



REMOVAL OF COPPER AND ZINC FROM WASTEWATER USING CHINA CLAY AS AN ADSORBENT

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ABSTRACT

Heavy metals are one of the most toxic materials to the environment. Adsorption is the process which is used for the removal of heavy metals from wastewater. Various adsorbents have been used to remove different type of heavy metal ions from wastewater especially those that are harmful to mankind. China clay was used as an adsorbent to remove copper and zinc from wastewater. Batch adsorption experiments were conducted to obtain the optimum conditions for copper and zinc. Effect of parameter like pH, adsorbent dose, contact time, temperature and initial metal ion concentration were also determined. The optimum conditions obtained were 360 min contact time, 200 mg adsorbent dose and pH 5.0 for copper and 180 min contact time, 200 mg adsorbent dose and pH 7.0 for zinc. The maximum adsorption capacity was found to be 89% for copper and 96.97% for zinc.

KEYWORDS: China clay, Adsorption, Heavy metals, pH.

INTRODUCTION

The tremendous increase in the use of heavy metals over the past few decades has inevitably resulted in an increased flux of metallic substance in aquatic environment. Industrial wastewater contains higher amount of heavy metals that can pollute the water when it is discharged to the nature. Toxic heavy metals of particular concern in treatment of industrial wastewaters include zinc, copper, nickel, mercury, cadmium, lead and chromium. Wastewater containing heavy metals originated mainly from metal plating facilities, mining operations, fertilizer industries, tanneries, batteries, paper industries and pesticides galvanizing plants, stabilizers, thermoplastics, pigment manufacture, etc.^[1] These industries discharge heavy metals and wastewater directly or indirectly into the environment especially in developing countries. Due to their toxicity and non-biodegradability, they tend to accumulate in living organism. Therefore they cause numerous diseases and disorders. Zn, Cu, Ni, Hg, Cd, Pb and Cr are considered as toxic metals of particular concern in wastewater treatment. Thus, treatment of industrial wastewater containing soluble heavy metals has become essential in order to increase the quality of water. Copper as an essential element plays an important role in all living organisms. It also widely used in industries such as high electrical and thermal conductivity, good corrosion resistance, ready availability, high recyclability and attractive appearance.^[2] Cu(II) is one of the heavy metals most toxic to the living organisms and it is one of more widespread heavy metal contaminants of the

environment. Extensive intake of Cu can causes hemolysis, hepatotoxic and nephrotoxic affects vomiting, cramps, convulsions, or even death.^[3] Zinc is a bluish white metal. Zinc is chemically active and alloys readily with other metals. It is used in many industries for preparing large number of zinc alloys and compounds. The excessive intake of zinc may cause toxic effects such as carcinogenesis, mutagenesis and teratogenesis as a result of bioaccumulation.^[4]

Many treatment processes that have been used to remove heavy metals from wastewater include precipitation, coagulation, ion exchange, electro dialysis, membrane filtration, flotation, reverse osmosis, and adsorption.^[5] Most of these processes are suffer from high cost. Adsorption is used many industries for water purification due to its low cost and applicability on large scale. Adsorption is commonly being done using activated carbon which adsorbs dissolved organic substances in the water treatment.^[6] To avoid the high cost of activated carbon many low-cost adsorbents have been used and tested to remove heavy metal ions. Different adsorbents have been used include rice husk ash^[1], wood sawdust Modified Sugarcane Bagasse^[7], modified flax shive^[8], waste biomass, waste activated sludge^[9], and Lignite^[10], chitosan.^[11] There are so many adsorbents have been used still new adsorbents are developed due to the increasing demand for treatment of industrial wastewater.

China clay is a mineral of kaolinite group. It does not

swell with addition of water. The alumina content present in it does not form isomorphous series with any other metallic compounds. It is generally used in the manufacture of different types of ceramic goods. It has been used by several workers^[12-16] as an adsorbent for water and wastewater treatment by adsorption process. It was collected from Patharghatt village of Bhagalpur district, Bihar (India). It was used as such without any pretreatment just after sieving through 53 μ m pore size sieve. The chemical analysis and characterization of China clay is given in table :1.

Table 1: Chemical analysis of China clay as Adsorbent.

Constituents	Percentage by weight
SiO ₂	46.22
Al ₂ O ₃	38.40
CaO	0.86
Fe ₂ O ₃	0.68
MgO	0.37
Loss of ignition	13.47

SCOPE OF STUDY

The scope of this study is to test wastewater for the removal of copper and zinc using China clay as an adsorbent. The wastewater was prepared in lab artificially. Batch studies were conducted using synthetic zinc and copper solution. The influence of pH, contact time, initial metal ion concentration, temperature and adsorbent concentration were investigated to optimize the conditions for maximum zinc and copper removal. The experimental data obtained were calculated and fitted using adsorption isotherms, various kinetic models and thermodynamic studies were conducted.

1. COPPER AND ITS IMPORTANCE

Copper is an important engineering metal and it is widely used for various engineering purposes. It is used for making of alloys. It is also used in ceramic and pesticides. In many industries like electrical appliances, electrical, electronics, automotive, white goods etc. copper is used in manufacture of wires. It is also used in copper forming industries. Copper compounds are used in fungicides, algicides, insecticides and wood preservatives. It is used in electroplating industry and manufacture of dyes. Copper compounds are added to fertilizers and animal feed as a nutrient to support plant and animal growth.^[17]

EMISSION OF COPPER

Copper enter into the environment through natural and anthropogenic sources. Air and water is contaminated by copper from mining, milling, electroplating industries, petroleum and refining melting plant. Copper is discharge into the industrial effluents of various industries like chloral- alkali, electroplating, paints and dyes, petroleum refining, fertilizers, mining and metallurgy, explosives, pesticides, iron and steel industries, burning of wood etc. Due to the direct discharge of industrial and municipal waste water is polluted.^[18] The main source of pollution

in copper industries are: Solids waste form mines, mine water and effluent from water treatment plants, sulphur containing gases, electrolyte from electro-refining plant, acid sponge from sulphuric acid plant etc.^[19]

ENVIRONMENTAL EFFECTS OF COPPER

Copper is regarded as one of the most basic toxic metals. The increase levels of copper in environment are posing a serious threat to mankind.^[20] It can cause harmful biochemical effects, toxicity and hazardous disease in human beings. Excessive intake of copper through air, water and food can cause harmful disease. Ingestion of 15-75mg of copper can cause gastro-intestinal disorder. Excessive intake of copper can cause hemolysis, hepatotoxic and nephrotoxic effects. Copper toxicity can cause irritation, corrosion, hepatic damage and central nervous system irritation followed by depression.^[21] Permissible limit for copper in drinking water is 0.05mg/L as per WHO norms and also 0.05 mg/L as per ISI prescribed limits, 1993.^[1]

2. ZINC AND ITS IMPORTANCE

Zinc is tremendously reactive metal that will combine with oxygen and other non-metals and will react dilute acids to release hydrogen. Zinc metal and zinc alloys are very resistant to corrosion. Due to its extensive usage in electroplating, metal plating, chemical manufacturing industries, etc. the demand of zinc has been increasing globally. Zinc is used in galvanization of steel to the manufacture of the negative plates in electrical batteries, preparation of alloys. Zinc is used in plastics, cosmetics, wallpaper, printing inks, photocopier paper etc. as a pigment. Zinc oxide used in ointments for burns and skin protection.

EMISSIONS OF ZINC

Zinc is widely used in many industries such as paint, batteries, fertilizers and pesticides, galvanization, pigment, polymer stabilizers, fossil fuel and combustion, electroplating, paper and pulp, pharmaceutical, textile mills, mining industries, etc. these industries are the main source of zinc pollution. The waste generated from these industries directly discharge to the environment and the water is polluted with zinc due to the excessive amount of zinc.^[22] Zinc is also available in some medicated shampoos contain zinc pyrithione to control dandruff. Residues of zinc from zinc-plated cold water tanks leach into tap water and are flushed away when water is used.

ENVIRONMENTAL EFFECTS OF ZINC

The excessive intake of zinc into the body through food, water or other dietary supplements can also affect human health. The recommended dietary allowances of zinc for man are 11mg/day and for women is 8mg/day.^[23] Beyond this limit it may cause many health problems like stomach cramps, nausea and vomiting. High level ingestion of zinc for several months can cause anemia, damage the pancreas and decrease the levels of cholesterol. Ingesting low level of zinc compounds like

zinc acetate and zinc chloride may cause skin irritation. Insufficient amount of zinc in diet can cause loss of appetite, decreased sense of taste and smell, decreased immune function, slow wound healing and skin sores.

STOCK SOLUTION PREPERATION

Stock solution of 10 mg/l Cu (II) ion is prepared dissolving copper sulphate pentahydrate (CuSO₄.5H₂O). 39.28 mg CuSO₄.5H₂O is added in distilled water contained in 1000ml volumetric flask. Stock solution of 10 mg/l of Zn is prepared by dissolving zinc sulphate heptahydrate (ZnSO₄.7H₂O). 43.96 mg of Zinc sulphate heptahydrate solution is added to distilled water contained in 1000ml volumetric flask. Hydrochloric acid and Sodium hydroxide were used to adjust the solution pH. Distilled water was used throughout the experimental studies.

BATCH ADSORPTION EXPERIMENT

Batch adsorption experiments of copper and zinc were carry out to determine the adsorption capacity of China clay at different metal concentrations ranging from 10 to 120 ppm and a fixed amount (50mg) of China clay in order to calculate the adsorption constant using different isotherms. 50 mL of different concentration of copper (II) and zinc (II) solutions ranging from 10–120 ppm were used. The China clay (50 g) was added to flasks and agitated at 25^oC and 120 rpm for 360 min for copper and 180 min for zinc. The initial and final concentrations of the solutions were measured were determined by Spetronic-20 Spectrophotometer at the maximum adsorption wavelength and the adsorption capacities of the adsorbent were calculated. After equilibrium was attained, the metal uptake capacity for each sample was calculated according to a mass balance on the metal ion using equation (1):

$$qe = \frac{(Co - Ce)V}{M} \quad \dots(1)$$

Table 1: Effect of pH on Cu(II) adsorption at 25 °C, 120 rpm and initial concentration 3.0 mg/L.

pH	FinalConc (mg/L)	Cu(II) adsorbed (mg/L)	% Removal
4	1.03	1.97	65.67
5	0.33	2.67	89.00
6	0.75	2.25	75.00
7	1.39	1.61	53.33
8	1.45	1.55	51.67
9	1.51	1.49	49.67

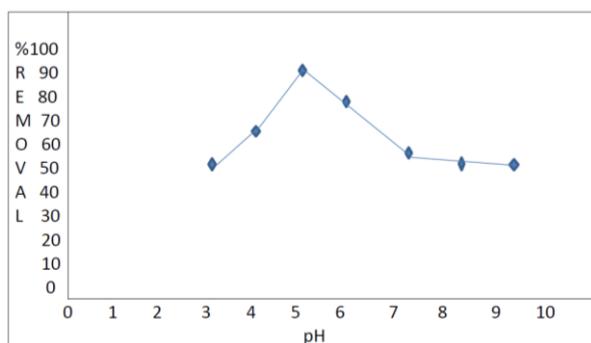


Figure 1: Effect of pH on adsorption of Cu(II).

Where M is the mass of adsorbent (g), V is the volume of the solution.

(L), Co is the initial concentration of metal (mg/L), Ce is the equilibrium metal concentration (mg/L) and qe is the metal quantity adsorbed at equilibrium (mg/g). Experiments were carried out at different initial pH values. The initial pH of the solution was adjusted with either HCl or NaOH. The percent removal of metals from the solution was calculated by the following equation.

$$\text{Percentage removal} = \left(\frac{Co - Ci}{Co} \right) \times 100 \quad \dots (2)$$

Where Co (mg/L) is the initial metal ion concentration and Ci (mg/L) is the final metal ion concentration in the solution.

A. COPPER 1. EFFECT OF pH

It is clear that pH influenced the removal efficiency of the copper ions in the aqueous solution. The results indicated that Cu (II) removal was increased to maximum and then decreased with pH variation from 4 to 9 at temperature 25^oC and agitation speed of 120 rpm. The maximum percentage removal of Cu (II) was about 89% (Figure:1) at pH 5. The dominant species of copper was free Cu(II) and was mainly involved in the adsorption process when the pH was lower than 5. When the pH greater than 5, copper ions started to precipitate as Cu(OH)₂.^[24] Increases in metal removal with increased pH can be explained on the basis of the decrease in competition between proton and metal cations for same functional groups and by decrease in positive surface charge, which results in a lower electrostatic repulsion between surface and metal ions. Decrease in adsorption at higher pH (>pH 5) is due to formation of soluble hydroxy complexes.^[25]

2. EFFECT OF CONTACT TIME

Figure:2 indicate that metal ions removal was increased with an increase in contact time before equilibrium was reached. All parameters such as dosage of adsorbent and pH of solution were kept constant. The results indicated that Cu (II) removal was increased from 15 to 89% with the contact time variation from 10 to 360 minutes. From 360 to 400 minutes, the percentage removal of Cu (II) remains constant (89%), which showed that equilibrium was reached at 360 minutes. Thus, the optimum contact time for maximum removal (89%) of Cu (II) was 360 minutes. This result is important because equilibrium

time is one of the important parameter for economical wastewater treatment system.

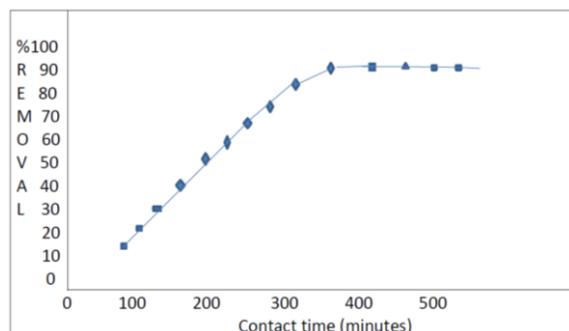


Figure 2: Effect of contact time on adsorption of Cu(II).

3. EFFECT OF ADSORBENT DOSE

Adsorption efficiency of Cu (II) adsorption was studied by varying the amount of adsorbents from 50 to 200 mg keeping other parameters (pH, and contact time) constant. The figure: 3 shows that percentage removal of the C(II) increases on increasing adsorbent dosages. This may occur due to the fact that the higher dose of

adsorbents in the solution provides the greater availability of active sites for the ions. The maximum percentage removal of Cu (II) was about 88% at the dosage of 200 mg. This result also suggest that after a certain dose of adsorbent, the equilibrium conditions reached and hence the amount of ions bound to the adsorbent and the amount of free ions in the solution remain constant even with further addition of the dose of adsorbent.

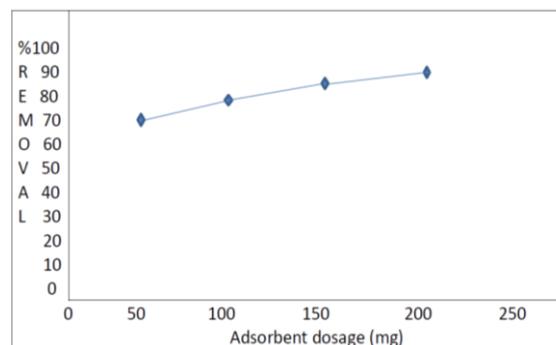


Figure 3: Effect of adsorbent dosage on adsorption of Cu(II).

Table 2: Effect of adsorbent dosage on Cu(II) adsorption at 25 °C, 120 rpm, at pH 5 and initial concentration 3.0 mg/L.

Amount Dosage(mg)	Final Conc(mg/L)	Cu(II) adsorbed (mg/L)	% Removal
50	0.83	2.17	72.33
100	0.73	2.27	75.67
150	0.41	2.59	86.33
200	0.36	2.64	88.00

4. EFFECT OF TEMPERATURE

The temperature dependence of the adsorption process is related with several thermodynamic parameters. The temperature showed the negative effect on adsorption of Cu(II) onto China clay. The temperature effect on removal of copper ion using China clay was studied within the range of 25 - 55°C. Other parameters such as dosage of adsorbent and pH of solution were kept constant. With increase in temperature from 25- 55°C the percentage removal of copper ions was decreased from 83.3% to 75.37%. It is clear that the low temperature favors copper ion removal (Figure:4). This may be due to a tendency for the Cu(II) ions to escape from the solid phase to the bulk phase with an increase in temperature of the solution. The result shows that adsorption mechanism related with removal of Copper is physical in nature. The adsorption process takes place from the electrostatic interaction, which is in

general related with low adsorption heat. This implies that the adsorption process was exothermic in nature.

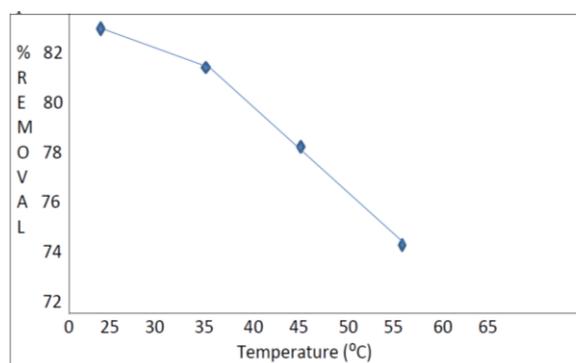


Figure 4: Effect of temperature on adsorption of Cu(II).

Table 3: Effect of temperature on Cu(II) adsorption at 25°C, 120 rpm, at pH 5, 50mg adsorption dosage and initial concentration 3.0 mg/L.

Temperature(°C)	Final Conc(mg/L)	Cu(II) adsorbed(mg/L)	% Removal
25	0.50	2.50	83.33
35	0.55	2.45	81.67
45	0.66	2.34	78.00
55	0.74	2.26	75.33

5. EFFECT OF INITIAL METAL ION CONCENTRATION

The effect of initial copper concentration on the copper adsorption rate was studied in the range (3 – 100mg/L) at pH 5, temperature 25°C, and 360 min contact time. It was observed that the percentage of removal decreased with increasing initial copper concentration (Figure:5). The poorer uptake at higher metal concentration was resulted due to the increased ratio of initial number of

moles of copper to the vacant sites available. For a given adsorbent dose the total number of adsorbent sites available was fixed thus adsorbing almost the equal amount of adsorbate, which resulting decrease in the removal of adsorbate, consequent to increase in initial copper concentration. Therefore, it was evident from the results that copper adsorption was dependent on the initial metal concentration.

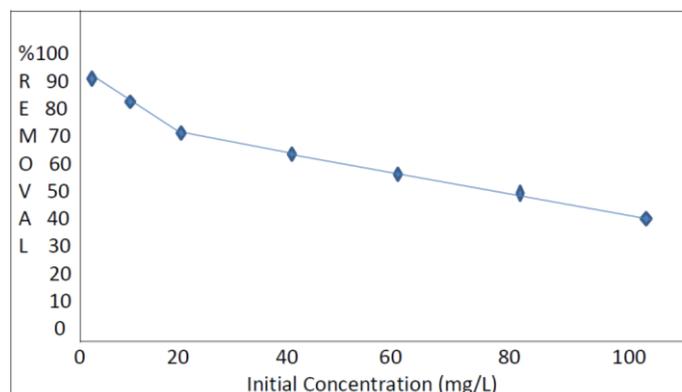


Figure-5: Effect of initial concentration on adsorption of Cu(II).

B. ZINC

1. EFFECT OF pH

It was observed that pH obviously influenced the percentage removal of zinc ions in the aqueous solution (Figure :6). The results indicated that Zn (II) removal was increased to maximum and then decreased with pH variation from 5 to 9 at temperature 25°C and agitation speed of 120rpm. The maximum percentage removal of Zn (II) was about 94.67% at pH 7. The dominant species of zinc was free Zn(II) and was mainly

involved in the adsorption process when the pH was lower than 7. When the pH greater than 7, zinc ions started to precipitate as $Zn(OH)_2$.^[26] Increase of metal removal with increased pH can be explained on the basis of the decrease in competition between proton and metal cations for same functional groups and by decrease in positive surface charge, which results in a lower electrostatic repulsion between surface and metal ions. Decrease in adsorption at higher pH (>pH 7) is due to formation of soluble hydroxy complexes.^[25]

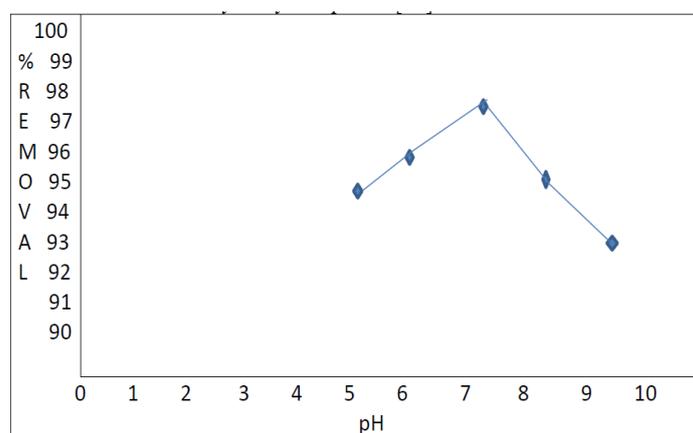


Figure 6: Effect of pH on adsorption of Zn(II).

Table 4: Effect of pH on Zn(II) adsorption at 25°C, 120 rpm and initial concentration 3.0 mg/L.

pH	Final Conc (mg/L)	Zn(II) adsorbed (mg/L)	% Removal
5	0.16	2.84	94.67
6	0.13	2.87	95.67
7	0.08	2.92	97.33
8	0.14	2.86	95.33
9	0.15	2.85	95.00

2. EFFECT OF CONTACT TIME

The effect of contact time on zinc adsorption process was determined by conducting adsorption experiments at different contact time between the adsorbate and adsorbent in the range of 10–180 minutes. The concentration of metal ions was 3mg/L, at constant pH 7.0 and temperature 25°C, while the amount of adsorbent added was 50 mg. The rate of percentage removal of zinc

was higher at beginning (figure:7). This may be due to the larger surface area of the adsorbent being available at beginning for the adsorption of zinc ions. Equilibrium was established after 180 minutes indicating that the adsorption sites are well exposed.^[27] All the batch adsorption experiments were conducted with a contact time of 10-180 minutes.

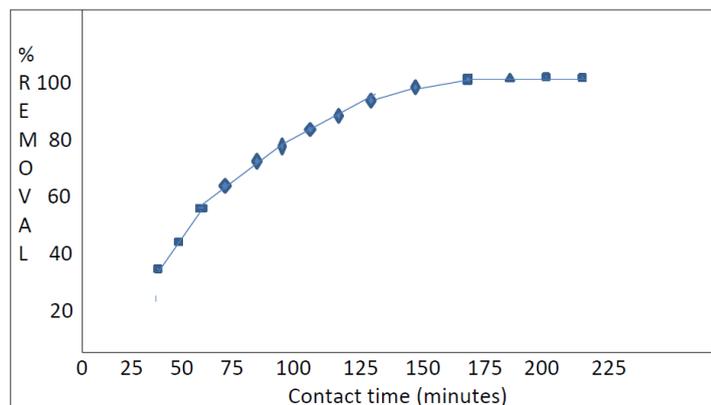


Figure 7: Effect of contact time on adsorption of Zn(II).

3. EFFECT OF ADSORBENT DOSE

Adsorption efficiency of Zn (II) adsorption was studied by varying the amount of adsorbents from 50 to 250 mg keeping other parameters (pH, and contact time) constant. It shows that removal efficiency of the zinc usually improved on increasing adsorbent doses (Figure:8). This may occur due to the fact that the higher dose of adsorbents in the solution provides the greater availability of exchangeable sites for the ions. It is also

clear that no further increase in adsorption after a certain amount of adsorbent. The maximum percentage removal of Zn (II) was about 95.67% at the dosage of 200 mg. After a certain dose of adsorbent, the equilibrium conditions reached and hence the amount of ions bound to the adsorbent and the amount of free ions in the solution remain constant even with further addition of the dose of adsorbent.

Table 5: Effect of adsorbent dosage on Zn(II) adsorption at 25°C, 120 rpm, at pH 7 and initial concentration 3.0 mg/L.

Amount Dosage(mg)	Final Conc(mg/L)	Zn(II) adsorbed(mg/L)	% Removal
50	0.26	2.74	91.33
100	0.18	2.82	94.00
150	0.17	2.83	94.33
200	0.14	2.86	95.33
250	0.13	2.87	95.67

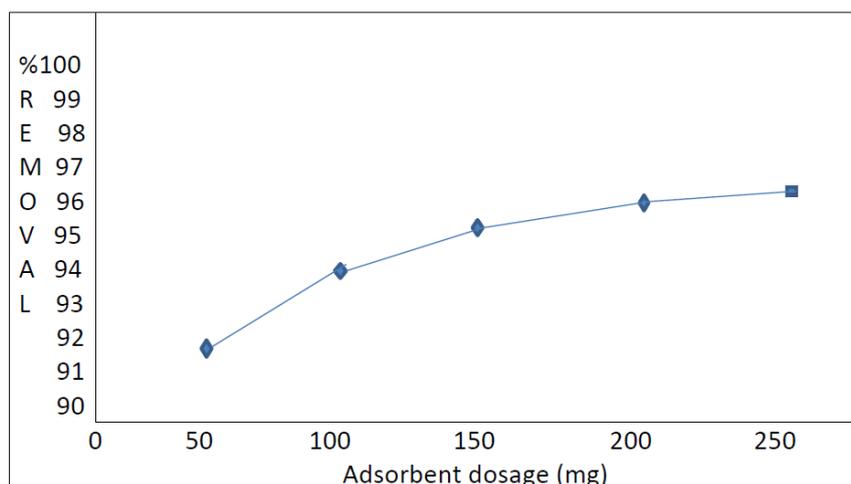


Figure 8: Effect of adsorbent dosage on adsorption of Zn(II).

4. EFFECT OF TEMPERATURE

The temperature dependence of the adsorption process is related with several thermodynamic parameters. The temperature showed the negative effect on adsorption of zinc onto China clay. The temperature effect on removal of zinc ion using China clay was studied within the range of 25 - 40°C. Other parameters such as dose of adsorbent and pH of solution were kept constant. With increase in temperature from 25- 40°C the percentage removal of zinc ions was decreased from 93.67% to 72%.

It is clear that the low temperatures are in favors of zinc ion removal (Figure: 9). This may be due to a tendency for zinc ions to escape from the solid phase to the bulk phase with an increase in temperature of the solution. The result shows that adsorption mechanism related with removal of zinc is physical in nature. The adsorption process takes place from the electrostatic interaction, which is in general related with low adsorption heat. This indicates that the adsorption process was exothermic in nature.

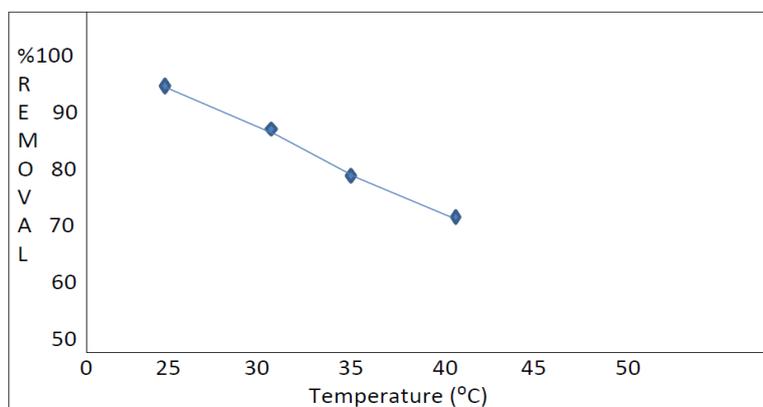


Figure 9: Effect of temperature on adsorption of Zn(II).

Table 6: Effect of temperature on Zn(II) adsorption at 25°C, 120 rpm, at pH 7, 50mg adsorption dosage and initial concentration 3.0 mg/L.

Temperature(°C)	Final Conc(mg/L)	Zn(II) adsorbed(mg/L)	% Removal
25	0.19	2.81	93.67
30	0.49	2.51	83.67
35	0.63	2.37	79.00
40	0.84	2.16	72.00

5. EFFECT OF INITIAL METAL ION CONCENTRATION

The effect of initial Zinc concentration on the copper adsorption rate was studied in the range (10-100mg/L) at pH 7, temperature 25°C, and 180 min contact time. It was observed that the percentage of removal decreased with increasing in initial zinc concentration (Figure:10). The poorer uptake at higher metal concentration was resulted due to the increased ratio of initial number of

moles of zinc to the vacant sites available. For a given adsorbent dose the total number of adsorbent sites available was fixed thus adsorbing almost the equal amount of adsorbate, which resulting in a decrease in the removal of adsorbate, consequent to an increase in initial zinc concentration. Therefore it was evident from the results that zinc adsorption was dependent on the initial metal concentration.

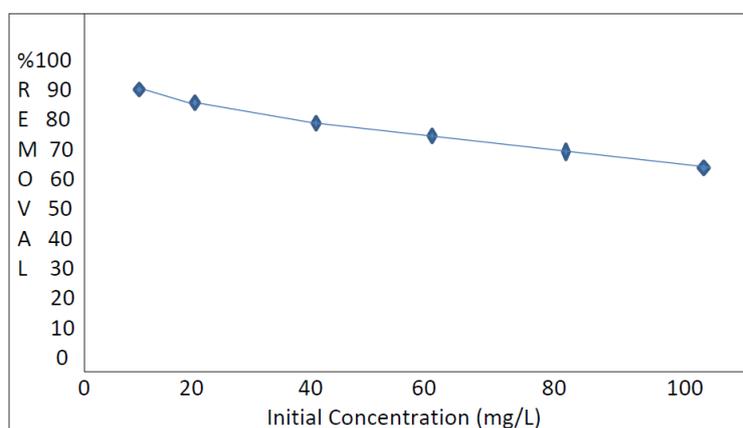


Figure 10: Effect of initial concentration on adsorption of Zn(II).

CONCLUSIONS

The present investigation is carried out to study the suitability of a novel indigenous adsorbent, China clay for the removal of heavy metal such as copper and zinc from the wastewater. Influence of process parameters such as pH, adsorbent dosage, temperature, contact time, initial metal ion concentration were at moderate levels such that they can affect the removal efficiencies of the heavy metals were concerned. The optimum pH of solution for Cu and Zn removal were found to be 5 and 7 respectively. Within the scope of the experimental investigation the optimum temperature was found to be 25°C. The optimum time for adsorption of zinc and copper was found to be 180 min and 360 min respectively. Initial metal ion concentration showed the negative effect on adsorption efficiency i.e. at lower levels the adsorption was higher.

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