to 10.4%. Similarly, the graph (in fig 12) shows that the % desorbability of cd (II) (% removal of desorption) at 0.5g/L, 1g/L, 2g/L, 3g/L, 5g/L decreased drastically from 95 to 53 %, 85.6 to 47.8%, 73.94 to 30 %, 66.88 to 24.7 %, 60.26 to 17.8 %.

These results indicate that the Cu (II) and Cd (II) adsorption on the mixed adsorbent is almost completely reversible and the bonding between the mixed adsorbent and adsorbed Cu (II) and Cd (II) ions is likely to be strong. It is relatively easy for the adsorbed Cu (II) and Cd (II) to be desorbed from the mixed adsorbent by achieving 90% and 94% desorption efficiency rate. It can be concluded that the desorption process with the same regeneration of adsorbent can be used for 9-10 cycles in the batch process to get completely saturated and the mixed adsorbent can be thrown away as it will not be recycled back. In comparison between Cu (II) and Cd (II), cadmium achieved more desorption rate at each adsorbent dosage and further predicted that regenerations studies can be used in the waste water treatment for the recovery of metal ions from the treated adsorbent.

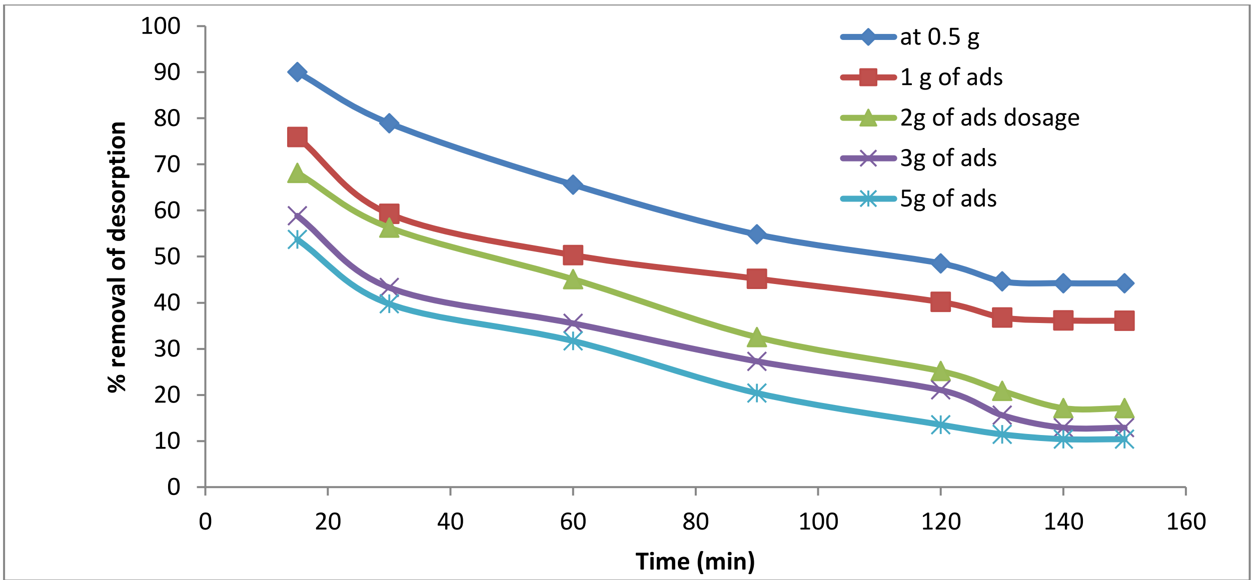

Fig 11 Effect of % removal of desorption vs time at different adsorbent dosage of Cu(II)

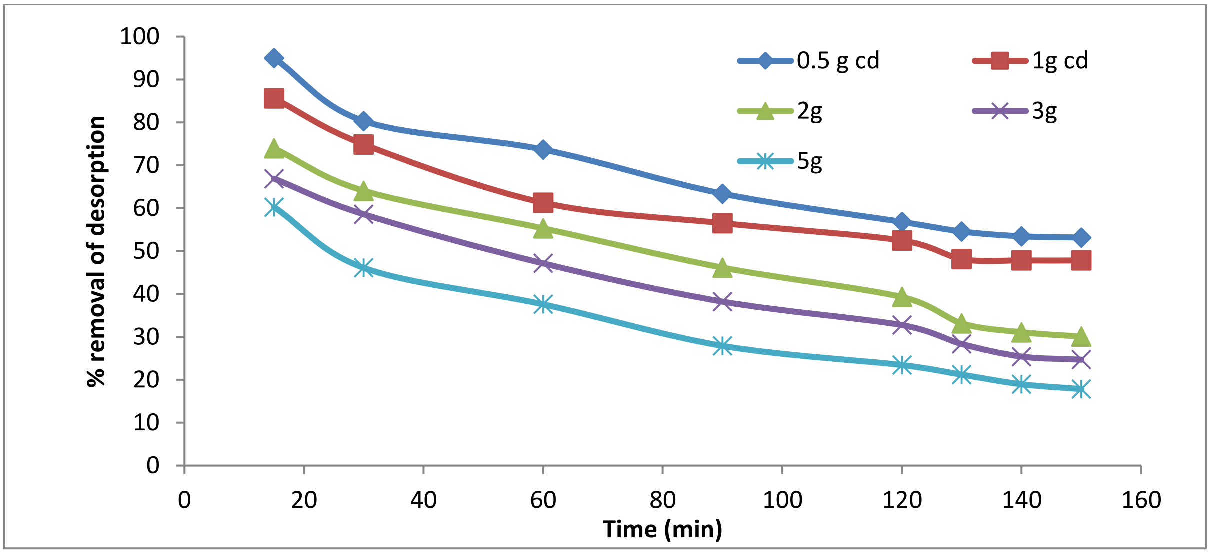

Fig 12 Effect of % removal of desorption vs time at different adsorbent dosage of cd (II)

Conclusion

In conclusion it can be further reported that orange peel can be treated as a low-cost agricultural adsorbent when compared to mixed adsorbent in terms of cheaply availability of raw material, as a bio sorbent, in terms of ease of usage. But in terms of surface area and porosity it is less when compared to mixed adsorbent. The regeneration capacity is also less when compared to the mixed adsorbent as the active sites are occupied by the metal ions or the pores are blocked and even the desorption studies are carried out the maximum % recovery of metal ions is difficult from orange peel. It can be concluded that regeneration, reuse of adsorbent and the recovery of solute are few important aspects of the adsorption which can render this wastewater treatment method more economic value and importance so that cost and excessive usage of the mixed adsorbent can be saved or minimized and it is an economically feasible to reduce the cost of the adsorbent.

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