

Characterization of alginate polymer and its application in copper removal from liquid wastes

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Abstract: Copper is one of the most dangerous pollutants that require removal from wastewater effluents before being discharged. Here are reported on the adsorption performance of a novel environmental friendly material, calcium alginate gel beads as a non-conventional technique for the successful removal of copper ions from aqueous solution. Batch equilibrium studies were carried out to evaluate the adsorption capacity and process parameters such as pH, adsorbent dosages, initial metal ion concentrations, stirring rates and contact times. It was observed that, the maximum removal of copper ions was occurred at pH 5.0 ± 0.02 . An adsorbent dose of 1 g/L was optimum for copper ions removal within an equilibrium time. For all contact times, an increase in copper ions concentration resulted in decrease in the percent of copper ions removal (91.98%–49.96%) and an increase in adsorption capacity (4.59 – 49.93 mg/g) for copper ions concentrations 5 and 100 ppm, respectively. The mechanical stirring speeds greatly enhance the mass transfer rate of copper ions onto the adsorbent indicating 250 rpm is the optimum. The removal of copper ions occurs rapidly within the two hours (equilibrium time), followed by a slow removal process. The Langmuir and Freundlich's isothermal models were used to describe the experimental adsorption. The equilibrium adsorption data were well fitted to Langmuir isotherms ($R^2 = 0.9959$) and the maximum adsorption capacities of the calcium alginate gel beads were found to be (87.5%, 17.5 mg/g) were obtained at the optimum conditions on a Jar test at temperature $25 \pm 3^\circ\text{C}$ for copper ions concentration 20ppm. The calcium alginate gel beads were characterized using Fourier transform-infrared (FT-IR) spectroscopy and Transmission electron microscopy (TEM).

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Key words: copper sorption, alginate polymer, Equilibrium, heavy metals, adsorption, isothermal models

1. Introduction

Due to the industrial, day-to-day human activities and technological advancements in this century, a large amount of liquid wastes are produced and disposed into the environment. The increased concern about the environment and health aspects due to the discharge of such liquid wastes containing toxic compounds have lead to stricter legislations concerning pollution control measures [1]. Toxic metals from mining, milling and surface-finishing industries can contaminate river waters and finally accumulate in marine sediments [2]. Heavy metals are elements having atomic weight between 63.545 and 200.5g, specific gravity greater than 4.0 and with an atomic density greater than 6.0 g/cm^3 . Heavy metals are among the worst group of pollutants of the environment. Heavy metals occur in immobilized form in sediments and as ores in nature as natural phenomena (volcanic activities or erosion). However due to various human activities like ore mining and industrial processes, the natural biogeochemical cycles are disrupted causing increased deposition of heavy metals in terrestrial and aquatic environment [1 and 3]. Heavy metals are one of the most persistent pollutants in water. Unlike other pollutants, they are

difficult to degrade, but can accumulate throughout the food chain, producing potential human health risks and ecological disturbances [4]. It has also severe effects include reduced growth and development, cancer, organ damage, nervous system damage and in extreme cases death [5]. Heavy metal pollution is a global issue, although severity and a level of pollution differ from place to place. At least 20 metals are classified as toxic with half of them emitted into environment in concentrations that pose great risks to human health. The common heavy metals that have been identified in polluted water include arsenic, copper, cadmium, lead, chromium, nickel, mercury and zinc. The release of these metals without proper treatment poses a significant threat to public health and the environment because of their toxicity, bio-accumulating tendency (biomagnifications), persistence and accumulation in food chain processes. Therefore, it is frequently desirable to measure and control the concentration of these substances [6, 7, 8, 9, 10 and 11].

Removal of heavy metals present in the environment is always of high importance in order to balance ecology with healthy life forms. Copper (Cu^{2+}) ions are extensively released from different

industries and its excessive entry into food chains results in serious health impairments, carcinogenicity and mutagenesis in various living systems. The activities of man through the growing and development of the small and medium scale enterprise has gradually kept on the increase of copper (II) ions discharge into the environment. Thousands of years ago, the use of copper was limited to making tools and other utensils, but now, it is widely used in electrical wire, coins, ornamental objects, jewelers, pharmaceuticals, fungicides and mining activities. These consequently have impact on the threshold limit. Copper toxicity can occur in plants growing in polluted soils, and animals grazing on these plants, through the food chain. In humans about 10-20mg of orally ingested Cu^{2+} may cause intestinal discomfort, dizziness and headaches, while ingestion of copper salts in excess of 500-100mg have caused fatal acute poisoning such as vomiting, diarrhea with bleeding, circulatory collapse, failure of the liver and kidneys and severe haemolysis. World Health Organization (WHO) defines the Cu^{2+} permissible limit of 1.5 mg/L in drinking water [12]. A wide variety of treatment technologies for the decontamination of this metal-polluted effluent have been investigated and developed. These are chemical

precipitation, ion exchange, adsorption, solvent extraction, membrane processes and electrochemical techniques while, it is difficult and sometimes very expensive to remediate Cu^{2+} by conventional treatment techniques. Adsorption process via the use of natural materials has been recently utilized because it is readily available; it has low energy consumption, eco-friendly, and cost effective [13 and 14]. A large number of technologies have been adapted and practiced so far to ensure the environmental safety against Cu^{2+} in the industrial effluents as showed in **Figure 1**.

Adsorption is the most attractive option due to the availability of cost effective, sustainable and high efficacy. Adsorption is a recognized method for the removal of heavy metals from wastewater having low concentration of heavy metal. The adsorption process offers flexibility in design and operation and in many cases produce high-quality treated effluent. Besides this, adsorption is reversible and adsorbents can be regenerated by suitable desorption techniques. Many low cost adsorbents have been developed and tested for heavy metal ion removal so far, which reflect varying adsorption efficiencies depending upon the type of adsorbents used [15 and 16].

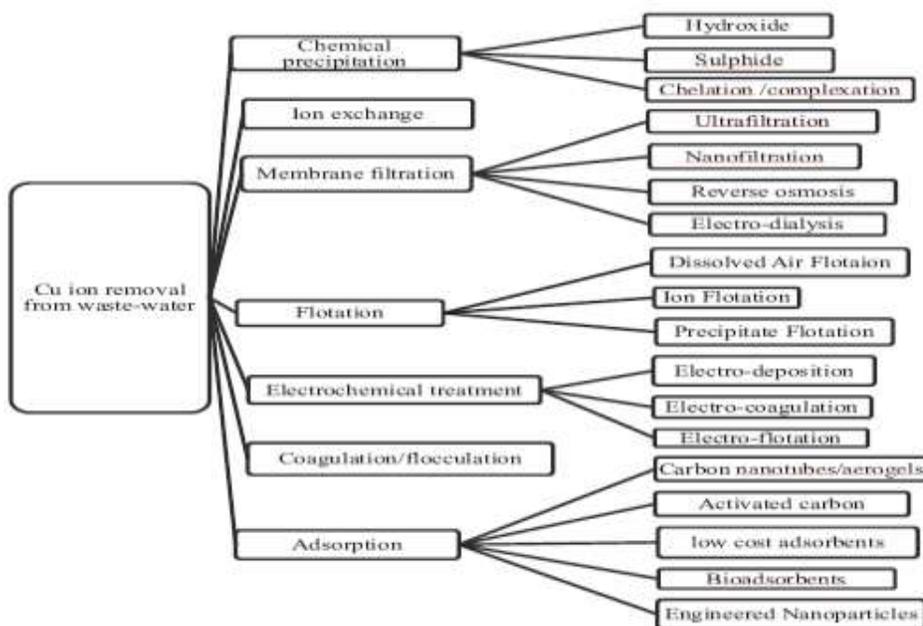


Fig. (1): Available treatment technologies for copper ion removal from wastewater

A search for a low-cost and easily available adsorbent had led to the investigation of materials of natural origin as potential metal sorbents [17, 18 and 19]. Calcium alginate beads could also stripped of metal ions by desorption which can be recycled and

reused for subsequent cycles [20 and 21]. Polymeric materials are generally necessary and provide additional advantages. These included easier handling, requiring less complex separation systems and provide a greater opportunity for reuse and

recovery. Alginic acid is a heteropolysaccharide of α -L-glucuronic acid and β -D-mannurinic acids and is found in many algal species especially inside the brown algae. This carboxylic polyelectrolyte is soluble in aqueous solutions and precipitates in the form of a co-acervate in the presence of multivalent metal ions like Ca^{2+} , Co^{2+} , Fe^{2+} , Fe^{3+} and Al^{3+} . The presence of carboxylic groups in the alginate structure enhanced the heavy metal ion adsorption capacity [22 and 23]. The purpose of this study therefore was to determine the ability of calcium alginate beads to remove copper ions from liquid wastes.

2. Materials and Methods

Adsorbate Solution

Copper sulphate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) was used as a source of copper ions. The aqueous stock solution (1000 ppm) of Cu^{2+} was prepared by adding 3.928 g from copper sulphate salt into 1L of bi-distilled water. The solutions of different concentrations (5–100 ppm) required for the adsorption studies were prepared by dilution of the stock solution.

Instrumentation

- A Transmittance Electron Microscope TEM (Inspect S. FEI Company, Holland) was used to characterize the surface of the Ca alginate beads.
- Functional groups in Ca alginate beads were determined by the Fourier transform infrared (FTIR) spectroscopy with a FTIR Spectrometer (Shimadzu S 201 PC spectrophotometer – Japan) in the transmittance % mode in the range 4000–400 cm^{-1} .
- Flame atomic absorption spectrophotometer AAS (Thermo Scientific ICE 3000 series, AA Spectrometer– Thermo Scientific) was used for the analysis of copper Cu^{2+} in aqueous solution.
- Environmental Shaker (GFL 3018 Model) and VELP Scientifica JLT6 leaching test Jar test was used for batch adsorption experiments.
- A (Cole Parmer) pH-meter was used, with a range of 0.00 to 14.00 and an accuracy of ± 0.02 . The pH meter was standardized using buffer solutions of pH values: 4, 7 and 10.
- Millipore (Elix) UV- Milli-Q Advantage A 10 System: - Doubled Distilled Water (DDW) from Millipore Instrument was used throughout the study as a source of bi-distilled water.
- All glassware used in the experiments was first washed with 10% nitric acid to eliminate any trace of residual metals. The glassware was then washed with tap water and then finally washed with distilled water.

Alginate Beads Preparation

Sodium alginate $\text{C}_6\text{H}_7\text{O}_6\text{Na}$ and calcium chloride CaCl_2 were used to prepare calcium alginate gel beads according to method described by **El-Naggar *et al.*, [24]**. Sodium alginate solutions (3% w/v) were prepared by mixing the fine sodium alginate powder with distilled water while stirring. The alginate gel solution (cross-Linker solution) was kept in refrigerator for half an hour then added drop wise into 100 ml of 2% CaCl_2 solution under gentle stirring at 25 ± 3 °C. Ca-alginate hydrogel spheres were formed into equal size unites of spheres ranged from 1.5 to 2.0 mm upon contact with the cross-Linker solution. The formed beads were washed several times with bi-distilled water then dried at 60°C for two hours and were used as a good adsorbent to remove copper ions from wastewater in batch adsorption experiments.

Batch Adsorption Experiments

Ca-alginate hydrogel spheres were immersed in 100 ml of the wastewater. Adsorption studies were carried out to synthetic wastewater containing copper ions in 500 ml Erlenmeyer flasks, as follows: 0.1g of alginate beads was immersed in 100 ml of the wastewater. The pH was firstly adjusted at 5.0 ± 0.02 , the stirring rate at 250 rpm on a Jar test at temperature 25 ± 3 °C. After finishing the process (2 hr.), the last stage, after settling time, a sample was taken from the supernatant and analyzed according to Standard Methods for the examination of water and wastewater [25].

The uptake percent was measured as:-

$$\text{Uptake \%} = (C_0 - C_e) / C_0 * 100$$

The metal uptake per gram was calculated from a metal mass balance yielding:-

$$Q = V (C_0 - C_e) / m$$

Where, (Q or q_e) is mg metal ions per g dry adsorbent; (V) is the reaction volume (L), (C_0) and (C_e) are the initial and residual metal concentrations (ppm), respectively, and (m) is the amount of dry adsorbent (g) [26].

3. Results and Discussion

The adsorption capacity of metal ions is expressed by the uptake percentage and the specific uptake (Q). In this study, batch experiments are used in the optimization of copper sorption by Ca-alginate beads.

Effect of pH:

The pH value of copper solution was adjusted using hydrochloric acid (HCl) 0.1N and sodium Hydroxide (NaOH) 0.1 N. Obtained results indicated that the pH of the solution is an important factor for the adsorption study. Batch experiments were occurred at Conc. 20 ppm (100 ml), Temp 25 ± 3 °C and Stirring 200 rpm and for 2hr. The uptake percent

is increased as pH of the solution increased and the maximum uptake occurred at $3 \pm 0.02 < \text{pH} < 7.0 \pm 0.02$. Results showed that the best uptake capacity of Cu^{2+} (87.5%, 17.5 mg/g) were obtained at $\text{pH} 5.0 \pm 0.02$ other those obtained at $\text{pH} 1.0 \pm 0.02$, 3.0 ± 0.02 and 7.0 ± 0.02 as shown in **Figure 2**.

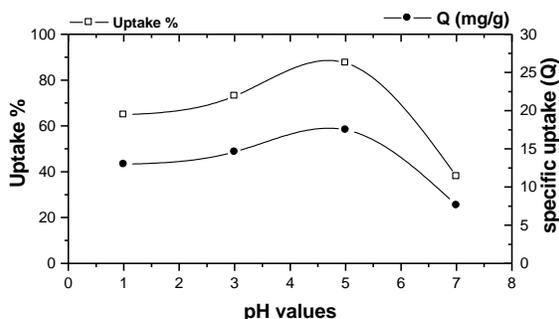


Fig. (2): Effect of solution pH on copper ion sorption

Effect of Cu^{2+} ion concentrations:-

It is found that, 0.1 gram of Ca-alginate beads could fix 91.98, 90.79, 87.5, 80.25, 73.76 and 49.96 % from 5, 10, 20, 30, 50 and 100 ppm Cu^{2+} solutions, respectively. Results also showed that one gram dry weight of Ca-alginate beads could accumulate 4.59, 8.88, 17.5, 23.97, 36.82 and 49.93 mg of Cu^{2+} from 5, 10, 20, 30, 50 and 100 ppm solutions, respectively at pH was adjusted 5.0 ± 0.02 , Temp 25 ± 3 , Stirring 200 rpm, Time 2hr as shown in **Figure 3**. Results obtained showed that the amount of Cu^{2+} accumulated increased with the increase in Cu^{2+} conc. According to correlation coefficient (R^2), the Langmuir's model is best fit for Cu^{2+} adsorption by Ca-alginate beads than Freundlich's model as shown in **Figures 4, 5**.

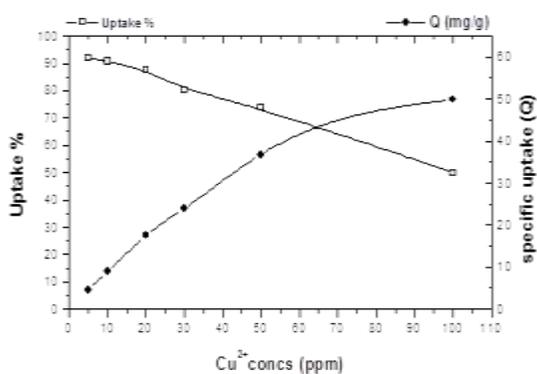


Fig. (3): Copper removal at different Cu^{2+} ion concentrations

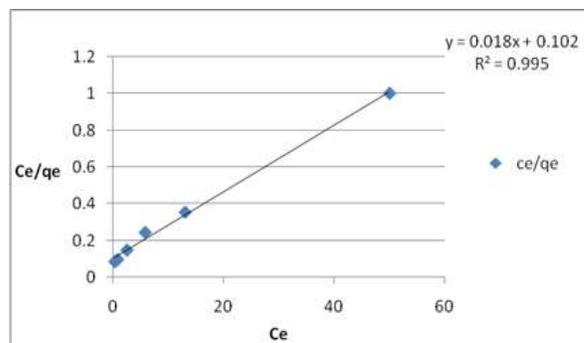


Fig. (4): Langmuir's isotherm for Cu^{2+} removal by Ca-alginate beads

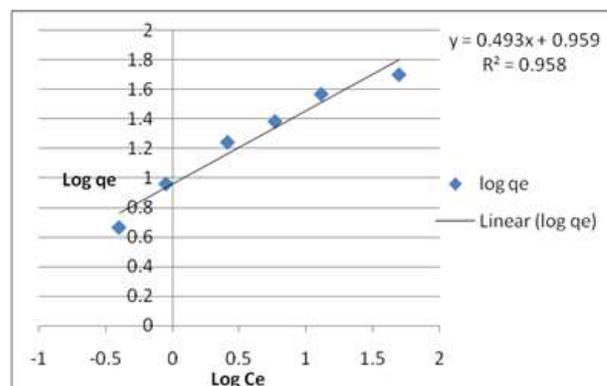


Fig. (5): Freundlich's isotherm for Cu^{2+} removal by Ca-alginate beads

Effect of adsorbent weights:-

Results showed an increase in the uptake percentage of Cu^{2+} with the increase in adsorbent weight from 0.1 to 0.5 g than from 0.5 g to 1.0 g. While, the mg uptake/g dry weight decreased with the increase in the adsorbent weight. The best uptake capacity were showed at adsorbent weight 0.1g, it achieves 87.5 % and 17.5 mg/g as shown in **Figure 6**.

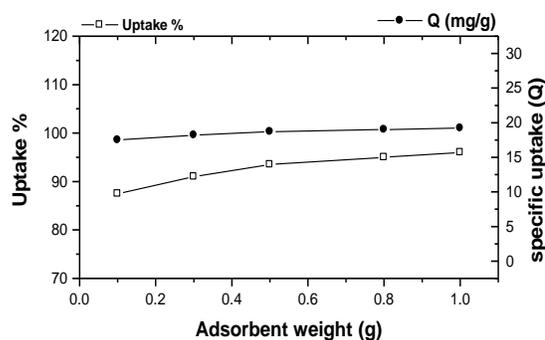


Fig. (6): Effect of adsorbent weights on copper sorption

Effect of contact times:-

Results showed that the Cu^{2+} concentration decreased from an initial value to an equilibrium value provided the contact time is sufficient. The time needed to reach equilibrium is defined as "equilibrium time". Results showed that the uptake capacity of Cu^{2+} ions increased with contact time till two hour and then the uptake capacity doesn't show any significant results as shown in **Figure 7**.

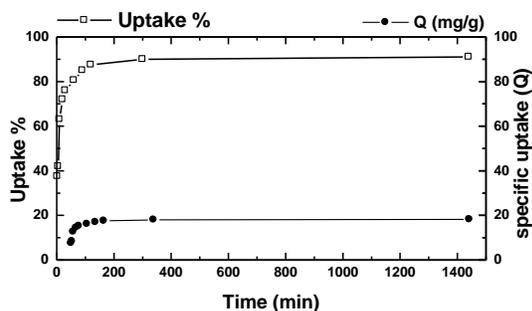


Fig. (7): Effect of Contact times on copper sorption

Effect of stirring rates:-

Results showed that the maximum uptake capacity 87.5 %, 17.5 mg/g and 90.5 %, 18.1 mg/g were obtained at stirring rates 200 and 300 rpm, respectively. The minimum uptake capacity were showed at low stirring rates (0, 50,100,200 and 300 rpm), respectively as shown in **Figure 8**. Results indicating that, the uptake of metal ions increased with the increase of stirring rate.

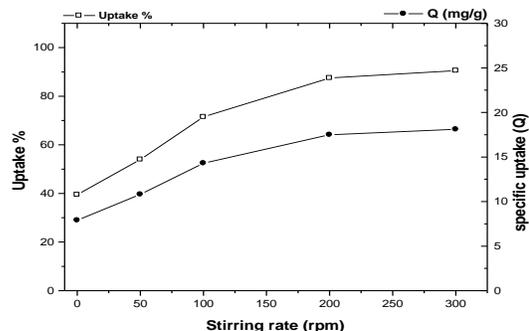


Fig. (8): Effect of stirring strength on copper sorption

Fourier Transform Infrared Spectrometry (FT-IR)

Another investigation related to the adsorption phenomenon is FT-IR. It is used for determination of functional groups in organic materials in frequency range from 500 to 4000 cm^{-1} . FT-IR is carried out to Ca-alginate beads before and after treatment process. The alginate beads were dried to almost nil moisture and send for FT-IR analysis. Spectral region consists of a set of peaks. This analysis had eventually confirmed the shifting and decrease in the band intensity at (1037.6 to 1029.9 cm^{-1}), shifting and decrease in the band intensity at (1662.5 to 1631.7 cm^{-1}) and shifting and sharp decrease in the band intensity at (3737.8 to 3436.9 cm^{-1}) after treatment. This decrease in the bands intensity was considered as adsorption bands as shown in **Figures (9, 10)**. Also, photographic pictures for Calcium alginate beads before and after treatment are showed in **Figure (11)**.

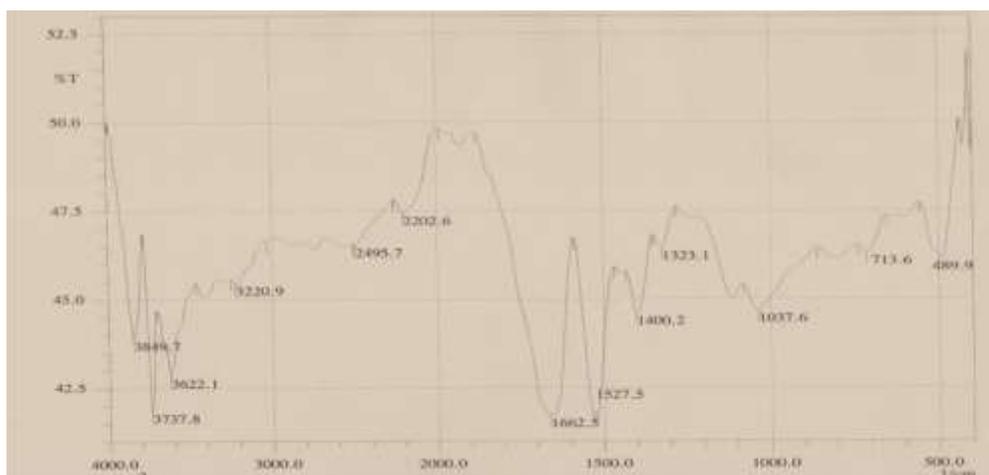


Fig. (9): FT-IR spectrum for Ca-alginate beads before treatment

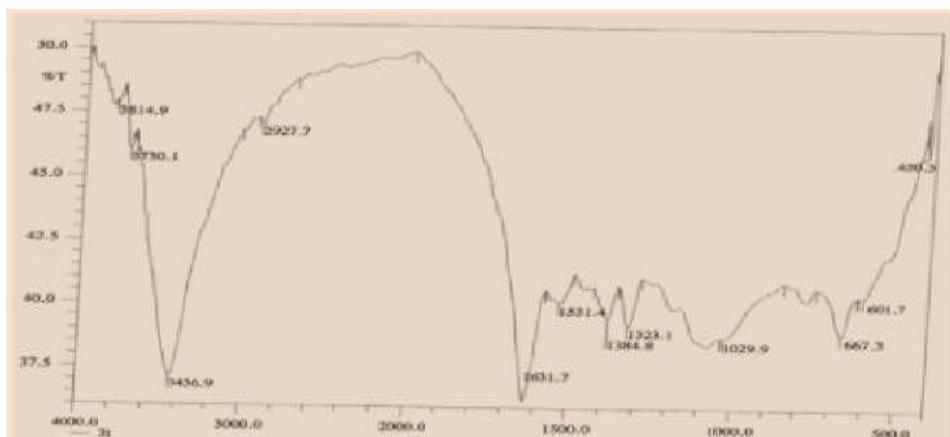


Fig. (10): FT-IR spectrum for Ca-alginate beads after treatment

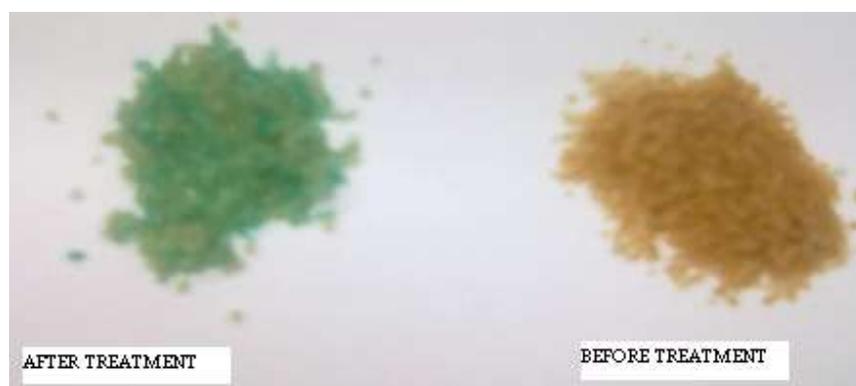


Fig. (11): Ca-alginate beads before & after treatment process

Transmittance Electron Microscopy (TEM):-

Ca-alginate beads before and after treatment were studied. The TEM micrograph of control Ca-

alginate beads is plain, smooth and clear while, Ca-alginate after treatment showed precipitation of metal ions all over the surface as shown in **Fig. (12)**.

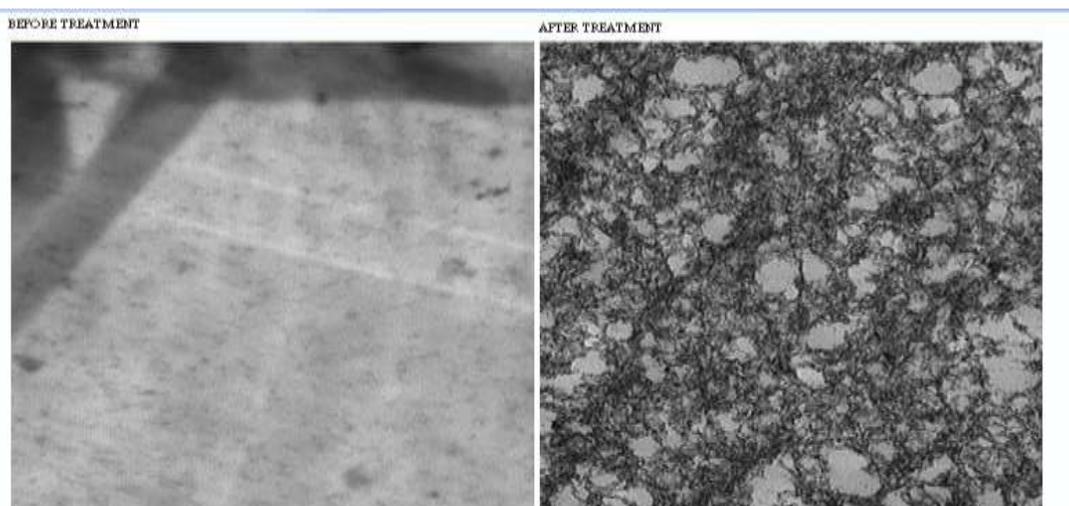


Fig. (12): TEM of Ca-alginate sorbent before and after copper sorption

Conclusion

Adsorption is considered a reliable, efficient and low-cost technique for metal removal from wastewater. The study revealed that the alginate gel beads could be used as an ideal material for the removal of Cu^{2+} ions about 87.5% from aqueous medium containing Cu^{2+} concentration 20 ppm and it would be applicable in the process development to treat industrial effluents. It is quite evident that adsorption is mainly dependent upon the surface chemistry, pH of solution, charge distribution over the adsorbent surface and metal ion concentration. Hydrogen ion (H^+) plays an important role on the effect of pH and an optimum pH of 5 was obtained for adsorption of the Cu^{2+} before precipitation of the hydroxides. The FT-IR analysis indicates that the main active groups were carboxylates and hydroxyl as being responsible for the adsorption. Overall adsorbents data for Cu^{2+} removal were found best fit to Freundlich's and Langmuir's isotherm which reflected the single and multilayer adsorption behavior.

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