



Removal of Cu (II) and Fe (II) from Industrial waste water using orange peel as adsorbent in batch mode operation

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Abstract : The current study focuses on the removal of Copper and Iron from industrial waste water using unconventional adsorbents. Chemically treated orange peel is available abundantly as agricultural based wastes. In this study the modification of the surface of an adsorbent was found to be more effective in the removal of copper and iron from the waste water which leads to achieve the higher adsorption capacity and % removal. This work is considered to be innovative because the economic feasibility of the modifications made is not yet available fully. The work was carried out in batch mode reactor. The influence of process parameters like pH, speed of agitation, adsorbent dosage, metal ion concentration, External temperature and contact time are studied in terms of % removal vs time. The maximum metal ion removal for Cu (II) is 87% at pH 6 and for iron it is 85% at pH 5. At 10 ppm concentration, the maximum removal was obtained as 93% for both metals at the same operating conditions. The maximum removal of metal ions at 1.5 g of adsorbent dosage for Cu (II) and Fe (II) are 96% and 94% respectively. At a temperature of 30°C the maximum removal of metal ions was obtained as 89% and 81% respectively for Cu (II) and Fe (II). At 180 rpm of agitation rate, the maximum % removal of metal ions was 89 and 85 for Cu (II) and Fe (II) respectively. At 90 minutes of contact time the maximum % removal achieved was 90 and 87 for Cu (II) and Fe (II) respectively.

Key words : Adsorption, pH, agitation rate, adsorbent dosage, Initial metal ion concentration, Contact time, Temperature.

1. 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 rainwater. 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[16-21].

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. And 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. The conventional adsorbents are not preferred due to their lesser efficiency and higher cost. So generally used biomass adsorbents are saw dust, paper waste, bagasse, coconut shell, tea powder, citrus peel etc. Orange peel considered as the most abundantly available biomass and which constitute the 75% of the citrus fruit family[5]. It has a very good quantity of cellulose, pectin, hemicelluloses and lignin content with various polar groups like COOH and OH which helps to increase the strength of bond formation and sometimes they also act as biopolymers [6][7][8][9][10].

In 1990's a new scientific area was developed to recover heavy metals and it was called bioremediation. The early reports described how abundant biological materials could be used to remove, at very low cost, even small amounts of toxic heavy metals from industrial effluents. The principle advantages of biological technologies for the removal of pollutants are they can be carried out in situ at the contaminated site, usually environmentally benign (no secondary pollution) and they are cost effective. Of the different biological methods, bioaccumulation and biosorption have been demonstrated to possess good potential to replace conventional methods for the removal of heavy metal ions.

2. Materials and Methods

2.1 Chemicals used

All the chemicals used in this experiment were in their pure form. The stock solution of Cu(II) was prepared in laboratory by dissolving 1 gram of copper salt in 1000 ml of deionized water. The same stock solution is used for various experimental runs. The Ph value of the solution is adjusted by the addition on 0.1N HCl and 0.1 N NaOH solutions.

2.1.1 Preparation of biosorbent by chemical treatment

The orange peel was collected from the local juice shops of Dehradun and then it is washed thoroughly by tap water and followed by rinsing with deionized water. Then the peel was treated with 0.1 N HNO₃ 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°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.

2.1.2 Instruments used for Adsorbent / biosorbent characterization

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 Spectroscopy (AAS) equipment.

2.1.3 Batch mode operation

Various batch mode studies were conducted by preparing 100 ml of solution using simulated water stock solution of suitable concentration in a 250 ml conical flask. The pH of the solution was adjusted by adding 0.1N NaOH and 0.1 N HCl solutions. Various metal ion solutions of 10-60 ppm were selected and pH was varied from 3 to 8. The rotational speed was varied from 90 rpm to 180 rpm. The adsorbent dosage varied from 0.25 to 1.5 grams in every run. Each conical flask was rotated for about 2 hours in orbital shaker equipment. Then all the solutions were centrifuged at 4000 rpm and the supernatant clear liquid was analysed for final Cu (II) concentration in Atomic Absorption Spectrometer. The removal capacity of the adsorbent was calculated by using the formula. After the analysis the equilibrium time and % removal of heavy metal ions were calculated. The data obtained in the present studies were used to calculate the equilibrium metal adsorptive quantity/capacity (mg/g) by using the mass balance relationship and the percentage removal of heavy metal ions. Experiments were conducted (three repetitions) simultaneously and the average values were reported. The equilibrium metal adsorptive capacity of the metal ions (q_e) and % removal were calculated by using mass balance given by

$$q_e = (C_o - C_e) \left[\frac{V}{M} \right] \quad (1)$$

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

Where 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. C_o , C_e is the initial and equilibrium concentration of metal ions in mg/l. M is the mass of the adsorbent in grams.

3. Results and Discussion

Various process parameters of the batch mode adsorption are considered and the effect of these parameters on adsorption % removal was studied and plotted in terms of graphs which will be studied in this section.

3.1 Effect of pH

pH is one of the most important environmental factor influencing not only site dissociation but also the solution chemistry of the heavy metals, hydrolysis, complexation by organic and/or inorganic ligands. Redox reactions, precipitation are strongly influenced by pH and on the other side strongly influence the speciation and the adsorption availability of the heavy metals. 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 orange peel by greater repulsive forces and therefore lower adsorption takes place. 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 as shown in the fig 1 and 2 respectively for Cu (II) and Fe (II). The study at pH higher than 6 were not conducted, because insoluble copper and ferric hydroxides get precipitated and restricted the true biosorption studies [11]. The experiment is conducted at a temperature of 30°C, 50 mg/L concentration for 60 minutes with an adsorbent dosage of 0.25 grams.

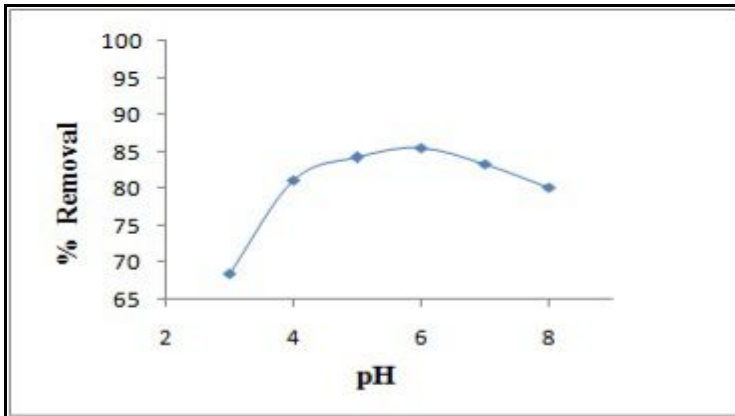


Figure 1 Effect of pH on copper adsorption

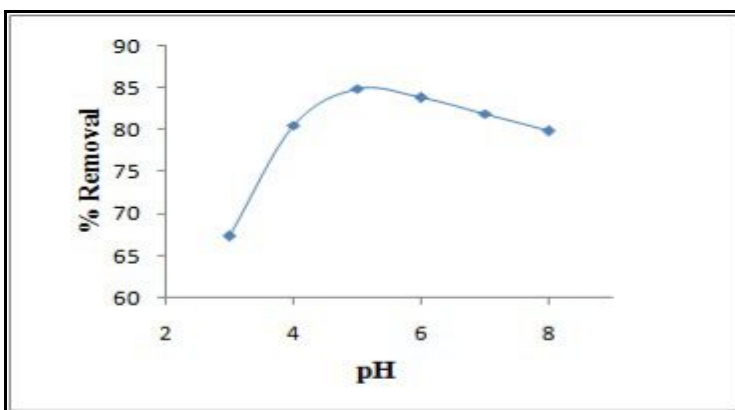


Figure 2 Effect of pH on Iron adsorption

3.2 Effect of Initial metal ion concentration

At low-ion concentrations, the ratio of surface active sites to the total metal ions in the solution was high and hence metal ions may interact with the adsorbent and be removed from the solution. Also, at high-concentration levels of metal ions are left unadsorbed in solution due to the saturation of binding sites on the biomass surface. However, amount of metal adsorbed per unit weight of adsorbent, q_e , is higher at high concentrations [10]. The experiment was conducted at a temperature of 30°C, 50 mg/L concentration at pH 6 for copper and 5 for iron with an adsorbent dosage of 0.25 grams. Increase of metal ion concentration from 10 to 60 mg/l decreases the % removal of metal ions from 93 % to 80% which indicates that the binding sites are occupied by the metal ions at high concentration and restricted the true adsorption studies as shown in fig 3 and 4 respectively for Cu (II) and Fe (II)

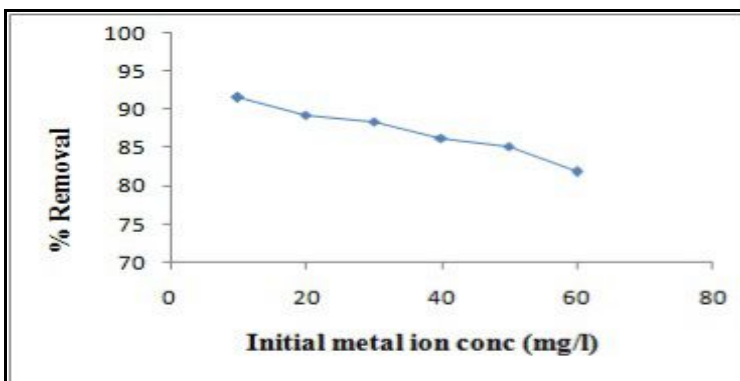


Figure 3: Effect of Initial Copper metal ion concentration on % removal

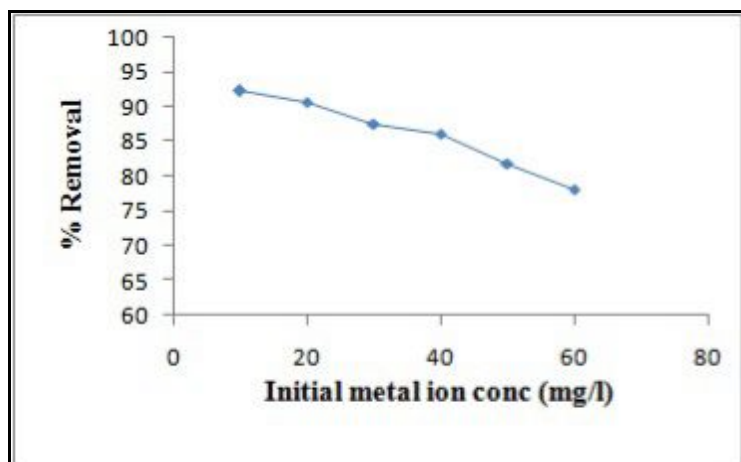


Figure 4: Effect of Initial Iron metal ion concentration on % removal

3.3 Effect of Adsorbent dosage on % removal

Biosorbent dose is a significant factor to be considered for effective metal removal as it determines sorbent- sorbate equilibrium of the system. It was observed that the amount of copper adsorbed varied with varying orange peel biomass concentration. The amount of copper adsorbed per unit mass of adsorbent was decreased with an increase in adsorbent dosage from 0.25 to 1.5 g. Dose of biomass added into the solution determine the number of binding sites available for adsorption. The number of adsorption sites or surface area increases with the weight of adsorbent and hence results in a higher percent of metal removal at a high dose as shown in fig 5 and 6 respectively for Cu (II) and Fe (II) [12]. The experiment was conducted at a temperature of 30°C, 50 mg/L concentration for 60 minutes at a pH of 6 for copper and 5 for iron.

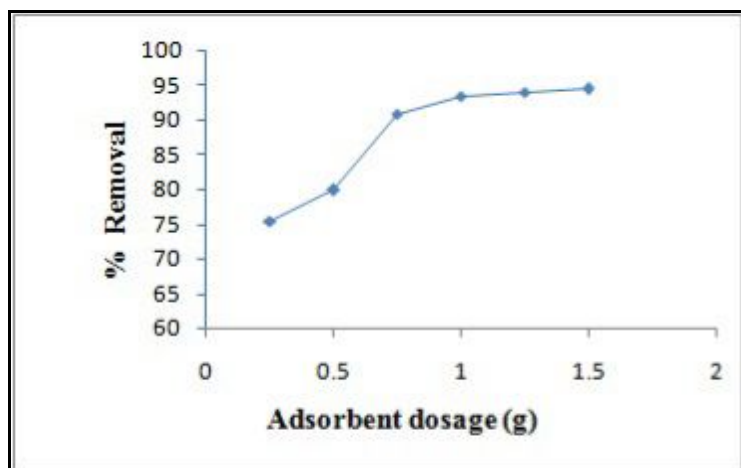


Figure 5 Effect of Adsorbent dosage on copper metal ion adsorption

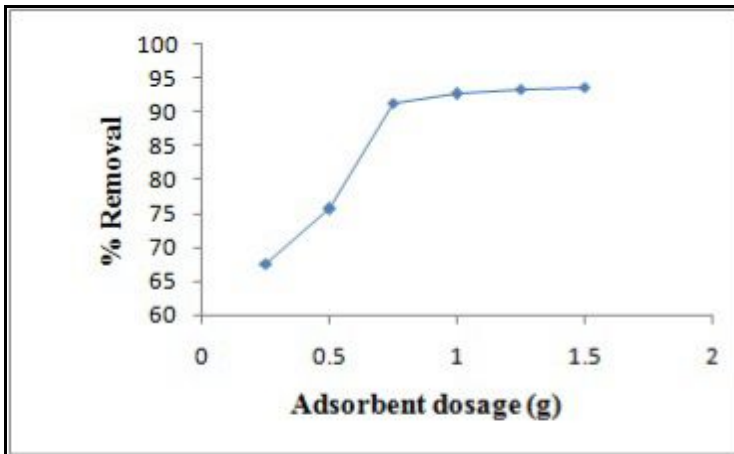


Figure 6: Effect of Adsorbent dosage on copper metal ion adsorption

3.4 Effect of temperature

From the below figure it is very clear that the adsorption process favours at low temperature. At elevated temperatures the particles will try to move away from the active surface. As per the theory of adsorption the rate of adsorption decreases with the increase in temperature [13]. The experiment is conducted with 50 mg/L concentration and 0.25 g orange peel for 60 minutes at the pH of 6 for copper and 5 for iron. As the temperature increased from 30°C to 45°C the % removal of Cu (II) decreased from 90% to 78% and Fe (II) decreased from 82% to 76% as shown in the fig 7 and 8 respectively.

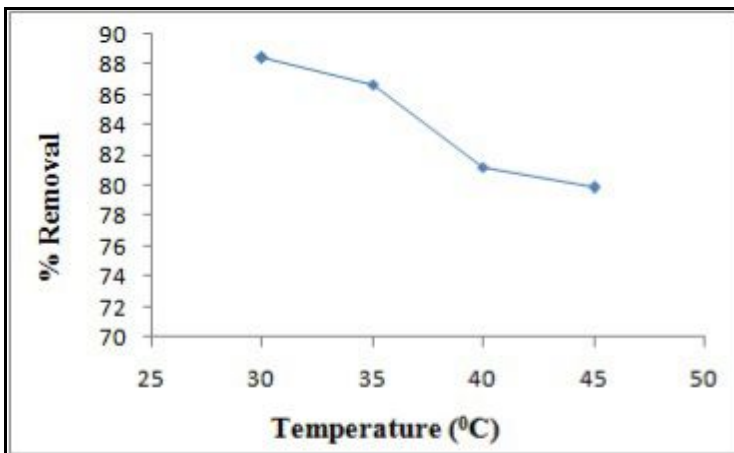


Figure 7: Effect of temperature on the adsorption of Copper

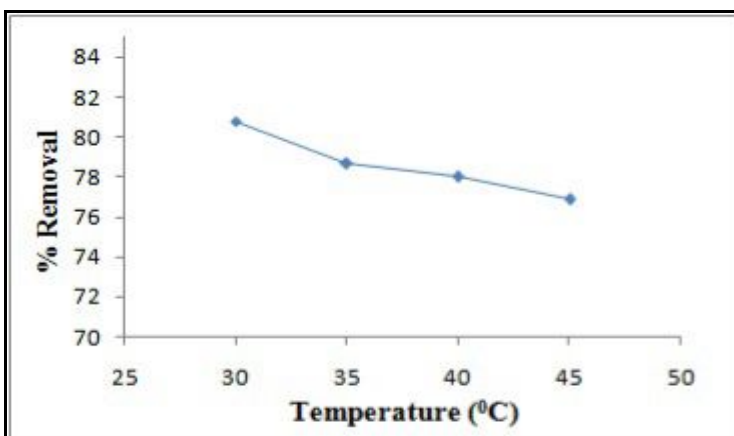


Figure 8: Effect of temperature on the adsorption of Iron

3.5 Effect of agitation speed

Agitation is an important parameter in adsorption, the main reason for this being that agitation helps in overcoming the external mass transfer resistance. At higher agitation speeds, that is, rapid stirring of the solution, the mass transfer resistance related to ion diffusion through the liquid film surrounding the orange peel particles is reduced as the film thickness reduces due to agitation, resulting in greater metal uptake. Agitation of the mixture not only results in a decrease in film transfer resistance but also results in the abrasion of orange peel producing freshly broken and highly reactive locations on the surface. So this mechanical effect increases the number of possible adsorption locations, resulting in an increase in the rate of adsorption. However, the production of fine particles due to abrasion, has its disadvantages, mainly that it becomes increasingly difficult to separate the solids from the liquid [14]. The experiment was conducted with 50 mg/L concentration and 0.25 g orange peel for 60 minutes at the pH of 6 for copper and 5 for iron. The temperature was kept constant at 30°C. The % removal of Cu (II) and Fe (II) increased from 76 to 90% and 75 to 85 % with the increase in agitation rate from 90 to 180 rpm as shown in fig 9 and 10 respectively.

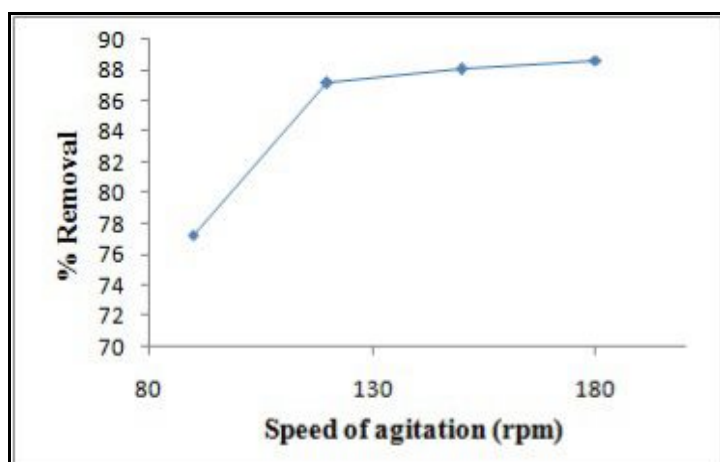


Figure 9 Effect of agitation on Copper metal adsorption

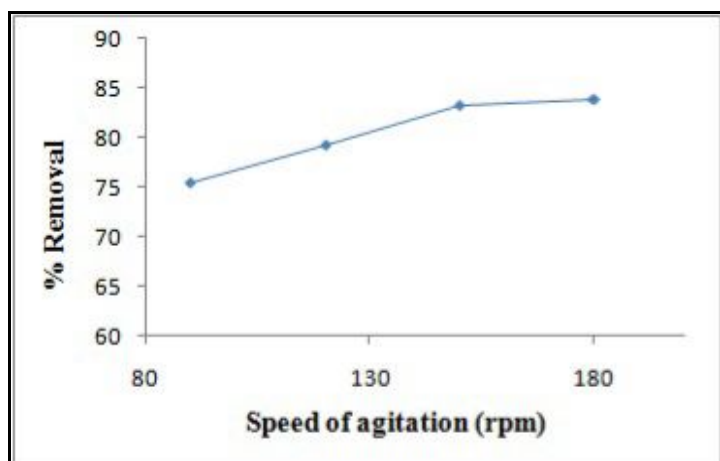


Figure 10 Effect of agitation on Iron metal adsorption

3.6 Effect of Contact time

It was very clear from the fig 11 and 12 for both Cu (II) and Fe (II) that the rate of adsorption increases with increase in the time of contact between adsorbent and metal ion solution. After certain amount of time all the active sites of the adsorbent will be either filled with metal ions or the solution itself is saturated. So increase in rate of adsorption ceases and percentage removal becomes constant [15]. The experiment is conducted with 50 mg/L concentration and 0.25 g orange peel at the pH 6 for copper and 5 for iron. The temperature of the metal ion solution was kept constant at 30°C.

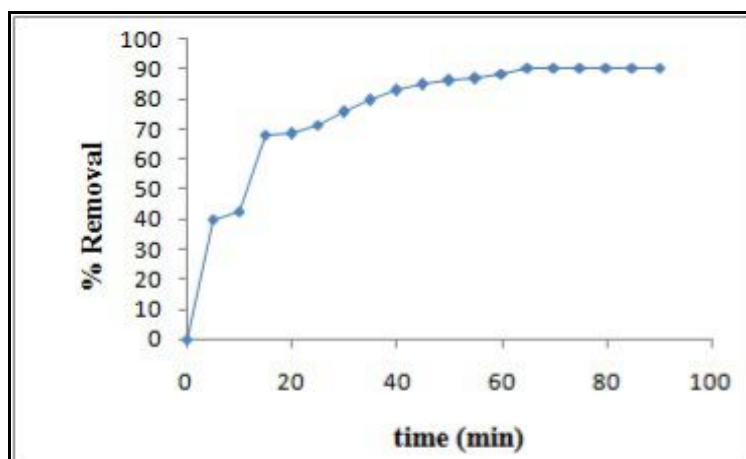


Figure 11: Effect of contact time on copper ion adsorption

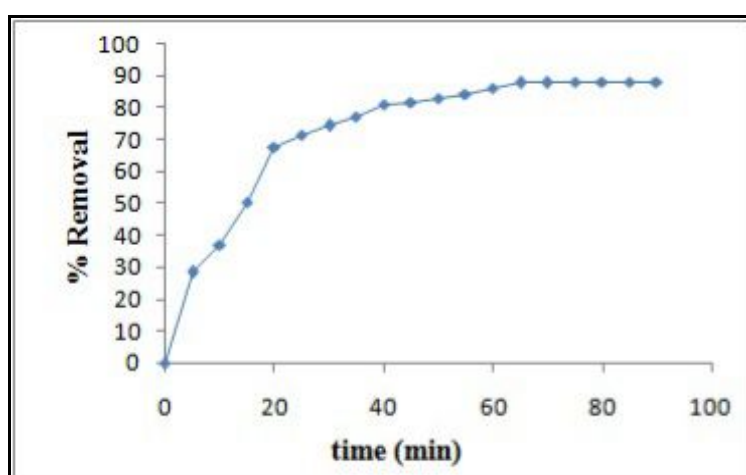


Figure 12: Effect of contact time on Iron ion adsorption

4 Conclusions

The potential of natural orange peel as a low cost material for the removal of iron and copper from synthetic metal solutions was studied. A number of experiments were performed in order to determine this potential; equilibrium adsorption capacity, % removal of metal ions. A summary of the conclusions of the experimental results are presented in this section. Results from batch equilibrium studies showed that natural orange peel was capable of removing heavy metals from solution. The maximum adsorption capacities observed were 6 for copper and 5 for iron. Kinetic studies indicated that the rate of adsorption of the heavy metals by orange peel was rapid for the first 40 minutes and then gradually decreased as equilibrium was approached. A maximum of 85 % metal ion removal was observed for both copper and iron. Various parameters like pH, initial ion concentration, temperature, adsorbent dosage, and Agitation rate and contact time were studied successfully. The maximum removal of metal ions at 1.5 g of adsorbent dosage for Cu (II) and Fe (II) are 96% and 81% respectively. At a temperature of 30°C the maximum removal of metal ions was obtained as 89% and 81% respectively for Cu (II) and Fe (II). At 180 rpm of agitation rate, the maximum % removal of metal ions was 89 and 85 for Cu (II) and Fe (II) respectively. At 90 minutes of contact time the maximum % removal achieved was 90 and 87 for Cu (II) and Fe (II) respectively.

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

Declaration by the Authors

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