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# The Role of Alginate as Polymeric Material in Treatment of Tannery Wastewater

**Marwa M. EL-Tayieb; M.M. El- Shafei; M.S. Mahmoud**
Sanitary and Environmental institute (SEI),
Housing and Building National Research Center (HBRC), Egypt

## ABSTRACT

This paper determines the use of alginate to prepare metal sorbing beads. Their metal binding properties were investigated with respect to toxic constituents present in tannery wastewater from chromium stage Elmontaza Tannery, Ain El Sira, Cairo, Egypt. Their behavior in batch experiments for the remediation process was studied for two hours of contacts in acidic medium. Alginate was found to be a promising material for simultaneous removal of heavy metal ions and toxic organics pollutants. Results obtained adsorption efficiencies for chromium (43.5 %), cadmium (51.6 %), copper (67.4%), lead (57.8%), nickel (73.02%), iron (51.02%) and manganese ions (74.8%). Also, Results showed decrease in color absorbance and organic loads from tannery wastewater; TDS (44.6 %), salinity (39.9 %), COD (64.3 %), BOD (61.1 %), ammonia nitrogen (78.6 %), nitrate (75.5 %) and phosphorous (55.8 %). The availability of recycling of Ca-alginate beads was also studied for three subsequent cycles. SEM examination and FT-IR technique were also studied.

**Keywords:** *Tannery, Polymerization technology, Heavy metals, Chromium.*

## 1. INTRODUCTION

The increase of industrial activities has intensified environmental pollution and the deterioration of ecosystems, especially aquatic, with the accumulation of pollutants, such as heavy metals, synthetic compounds, nuclear wastes, etc. In recent years, increasing concern about the effect of toxic metals in the environment has resulted in more strict environmental regulations for industrial applications that discharge metal bearing effluents **{1}.**

Tanneries are typically characterized as pollution intensive industrial complexes which generate widely varying and high-strength wastewater. Major problems are due to wastewater containing heavy metals, toxic chemicals, chloride, lime with high dissolved and suspended salts and other pollutants. In Egypt, the tannery wastewater is discharged directly to the main domestic sewage pipeline without proper treatment which adds difficulties to the sewer system and to the wastewater treatment plants **{2}.**

The need for cost effective and efficient methods for the removal of metals has resulted in the development of new separation technologies. Precipitation, adsorption–ion exchange, flocculation, absorption, electrochemical processes and/or membrane processes such as electrodialysis, nanofiltration and reverse osmosis, are commonly applied for the treatment of industrial effluents. Adsorption has been found to be superior to other techniques for water reuse in terms of the initial cost, simplicity of design, and easiness of operation **{3}.**
Polymerization technology is considered as an essential step for an adsorption scale-up. Polymerization provides particles with adequate size, density and mechanical strength required by continuous systems. Besides, Polymerization can save the cost of separating from the treated solution which can represent up to 60% of the total cost. This process also enables regeneration in various adsorption–desorption cycles. Natural polysaccharide gel matrixes such as alginate are widely used and are a cost effective alternative to synthetic polymers. Alginate, a linear copolymer 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. The capability of this copolymer to form stable biodegradable gels in the presence of divalent and multivalent cations like $Ca^{2+}$, $Co^{2+}$, $Fe^{2+}$, $Fe^{3+}$ and $Al^{3+}$ was studied **{4, 5, 6}.**

Ca-alginate, the polymeric matrix, offering advantages such as biodegradability, hydrophilic properties, natural origin, and abundance combined with its ability to form stable hydrogels due to the presence of specially coordinated carboxylic binding sites. The polymeric matrix also determines the mechanical strength and chemical resistance of the final particle, which would be utilized for successive adsorption–desorption process **{7}.**

These polymeric materials have several advantages included easier handling, requiring less complex separation systems and provide a greater opportunity for reuse and recovery **{8, 9}.**

The aim of this work is to study the sorption capacity of alginate in the form of calcium beads prepared via the dripping technique to remove toxic constituents from tannery wastewater; also morphological characteristics and availability to be recycled were studied.

## 2. MATERIALS AND METHODS

### 2.1 Samples Collection Site

Samples of wastewater from contaminated sites with tannery wastewater - chromium stage – Elmontaza Tannery, Ain El Sira, Cairo, Egypt, were collected. The collected samples were then mixed to become one sample, analyzed within 8 h and stored in a refrigerator at 4ºC. The physicochemical characteristics of tannery wastewater sample are listed in **Table (1).**

**Table (1): Physicochemical analysis for tannery wastewater sample**

| Constituents | Values | Units | Constituents | Values | Units |
|---|---|---|---|---|---|
| **Color** | Dark Green | | **Nitrite** | 30 | mg/L |
| **pH** | 4.01 | | **Phosphorous** | 15 | mg/L |
| **TDS** | 57.87 | Ppt | **Oil and Grease** | 28.3 | mg/L |
| **EC** | 63.6 | ms/cm | **Chromium** | 500 | mg/L |
| **DO** | 45.0 | % | **Cadmium** | 15.5 | mg/L |
| **COD** | 550 | mg/L | **Copper** | 2.7 | mg/L |
| **BOD** | 120 | mg/L | **Lead** | 15.4 | mg/L |
| **ammonia nitrogen** | 200.11 | mg/L | **Nickel** | 5.3 | mg/L |
| **Nitrate** | 25 | mg/L | **Iron** | 10.8 | mg/L |
| **Salinity** | 73.2 | mg/L | **Manganese** | 2.1 | mg/L |

### 2.2 Alginate Beads Preparation

3% w/v sodium alginate solutions were prepared by mixing the fine sodium alginate powder with distilled water while stirring. 10 ml of 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°C. Ca-alginate hydrogel spheres were formed into equal size unites of spheres ranged from 2.5 to 3.0 mm upon contact with the cross-Linker solution and were left over night to stabilize. The excess of cross-linker solution was removed by filteration and was washed several times with bi-distilled water. Beads were then used to remove heavy metals and other pollutants from wastewater in batch adsorption experiments.

### 2.3 Instrumentation

- **Multi parameter analyzer - HANNA – HI 9828 - Italy - pH / ORP / EC / DO** was used for measuring of pH, temperature, EC, DO, TDS and salinity.

- **iCE 3000 Series AA Spectrometer– Thermo Scientific)** was used for quantitative determinations of heavy metal ions.

- **T70+ UV/VIS Spectrophotometer – PG instruments Ltd** was used for colorimetric spectrophotometer measurements.

- **Environmental Scanning Electron Microscope ESEM** was employed to characterize the surface morphology of Ca alginate beads with EDAX analyses.
- **Shimadzu S 201 PC spectrophotometer – Japan** was used for infrared spectroscopy of Ca alginate beads .

- **VELP Scientifica JLT6 leaching test Jar test** was used for batch adsorption experiments.

### 2.4 Batch Adsorption Experiments

Study was carried out to tannery wastewater sample in 500 ml Erlenmeyer flasks, as follows: Ca-alginate hydrogel spheres were immersed in 100 ml of the real tannery wastewater. The pH was firstly adjusted at 5.0 ± 0.2, 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, **{10}.**

The uptake percent was measured as:-

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

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

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

Where, (Q) is mg metal ions per g dry adsorbent; (V) is the reaction volume (L), (C0) and (Ce) are the initial and residual metal concentrations (mg/l), respectively, and (m) is the amount of dry adsorbent (g) **{11}.**

## 2.5 Recycling of Ca-Alginate Beads Experiments

Recycling or reusability of Ca-alginate beads was studied for three consecutive cycles. The accumulated beads after each cycle were eluted using 0.05N $HNO_3$ for one hour on a rotary shaker (250 rpm). Then the beads were washed with bi-distilled water three times until the pH of washing reach 6 – 6.5.

## 3. RESULTS AND DISCUSSION

Tannery wastewater is one of the most important sources of environmental pollutants. The biodegradability of tannery wastewater was represented by low BOD value to less than 1/3 of COD value (i.e. 0.22) due to the presence of high metal ions concentrations especially chromium ions and high concentrations of salts. This is also confirmed by many other studies **{12}**.

## 3.1 Treatment by Ca-alginate Beads

Treatment of tannery wastewater by Ca-alginate beads showed noticeable decrease in color intensity, organic loads and metal ions concentration. The color intensity of Ca-alginate beads before and after treatment was showed in **Figure (1).** For organic loads, the removal efficiencies were for COD (64.3%), BOD (61.1%), ammonia nitrogen (78.6%), nitrate (75.5%), phosphorous (55.8%), TDS (44.6%), EC (44.7%) and salinity (39.9%) as showed in **Figure (2).** For heavy metals, the removal efficiencies were for chromium (43.5 %), cadmium (51.6 %), copper (67.4%), lead (57.8%), nickel (73.02%), iron (51.02%) and manganese ions (74.8 %) as showed in **Figure (3).** Results showed difference in the uptake percent. The decrease in the uptake percent could be explained by; at lower initial metal ion concentrations, sufficient adsorption sites are available for adsorption. However, at higher concentrations the numbers of ions are relatively higher compared to availability of the adsorption sites. This decrease may be also attributed to the negative effect of both metals on each other for removal or the difference in ionic radii of metal ions. Also, results showed difference in the specific uptake. The increase in specific uptake could be explained by with a fixed adsorbent weight the competition of metal ions on the adsorbent surface was increased and so, increased in metal ions accumulated until reach saturation of active sites. Almost similar explanation was also reported by **{13, 14, 15}.**

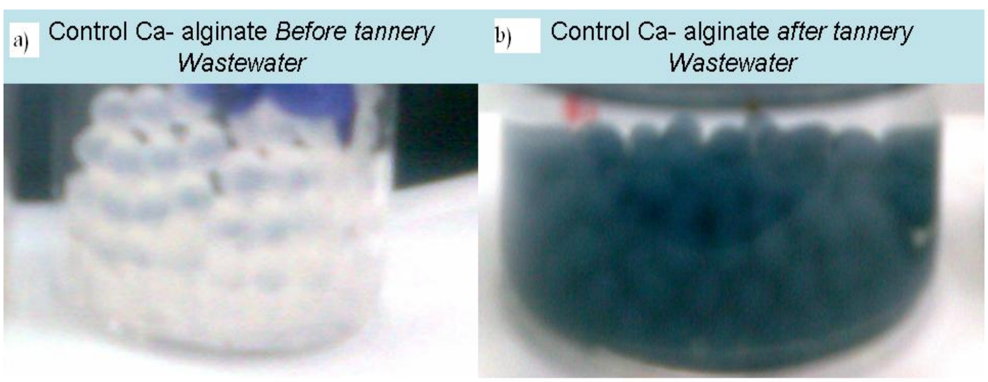



**Fig. (1): Ca-alginate beads (a) before and (b) after tannery wastewater treatment**

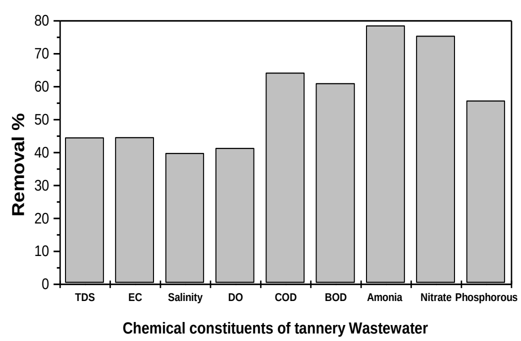



**Fig. (2) Removal percentage of chemical constituents after treatment by Ca-alginate beads**

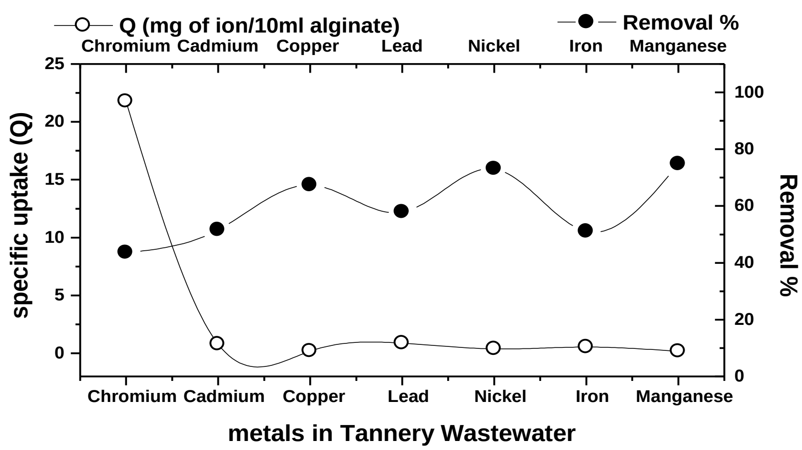



**Fig. (3) Heavy metals adsorption capacities after treatment by Ca-alginate**

## 3.2 Evaluation of Recycling of Ca-alginate Beads

Recycling or reusability of Ca-alginate beads in treatment of tannery wastewater was studied for three cycles. It was found that, there is noticeable decrease in the treatment efficiency when Ca-alginate beads were reused. The color absorbance at λ: 580 nm and 418 nm was investigated within three cycles indicating that first cycle was more efficient (had low absorbance) then second cycle then third cycle as showed in **Figure (4).** Removal percentages of organic loads were determined; COD (64.3%, 56.8%, 49.3%), BOD (61.1%, 53.8%, 46.1%), ammonia nitrogen (78.6%, 71.1%, 63.6%), nitrate (75.5%, 68%, 60.5%), phosphorous (55.8%, 48.3%, 40.8%), TDS (44.6%, 37.1%, 29.6%), EC (44.7%, 37.2%, 29.7%) and salinity (39.9%, 32.4%, 24.9%) at 1st cycle, 2nd cycle and 3rd cycle, respectively as showed in **Figure (5).** Removal percentages of heavy metals were also determined; chromium (43.5 %, 36 % and 28.5%), cadmium (51.6 %, 41.9 % and 31.6 %), copper (67.4 %, 55.6 % and 33.3 %), lead (57.8 %, 51.3 % and 44.2%), nickel (73.02 %, 65.5 % and 52.8 %), iron (51.02 %, 40.6 % and 23.1%) and manganese ions (74.8 %, 52.4 % and 28.1%) at 1st cycle, 2nd cycle and 3rd cycle, respectively as showed in **Figure (6)**. These results indicated that first cycle was more efficient then second cycle then third cycle. This could be explained by the presence of free active adsorption sites available for uptake on bead surface. Further addition of raw wastewater resulted in competition of ions for complexation with the active binding sites leading to decrease in the uptake process. These results and observations were paralleled to that obtained by **{16}.**

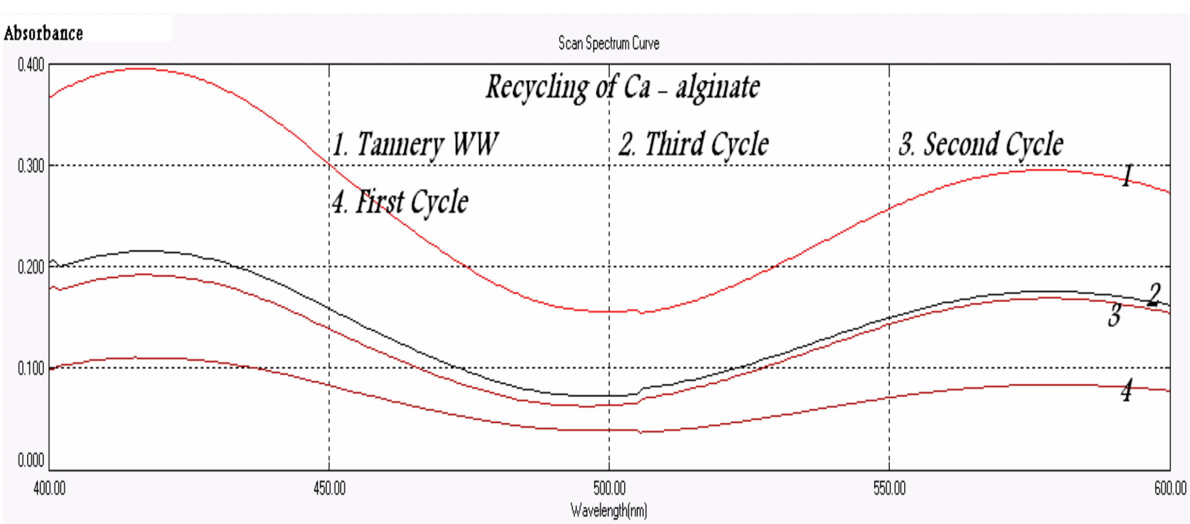



**Fig. (4): Scan spectrum curve of tannery wastewater sample after recycling of Ca-alginate beads**

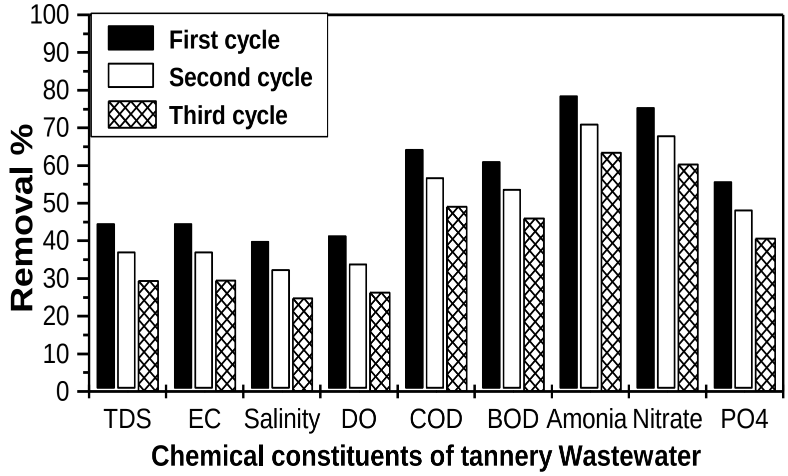



**Fig. (5) Removal percentage of chemical constituents after recycling of Ca-alginate beads**

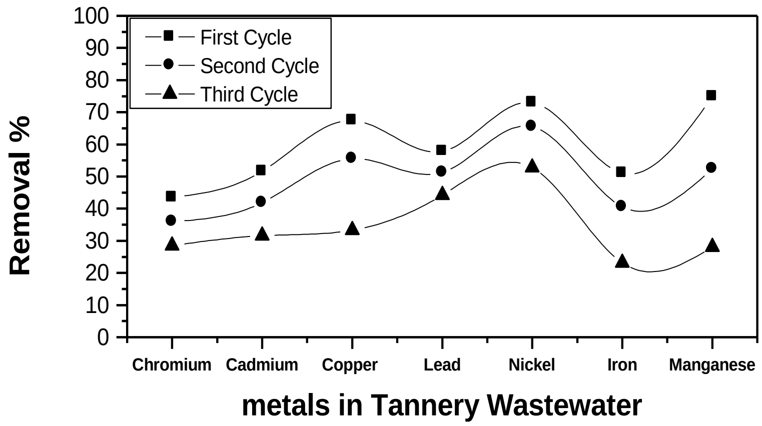
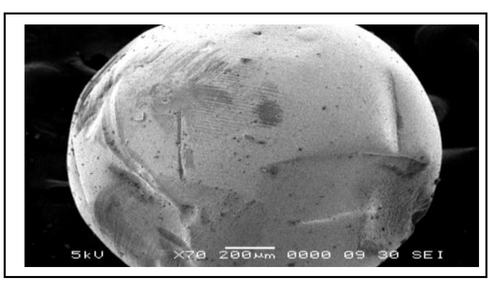



**Fig. (6) Heavy metals adsorption capacity after recycling of ca-alginate beads**

## 3.3 SEM Examination

SEM micrograph for control Ca-alginate beads before tannery wastewater treatment showed plain, smooth and clear surface as shown in **Figure (7).** SEM micrograph for Ca-alginate-beads after tannery wastewater treatment showed precipitation on the bead surface as shown in **Figure (8).** EDAX of Ca-alginate beads after treatment showed precipitation of C (60.64 %), O (22.06 %), P (0.75 %), S (1.28 %), Cl (0.38 %) and Cr (14.90 %) as shown in **Figure (9).** Almost similar observation was obtained by **{13, 17}**.



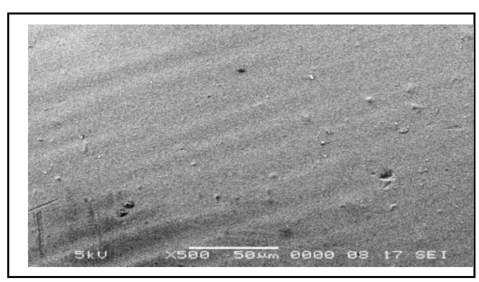


**Fig. 7. Ca-alginate bead before tannery wastewater treatment**

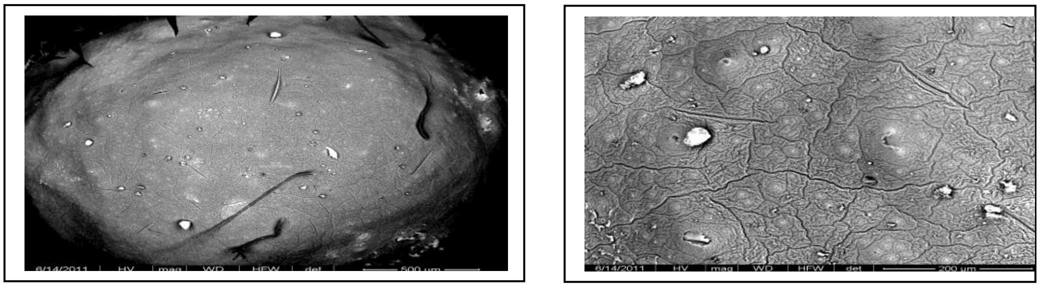


**Fig. 8. Ca-alginate bead after tannery wastewater treatment**

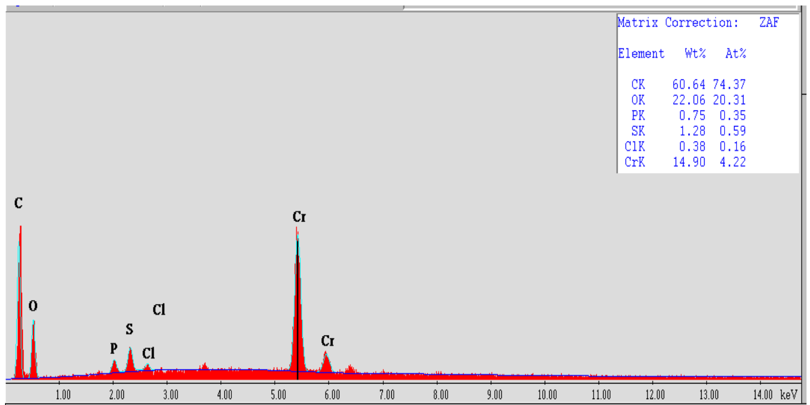



**Fig. 9. EDAX analysis for Ca-alginate bead after tannery wastewater treatment**

## 3.4 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 frequency range from 500 to 4000 Cm-1. This analysis had eventually confirmed the functional groups in relation to adsorption occurred and to change in chemical composition. FT-IR is carried out to Ca-alginate beads as shown in **Figures (10).** Results of FT-IR analysis confirmed that the Ca-alginate-beads had several binding sites which can involved in the uptake process. The most likely binding sites were carboxyl groups where, carboxylic acid dimers display very broad at 1400.2 and 3220.9 cm−1, intense O–H stretching absorption at 3622.1 cm−1 were present. Similar explanation was obtained by **{7, 5, 9}**.

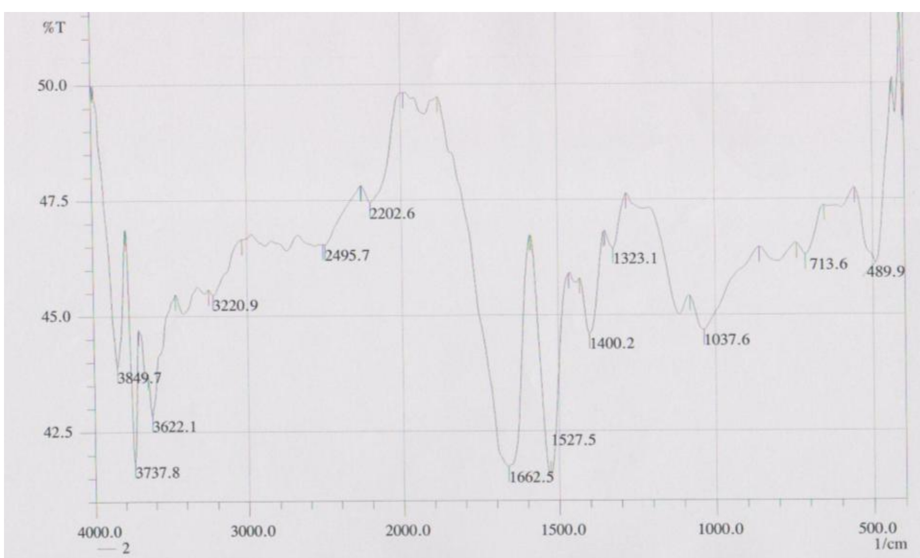



**Fig. (10): FT-IR spectrum for Ca-alginate beads**

## 4. CONCLUSION

Current interest in the state of environment has resulted in increased research to evaluate the global impacts of pollution on the biosphere. In order to fight damage to the environment by organic and inorganic pollutants, there are needs to develop treatment technologies. Alginate in the form of calcium cross-linked beads, exhibit high uptake capacity for chromium, cadmium, copper, lead, nickel, iron and manganese ions depend on their initial ion concentration with removal efficiency from 43.5% to 74.8%. Ca-alginate beads have been also shown to take up organic loads from tannery wastewater such as TDS, salinity, COD, BOD, ammonia nitrogen, nitrate and phosphorous depend on their initial concentration with removal efficiency from 39.9 % to 78.6 %. The adsorption experiments were obtained with the initial pH 5.0. Our findings also revealed that the ability of Ca-alginate beads to be recycled for three subsequent cycles with little decrease in the removal efficiencies. So, it can be concluded that Ca-alginate beads is considered to be low cost effective material in treatment of color, organic contents and metal-polluted industrial wastewater.

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