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DIFFERENT PARAMETERS FOR THE REMOVAL OF CU (II) AND CD (II) IONS FROM WATER AND WASTEWATER BY BATCH ADSORPTION PROCESS ON RED MUD AS LOW COST ADSORBENT.

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ABSTRACT
In the present study, adsorption effect of Red Mud on Cu (II) and Cd (II) removal from water and wastewater was examined. Characterization of the adsorbent was done using Perkin Elmer Spectrophotometer, Model 783 and 621 in the range of 4000-200 cm^{-1}. To obtain the optimized adsorption conditions, many parameters were studied as pH, agitation time, dosage of adsorbent, initial concentration of adsorbate, temperature and finally speed of rotation. pH = 6 was chosen as an optimum pH value for Cu (II) adsorption while pH = 5 was the optimum pH value for Cd (II) adsorption.

KEYWORDS: Red Mud as adsorbent; Cu (II) and Cd (II) removal.

1. INTRODUCTION
The growth of industrial technology is one of the main reasons of pollution rising, that's why many techniques were developed to minimize such dangerous pollutants and avoid their hazardous effects whether on human, animals or plants. Toxic heavy metals cause a serious health hazards in case that their concentrations exceeded the permissible limit. Even if the metals concentrations do not increase the permissible limits, there is a possibility of long-term heavy metals contamination where they accumulate within biological systems[1] Copper has two valences: cuprous, Cu (I) and cupric, Cu (II). Cu (II) is the most common species of special concern in aqueous solution.[2] Copper is introduced into in environment, water from brass manufacture, copper mining, electroplating industries, smelting operations and excessive use of Cu-based agricultural chemicals.[3] Beyond permissible limit, copper causes gastrointestinal problems, various diseases and disorders; it can cause fatigue, headache, insomnia, skin rashes, liver damage, depression, genetic disorders as Wilson's disease, learning disorders and copper may accumulate in each organ of the body (brain, heart, kidneys, pancreas and skin).[4,5] There is a direct link between inhalation of copper-containing spray by workers and spread of lung cancer between them which refers to the carcinogenicity of copper.[6]

Cadmium is of major concern because of its non-degradable nature and its frequent handling in developing countries.[1] Cadmium pollution arises from smelting, e-waste, waste batteries, paint sludge, incineration and fuel combustion.[7] Despite the importance of cadmium in industries as metal plating, Ni–Cd rechargeable batteries, manufacture of phosphate fertilizers , mining, stabilizers, pesticides, pigments, plastics, dyes and textile operations and alloy industries, excess cadmium can affect badly on human health and It causes many acute and chronic disorders as: emphysema, "itai–itai" disease, renal dysfunction, liver damage, destruction of red blood cells, bone degeneration, hypertension and atrophy of testes.[1,3,8,9] In addition, cadmium is carcinogenic, cause lung fibrosis, dyspnea.[10] Hence, Cu (II) and Cd (II) removal from water and wastewater is of a great interest for scientists. Several treatment techniques have been vastly used to remediate industrial effluents by removing the toxic heavy metals such as chemical precipitation, complexation, ion exchange, evaporation, solvent extraction, membrane filtration, oxidation/reduction processes, electro dialysis, reverse osmosis, coagulation and biological treatment[11, 12] whilst these techniques could be high-cost, ineffective specifically at low concentrations of the heavy metal ions that exist in the wastewater and require sensitive operating conditions which restrict their applicability in industry.[11,13,14]

Comparing to the other purification techniques, adsorption is one of the most economical, effective and thrifty technique which has been used worldwide for the removal of heavy metals from aqueous solution and wastewater and in many industrial applications.

Adsorption method has various advantages over other methods as following.
1) The low generation of residues,
2) Simple and easy metal recovery,
3) It produces a high-quality treated effluent suitable for reuse,
4) Both of design and operation processes are simple and flexible,
5) Since adsorption is sometimes reversible, so the adsorbent regeneration is possible and
6) Adsorbent materials are abundant in nature. It is just required choosing the appropriate adsorbents under optimum operation conditions with a minimal processing to decrease the cost.[15-21]

Industrial waste materials are considered effective adsorbents for toxic heavy metal removal because of the presence of functional groups that exist in their main components which facilitate the metal binding and it forms chelates or metal complexes. Also, they are eco-friendly, cheap, available in abundance, renewable. The industrial waste materials can be used as it is in the natural form (without modification) for the removal of metal ions or after physical or chemical treatment.[12,13]

2. MATERIALS AND METHODS

2.1. Instrumentation

The pH values for all the experiments were determined by Jenway 3510 pH Meter which has been calibrated before using with pH 4, 7 and 10 buffer solutions. Batch adsorption experiments were carried out with a stoppered pyrex glass flask that contains 100 mL of metal single-component solutions to examine Cu(II) and Cd(II) adsorption onto Red Mud. Both of the initial concentration and the residual heavy metal ion content were determined by Thermo Scientific atomic absorption spectrophotometer (AAS).

2.2. Adsorbent Preparation

Red Mud is a waste product obtained from aluminium industries. It has been used in the manufacture of different types of ceramic products since long time. Production of bricks[22-24] thermal insulators[25], acoustic tiles[26], corrosion inhibition primer[27], heavy clay products[28] and additive for concrete and mortar[24] are prepared from it. Red Mud has been used as desulphurising agent for the removal of hydrogen sulphide and industrial gases.[29-30] It has also been found useful for wastewater treatment.[31-34] Recently, it has been used as a cheap adsorbent for the removal of organic substances like 1- butanethiol from kerosene oil.[35] Red Mud was obtained from Hindustan Aluminium Corporation, Mirzapur, U.P (INDIA). The sample was subjected to repeated washing to remove free alkalis, heated in oven, cooled at room temperature and passed through 53µm pore size sieve. The Chemical analysis of Red Mud was given below.

Table1: Chemical analysis of Red Mud as Adsorbent

Constituents	Percentage by weight
Fe_2O_3	39.45
Al_2O_3	22.65
TiO_2	13.80
SiO_2	8.55
CaO	5.20
Loss of ignition	10.25
Particle size	53 µm
Mean Particle size diameter	$48x10^{-4}$ cm
Surface area	10.27 $m^2 g^{-1}$
Porosity	0.197
Density	2.632 gcm^{-3}

The Infra-red spectrum of adsorbent was recorded in KBr and nujol null using Perkin Elmer Spectrophotometer, Model 783 and 621 in the range of 4000-200 cm^{-1}.

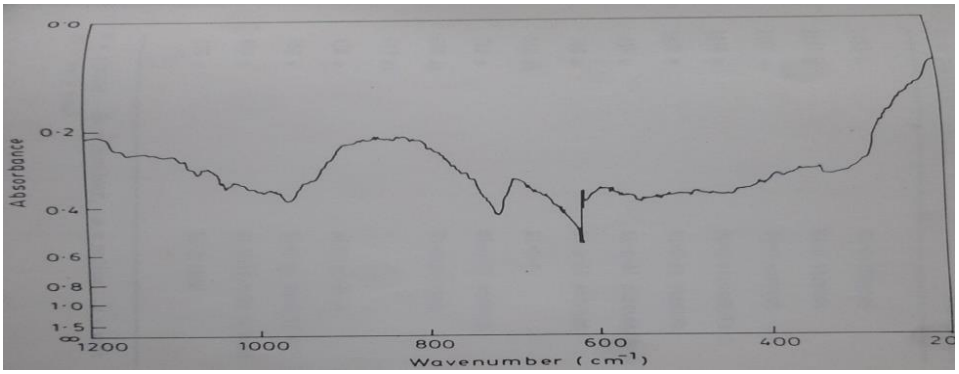

Figure 1: Infra-red spectrum of Red Mud.

2.3. Experimental Method

Aqueous solutions of copper and cadmium were prepared by using analytical grade of copper sulphate pentahydrate ($CuSO_4 . 5H_2 O$) and cadmium nitrate tetrahydrate ($Cd(NO_3)_2 \cdot 4H_2 O$) (obtained Merck, Germany). The solutions of Cu(II) and Cd(II) were prepared from stock solutions containing 1000 mg/L of Cu(II) and Cd(II), respectively by dissolving the desired amount of ($CuSO_4 . 5H_2 O$) or ($Cd(NO_3)_2 \cdot 4H_2 O$) in 500 mL of distilled water. Preparing the desired various concentrations of solutions were done by suitable dilution from the stock solution. Before the adsorbent is exposed to the metal solutions, pH values of a range: 2 to 6 are adjusted by micro-additions of (0.1N NaOH or HCl) to determine the optimum pH value for adsorption. After choosing the optimal pH for each metal adsorption, only this pH value was applied in any further adsorption tests. Blank solutions containing no Cu (II) or Cd (II) were used for each series of adsorption trials. The reported value of metal ions into 500 mL conical flask at 200 rpm for four hours at 50^0 C.

To determine adsorption capacity, the following expression was used.

$$qe = (Co - Ce)\, V/W \qquad (1)$$

Where qe (mg/g): adsorbed amount of the copper or cadmium metals per unit mass of adsorbent, Co (mg/L): the initial heavy metal concentration and Ce (mg/L): the heavy metal ion concentration at equilibrium, V (L) represents the adsorbate volume and W (g) is the adsorbent mass.

The removal percentage (%R) of Cu (II) or Cd (II) ions was determined by applying the equation.

$$\% R = (Co - Ct) \times 100/ Co \qquad (2)$$

Where Ct (mg/L): the concentration of single metal ion at a given time t (minute).

3. RESULTS AND DISCUSSION

3.1 Effect of time

The percent removal of copper (II) and cadmium (II) ions by adsorbent (1.0 g) was loaded into 100 ml of 30 mg/L of metal solution and then shaken for 60 minutes at pH 6.0 for Cu (II) ions and pH 5.0 for Cd (II) ions solution. As shown in Figs 1 & 2, the removal percentage of Cu (II) and Cd (II) ions by adsorbent was 79.50 and 78.80%, respectively.

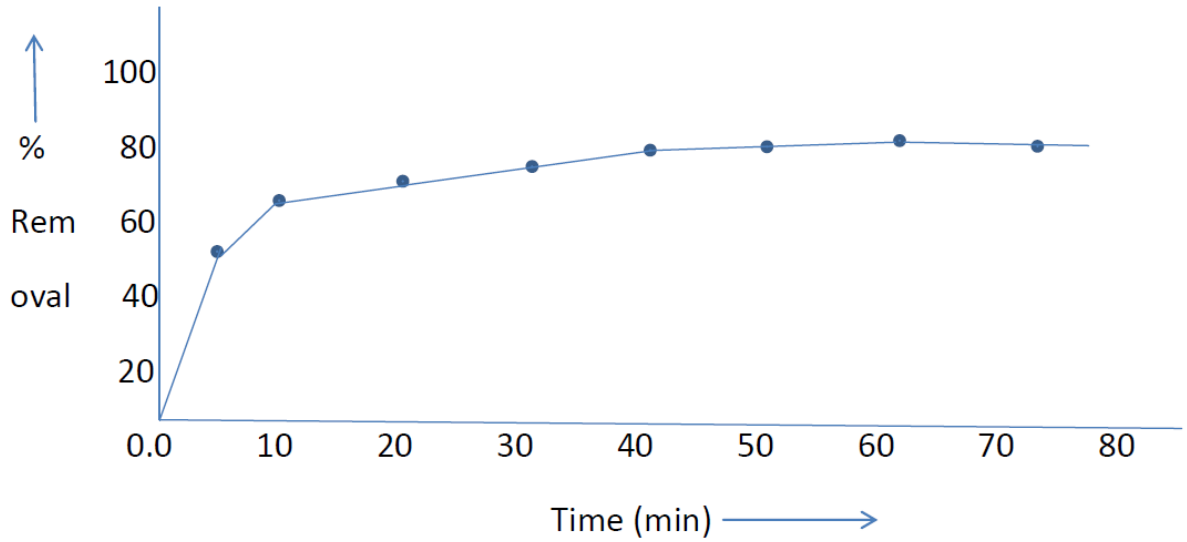

Figure 1: Percentage removal of Cu (II) ions on Red Mud against Time (temperature: 298 K, agitation speed: 300 rpm, initial concentration: 30 mg/L, 1.0 g of adsorbent and pH: 6 for 60 minutes).

3.2 Effect of pH

The variation in pH values in the adsorption process has a double effect.

(i) it influences the charge of the adsorbent surface, and
(ii) it affects the adsorbate speciation and its degree of ionization.[36]

The effect of pH on the adsorption efficiency of Red Mud for the removal of Cu (II) and Cd (II) ions was performed by mixing the suitable dose of adsorbent (1.0 g) with 100 mL of 30 mg/L concentration of metal ions solution. Figure 3 shows the effect of pH variation on percentage removal of Cu (II) and Cd (II) ions on adsorbent surface. The percentage removal of Cu (II) ions at equilibrium increased from 4.70% to 88.70% with increasing pH from 2 to 6 while there is severe increase in the Cd (II) removal from 11.10% to 94.60% at equilibrium upon rising the pH values from 2 to 5 then the percentage removal decreased to 91.40% at pH 6.As shown in Figure 4, the effect of pH variation on adsorption capacity of Cu (II) and Cd (II) ions respectively. The adsorption capacity at equilibrium (qe) of Cu (II) ions increased from 1.40 to 26.70 mg/g with increasing pH from 2 to 6 whereas for Cd (II) ions the qe values increased from 3.32 to 28.60 mg/g as pH values increased from 2 to 5 then the qe value decreased to 28.50 mg/g at pH 6.

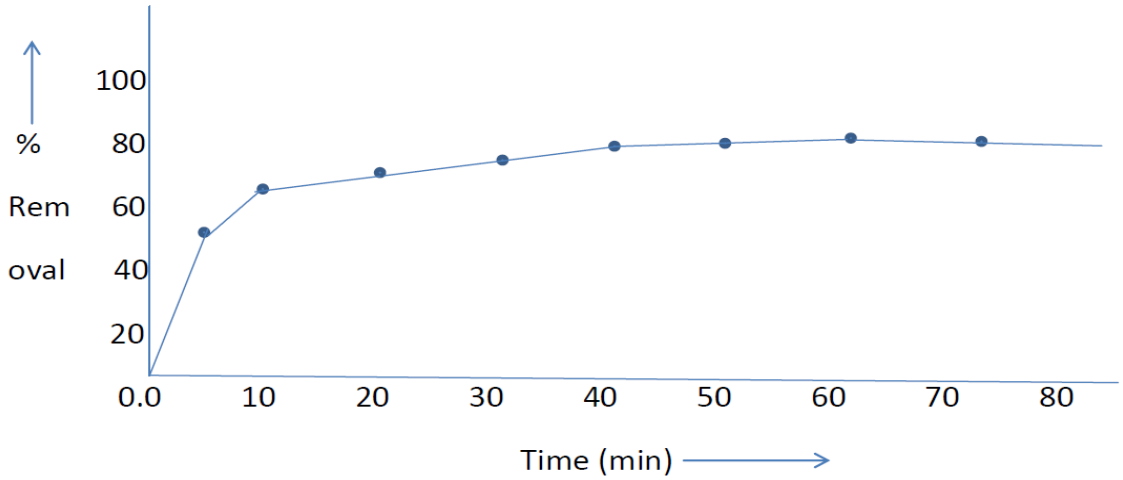

Figure 2: Percentage removal of Cd (II) ions on Red Mud against Time (temperature: 298 K, agitation speed: 300 rpm, initial concentration: 30 mg/L, 1.0 g of adsorbent and pH: 6 for 60 minutes).

In case of Cu (II) ions, If the pH value increased above pH 6 precipitation occurs and this restrains the adsorption process due to the partial hydrolysis of copper ions and as a result the insoluble $Cu(OH)_2$ precipitate is formed.[37] In the same way, Cd (II) ions precipitate at high pH as $Cd(OH)_2$ because of rising the OH– concentration in the solution. That's why, pH 6 was selected as an optimum pH value for Cu (II) adsorption while it was pH 5 in case of Cd (II) adsorption.

There are three main reasons for the low efficiency of heavy metals removal at a low pH.

(i) The H+ ions are existed in high concentration in the solution and thus a competition is engendered between them and the metal ions for the binding sites of adsorbent.[38]

(ii) because of protonation, the positive charge is spread on adsorbent surface. Subsequently, an electrostatic repulsion arises between the charged adsorbent surface and Cu(II) or Cd(II) ions in solution; the adsorption becomes undesirable.[12]

(iii) Adjusting the solution pH by using HCl lead to presence of Cl species in solution which form $CuCl^+$ and $CdCl^+$ complex with a relatively large molecular size if it is compared to that of the free metal ions and this may frustrate the adsorption, resulting decrease in metal uptake. But on the other side, this is considered a very limited effect.[12] In contrast; the hydronium ion concentration is diminished when the pH value is increased and this lead to de-protonation of adsorbent surface. Thereafter, Cu (II) or Cd (II) ions uptake is increased.[39]

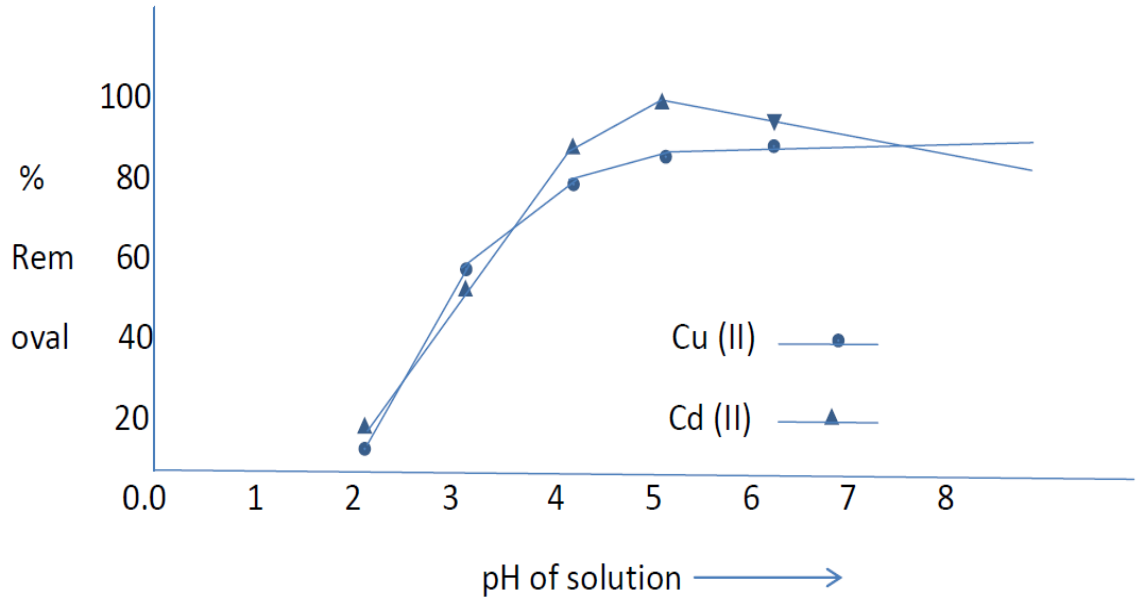

Figure: 3. *pH* variation effect on Cu (II) and Cd (II) ions removal (temperature: 298 K, agitation speed: 300 rpm, initial concentration: 30 mg/L and 1.0 g of adsorbent).

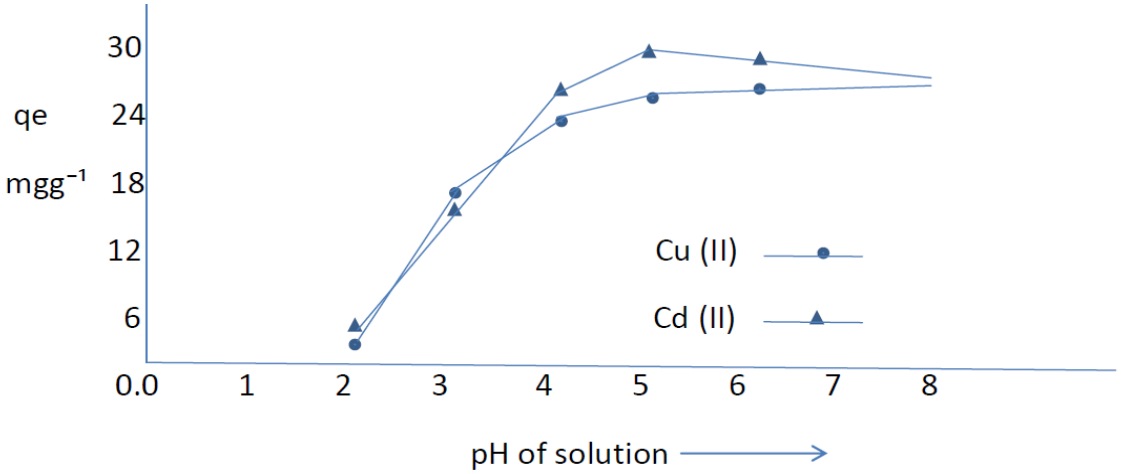

Figure 4: *pH* variation effect on Cu(II) and Cd(II) ions adsorption capacity at equilibrium on adsorbent (temperature: 298 K, agitation speed: 300 rpm, initial concentration: 30 mg/L and 1.0 g of adsorbent).

3.3. Effect of agitation time

Agitation time is one of the most important factors that affect the adsorption process. The percentage removal of copper and cadmium ions is determined by changing the agitation time between the adsorbate and adsorbent. For copper ions solution, the optimum pH was 6 while for cadmium ions solution, the optimum pH was 5. The effect of agitation time (1, 3, 5, 7, 10, 15, 20, 30, 45 and 60 minutes) on the percentage removal of adsorbent for both of Cu (II) and a Cd (II) ion with an applied dose of adsorbent (1.0 g /100 ml metal solution) is shown in Figure 5.

A two-phase behavior was noticed: the first rapid adsorption phase which is followed by a next phase of slow adsorption. The fast increase in percentage removal of metal ions at the beginning occurred where the binding active sites of adsorbent surface rapidly chelate Cu (II) or Cd (II) ions. The occurrence of a second phase of low adsorption until saturation process is verified can be interpreted by saturation of the adsorbent pores at the former phase of adsorption where the adsorbate (copper or cadmium ions) are attached on the adsorbent surface. So, the numbers of metal ions that may be adsorbed on the surface become limited where the solute diffuses slowly into the interior of the adsorbent.[40] Also, the remaining vacant surface sites are difficult to be filled with metal ions where a repulsive force is engendered between the metal ions which have been already adsorbed on adsorbent surface and the residual metal ions in the liquid phase which have not been adsorbed yet.[41] For Red Mud adsorbent, fifteen minutes only was enough to fulfill the equilibrium; after which, no noticeable change happened until sixty minutes (Figure: 5). Nevertheless, an agitation time of thirty minutes was chosen for the later experiments. It was noted that, at equilibrium the elimination percentage of copper ions onto adsorbent reached 88.70% while the elimination percentage of cadmium ions reached 94.57%. This result showed the selectivity of adsorbent (suggested a stronger affinity of adsorbent towards cadmium than of copper) and this is because of the variance in molecular weight, size and the ionic radius of the heavy metals used.[42-43] In the present study, It does not take a long contact time to achieve equilibrium which refers to a fast adsorption rate of Cu (II) and Cd (II) ions onto adsorbent.

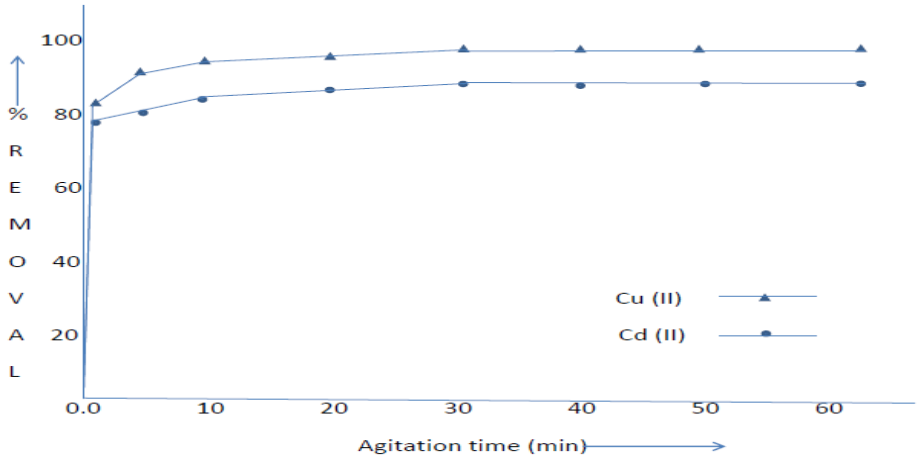

Figure 5: Effect of agitation time on the percent removal of Cu (II) and Cd (II) ions adsorbent (temperature: 298 K, agitation speed: 300 rpm, initial concentration: 30 mg/L and 1.0 g of adsorbent for 60 minutes).

3.4. Effect of adsorbent dosage

The effect of adsorbent dosage on percentage removal of Cu (II) and Cd (II) ions was investigated using different doses at optimum pH using 100 mL solution of 30 mg/L metal ions concentration. As shown in Figures 6 & 7: In case of Cu (II) ions: upon increasing the adsorbent dose from 0.5 to 4.0 g and until 10.0 g, the percentage removal of copper ions rose from 85.54 to 100.0%. In case of Cd(II) ions: results show complete removal of cadmium ions from solution through the experiments with the increase in adsorbent dose from 0.5 to 2.0 g and until 10.0 g, no noticed change occurred where the percentage removal of cadmium ions rose from 91.26 to 100%.

It is reasonable to assume that the higher the absorbent dosage, the greater the percent removal of heavy metal ions where the adsorbent surface area will increase and thus more available binding sites on the surface are ready for heavy metals ions chelating.[44]

However, *qe* values (mg/g) for both of Cu (II) and Cd (II) ions diminished progressively upon increasing the adsorbent dose as shown in Figures 6 & 7. For Cu (II) ions, *qe* value decreased from (51.67 mg/g at 0.5 g) to (2.996 mg/g at 10.0 g) and for Cd (II) ions, the *qe* value decreased from (58.79 mg/g at 0.5 g) to (3.025 mg/g at 10.0 g). This occurred due to the accretion in number of unsaturated binding active sites which are ready for adsorption with the adsorbent dose increment so the number of metal ions in solution became insufficient with respect to the available binding sites.[45] Also, increasing the adsorbent mass upon a certain limit causes aggregation of adsorbent particles and as a result, the adsorbent total surface area exposed to adsorption process decreases and the diffusion path length increases.[12]

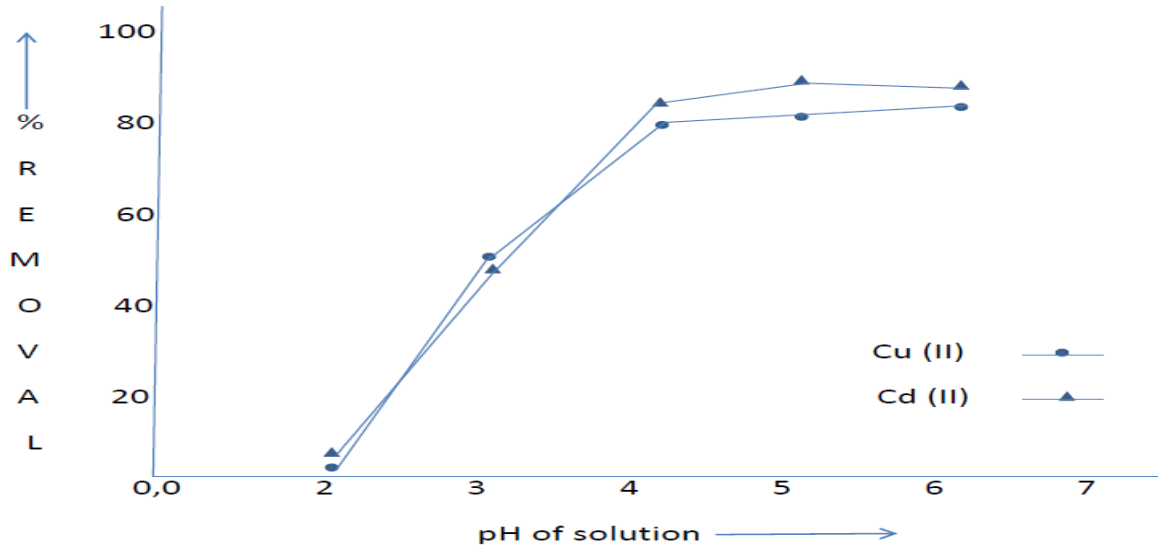

Figure 6: pH variation effect on Cu (II) and Cd (II) ions removal onto adsorbent (temperature: 298 K, agitation speed: 300rpm, initial concentration: 30 mg/L and 1 g of adsorbent).

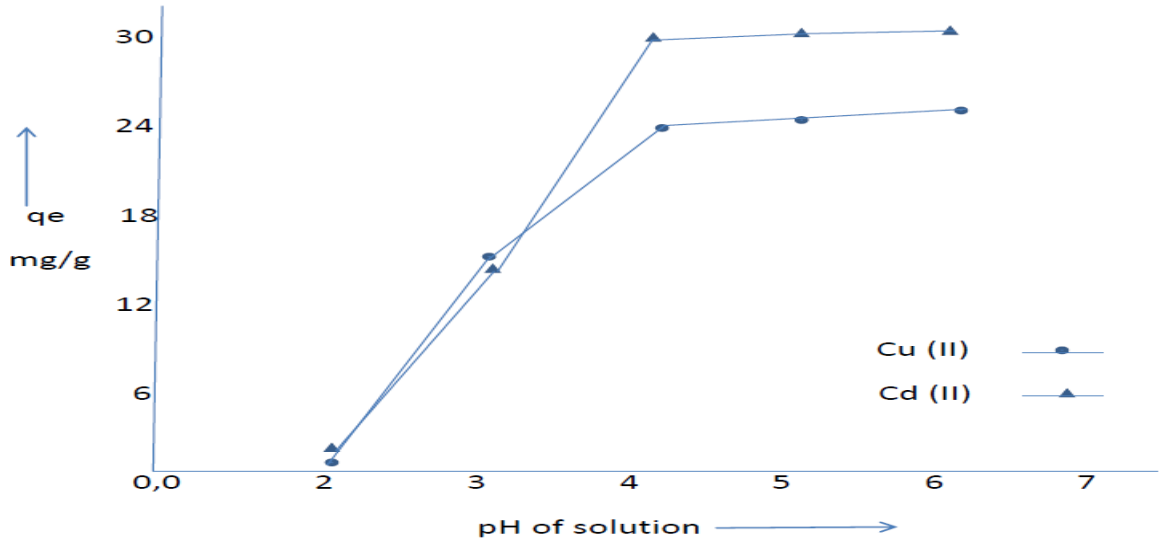

Figure 7: pH variation effect on Cu (II) and Cd (II) ions adsorption capacity at equilibrium onto adsorbent (temperature: 298 K, agitation speed: 300 rpm, initial concentration: 30 mg/L and 1 g of adsorbent).

3.5 Effect of temperature

Temperature is directly related to the kinetic energy of the metal ions in the solution. Any change in temperature subsequently results in a change in the diffusion rate of adsorbate. In addition, the change in temperature will affect the *qe* value of the adsorbent for a specific adsorbate. The adsorption of both of Cu (II) ions and Cd (II) ions on adsorbent was examined at 298,303, 308 and 313 K.

As presented in Figures 8 & 9, the temperature had a dramatic effect on the adsorption process where the percentage removal and *qe* values for both of Cu (II) and Cd(II) ions increased until reaching maximum then decreased. Upon rising the temperature from 298 K to 303 K , Percentage removal increased from 89.10 to 95.34 % in case of Cu(II) ions adsorption while it increased from 95.32 to 99.95 % in case of Cd(II) ions. Increasing the temperature above 303 K and up to 313K caused a gradual decrease in percentage removal to be 80.50 % and 91.15 % for Cu(II) and Cd(II) ions respectively at 313 K. In the same way, *qe* value of Cu(II) ions adsorption onto adsorbent increased from 26.80 mg/g at 298 K to be 28.95 mg/g at 303 K followed by gradual decreasing to be 24.15 mg/g at 313 K and *qe* value of Cd(II) ions onto adsorbent increased from 28.80 mg/g at 298 K to be 30.20 mg/g at 303 K then decreased until it became 26.98 mg/g at 313 K. This behavior refers that the process is dominated by the interactive forces between the adsorbent and the adsorbate metal ions.[46] The results indicate that chemisorption occurred where the rate of adsorption first increased then decreased with the increase of temperature.[47] Thus, it is inconvenient for the adsorption process to apply high temperature. The decrease of adsorption when the temperature is risen above 303 K was due to: degradation of the adsorbent. Where the bond rupture is occurred at elevated temperature and there is a possibility that some of the surface active sites are damaged which in turn decreases the material adsorption capacity or even desorption process becomes more favored than the adsorption process.[48-49] This change in adsorbent structure results in what is known as "material deterioration".[50] In addition, increasing the temperature makes the boundary layer thickness to be decreased and this is due to the increased tendency of earlier adsorbed copper and cadmium ions to be desorbed from the adsorbent surface to the solution phase again which affect inversely on adsorption pathway.[51] Li Q et al.[52] used peanut husk for removing Pb (II), Cr (III) and Cu (II) from aqueous solution and studying the temperature effect on adsorption revealed that: as the temperature increased from 10^0 C to 60^0 C, the adsorption removal rose at the beginning and then came down. Similar results were obtained by Mohanty S et al.[53] who reported that the adsorption percentage of Cr (VI) ions onto coconut shell activated carbon increased to reach maximum at 30^0 C but it is gradually decreased with increase in temperature up to 50^0 C.

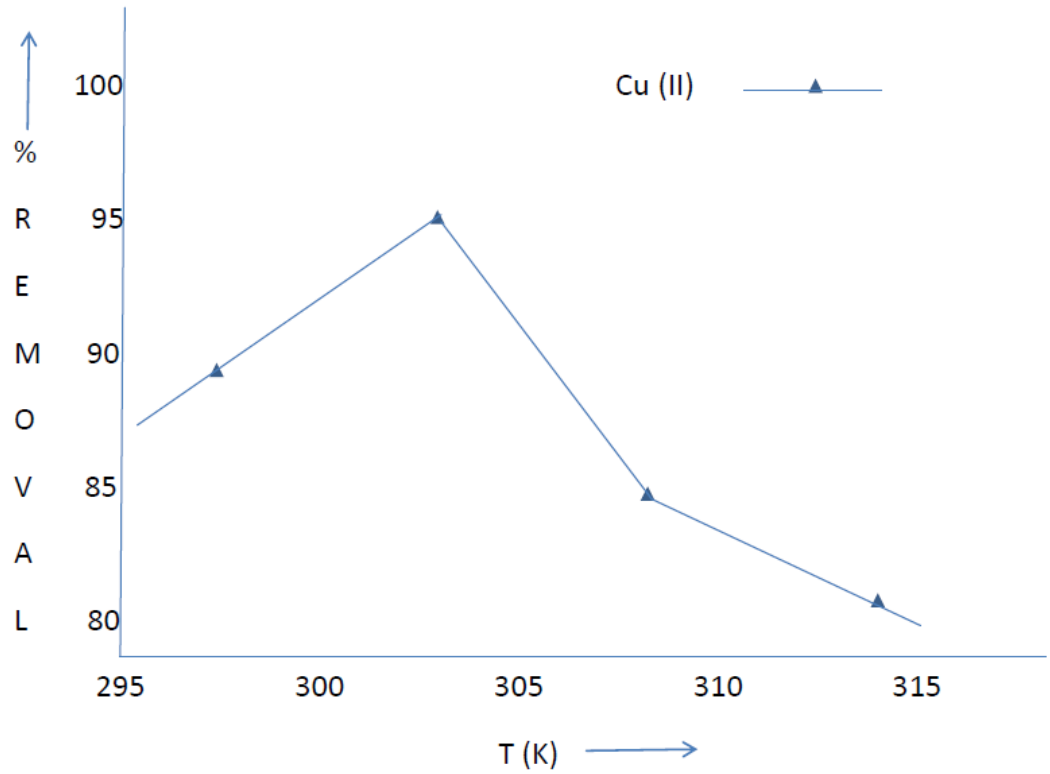

Figure 8: Temperature effect on the percentage removal of Cu(II) ions agitation speed: 300 rpm, initial concentration: 30 mg/L, 1.0 g of adsorbent and pH: 6 for 30 minutes.

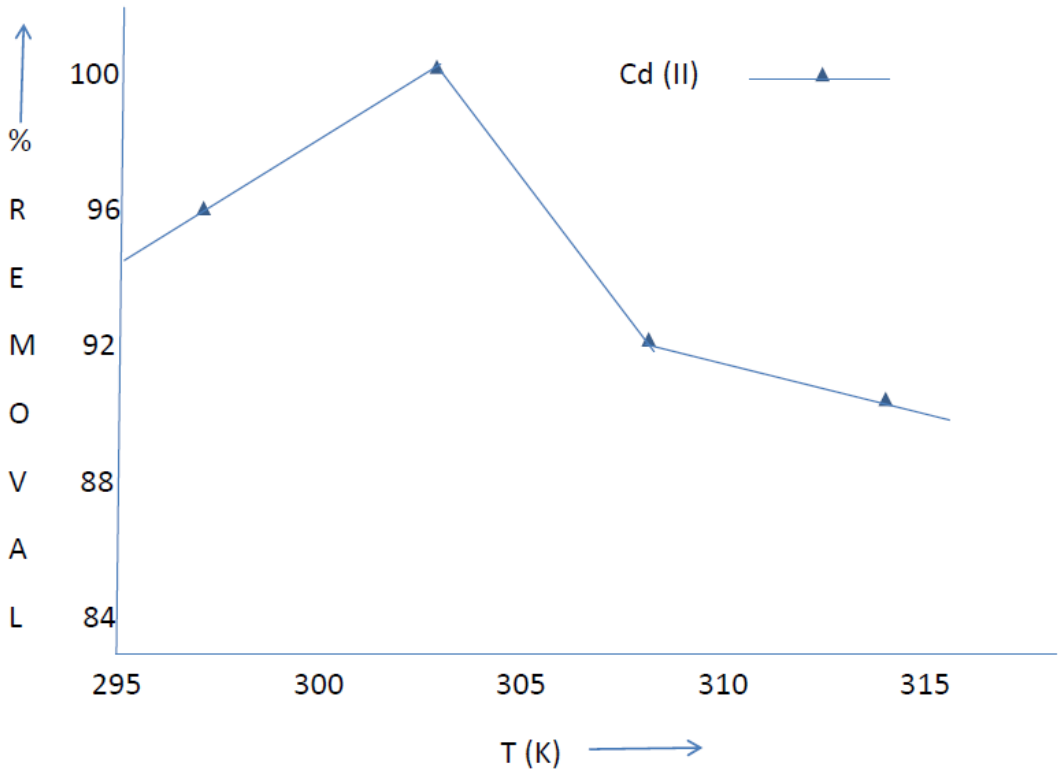

Figure 9: Temperature effect on the percentage removal of Cd(II) ions agitation speed: 300 rpm, initial concentration: 30 mg/L, 1.0 g of adsorbent and pH: 5 for 30 minutes.

3.6. Effect of rotation speed

The effect of different rotation speeds (100, 200, 300, 400 and 500 rpm) on adsorption of both of copper and cadmium ions onto adsorbent was studied using 100 ml solution containing 30 mg/L of metal ions. Figures 10 & 11 refer that upon increasing the rotation speed, the percent removal and *qe* values of adsorbent increased until a certain point (300 rpm) then decreased. For Cu (II) ions, % removal increased from 84.95 to be maximum of 88.70% upon raising the rotation speed from 100 to 300 rpm and *qe* increased from 25.70 to 26.70 mg/g. However, promoting the rotation speed more than 300 rpm decreases the Cu (II) ions percent removal and adsorption capacity at equilibrium where percentage removal and *qe* decreased from 88.70% and 26.70 mg/g at 300 rpm to 84.20% and 25.35 mg/g respectively at 500 rpm. Adsorption of Cd (II) ions showed a similar behavior where percentage removal increased from 92.70 to be maximum of 95.30% upon increasing the rotation speed from 100 rpm to 300 rpm and *qe* increased from 27.70 to 28.80 mg/g. While, increasing the rotation speed from 300 rpm to 500 rpm decreased the Cd (II) ions percentage removal and *qe* from 95.30% and 28.80 mg/g at 300 rpm to 92.50% and 27.90 mg/g respectively at 500 rpm. These results may be interpreted as following; the low rotation speed cannot disseminate the adsorbent particles duly in the metal solution and these particles may be accumulated.[54] This accumulation is a plausible reason that some of the adsorbent active binding sites will be buried and in this case not all of the adsorbent layer active sites are available for the heavy metal ions adsorption. So, the rotation speed should be appropriate enough to ensure that all the surface active sites are available and able to bind metal ions.[55] Furthermore, increasing the rotation speed minimize the resistance of the external mass because of reducing the thickness of the external boundary layer.[56] On the other side, the decrease in percent removal and *qe* after 300 rpm (for both of Cu and Cd ions adsorption) is attributed to an increase in desorption tendency of adsorbate ions.[55] Moreover, the higher agitation speed distributes the adsorbent particles strenuously in the solution and adsorption time will not be adequate for giving the adsorbent a chance to bind metal ions.[83] Similar trend was reported by Anwar J et al.[57], who studied the effect of agitation speed of pea pods on adsorption of chromium from aqueous solution. In the range of 50-250 rpm, the results showed that the adsorption percentage of chromium ions increased upon increasing the agitation speed from 50 rpm to 100 rpm after which, the adsorption percentage decreased until 250 rpm.

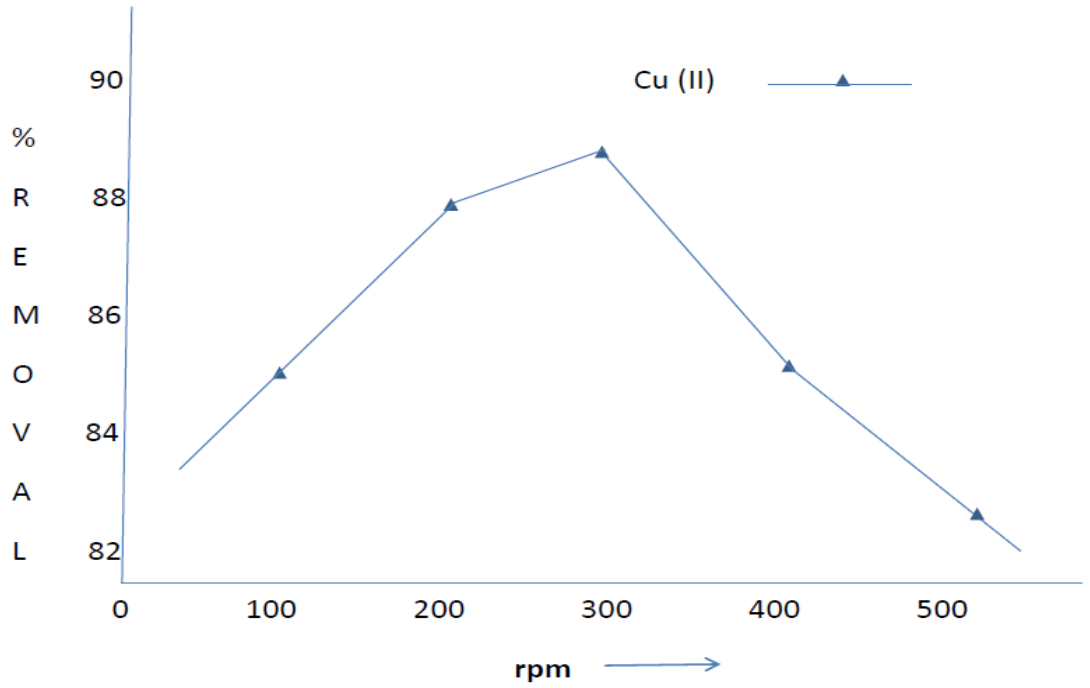

Figure 10: Rotation speed effect on the percentage removal of Cu (II) ions Temperature 298K, initial concentration: 30 mg/L, 1.0 g of adsorbent and pH: 6 for 30 minutes.

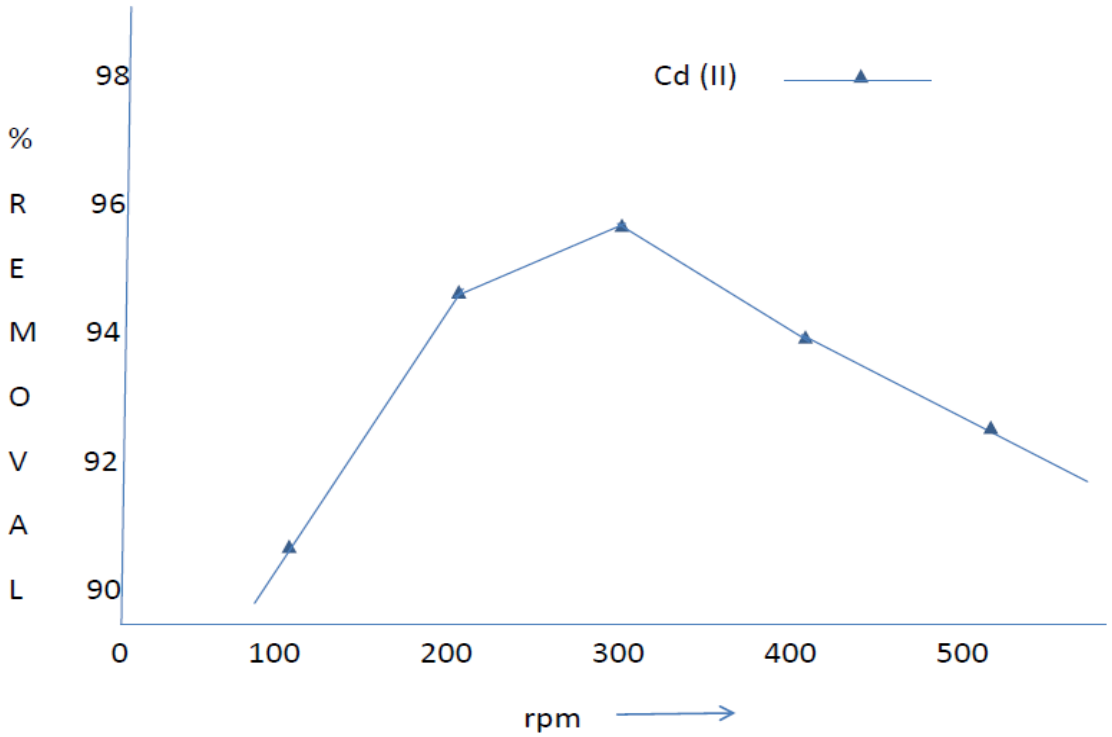

Figure 11: Rotation speed effect on the percentage removal of Cd (II) ions Temperature 298K, initial concentration: 30 mg/L, 1.0 g of adsorbent and pH: 5 for 30 minutes.

4. CONCLUSION

The aim of the present investigation is to show the adsorption capability of Red Mud adsorbent for removing of Cu (II) and Cd (II) ions from aqueous solutions. The results revealed that chemisorption as well as physisorption mechanisms are involved during the adsorption process of copper and cadmium ions on adsorbent. Red Mud are safe, low-cost, rapid and efficient adsorbents for the removal of Cu (II) and Cd (II) cations from aqueous solutions a relative small doses of 4 g and 2 g of adsorbent /100ml were enough for complete removal (100.0%) of 30 mg/L Cu (II) and Cd (II) ions solution, respectively. That's why Red Mud as environmentally acceptable adsorbent with high

performance for removal of some toxic heavy metal ions could have a promising future for wastewater treatment.

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