

Optimum conditions for removal of some heavy metal ions from aqueous solutions using cellulose acetate

Ahmed S. Al-Rawi^aTahseen A. Zaidan^bIsmail K. Ibrahim (Al-Khateeb)^c

^{a, c} Department of Chemistry, College of Science, University of Anbar, Ramadi, Iraq.

^bDepartment of Chemistry, College of Applied Science, University of Anbar, Heet, Iraq

Abstract This study describes the ability of cellulose acetate to remove heavy metals (Hg^{+1} , Cd^{+2} , and Pb^{+2}) from aqueous solutions. The extraction operation of these ions was carried out by using the column tech. Different particles size of cellulose acetate ($38 > \mu\text{m}$, $38\text{-}53\mu\text{m}$, $53\text{-}106\mu\text{m}$), different retention times (1 min, 5 min, and 10 min), and various pH (2, 6.7, and 10) to select the optimum conditions for the recovery of these ions were used. Flame and flameless atomic absorption spectroscopy were used to determine the concentration of these ions. The obtained results reveal that the percent adsorption for removal of most ions at (pH = 6.7, particle size less than $38 \mu\text{m}$, and 3 min retention time) was approximately 90%.

Keywords: cellulose acetate, heavy metal, column tech, ions removal, adsorption

1. INTRODUCTION

The rapid development of industry has led to an increase in the pollutants discharged and an increased release of heavy metals into the environment. These represent a serious threat to human health, ecology systems, and bioresources[1]. All of these reasons have led to a remarkable increase in the number of studies seeking to find suitable solutions to reduce or even eliminate heavy metals pollution. There are many processes for removing heavy metals from aqueous solutions, such as ion exchange, chemical precipitation, microfiltration, chemical reduction, membrane filtration, reverse osmosis, and adsorption[2]. Among the different treatment methods, adsorption appears to be the optimum approach on account of its low cost and high efficiency. Recently, cellulose and its derivatives have been used to remove heavy metal ions from aqueous solutions, and the removal depends on several factors, such as the chemical properties of cellulose, the acid and alkaline properties of solutions, the nature of the metallic ion itself (its radius, charge value and strength), the concentration of the metal ion and its competing ions in the solution, and the temperature[3]. Cellulose and its derivatives have a high adsorption capacity on their surfaces. Physically, cellulose is characterized by a fibrous composition and the main fiber forms from microfibrils and together they form many channels inside it. Chemically, it is formed from chains of glucose units bonded by glycoside bonds that are rich in functional groups that can be replaced and modified (Fig.1)[4,5]. The aim of this study is to study the possibility of removing metal ions from polluted water from various industries using cellulose derivatives, assess the performance and effectiveness of these materials in the adsorption of heavy metal ions, and determine

the particle size effect, retention time, and pH of the medium on the adsorption capacity.

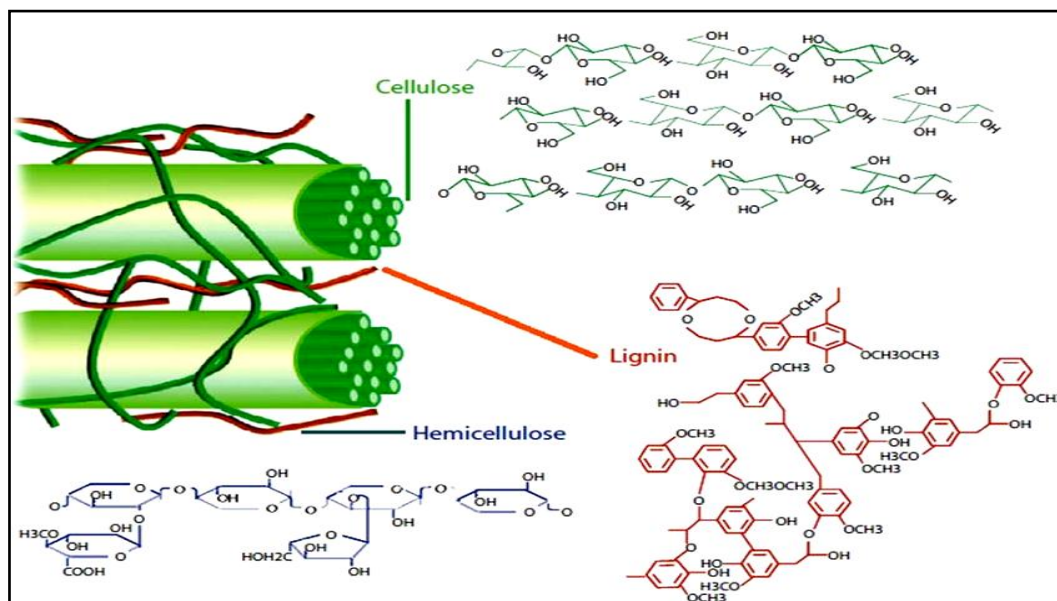


Figure 1. The physical and chemical constitution of cellulose composition

2. MATERIALS AND METHODS

2.1. Materials

Iraqi cotton raw was used for the preparation of cellulose acetate, after being bleached. All chemicals and reagents that were used were from Merck Company and had a high purity of not less than 99.5%.

2.2. Cellulose extraction

10 g of cotton was soaked with 17.5 % potassium hydroxide solution and added with the solid at a liquid ratio of 1:10. The mixture was kept at room temperature for 1 hour. After that, it was filtered, left for 24 hours at a temperature of 60°C , then washed with deionized water to remove the alkaline effect to reach $\text{pH} = 7$. The purified cellulose was dried for 48 hours at a temperature of 60°C [6].

2.3. Cellulose acetate preparation

10 grams of ZnCl_2 anhydrous were dissolved in 85 ml of glacial acetic acid. Next, 5 grams of the extracted cellulose were added in batches, then mixed well and left for 15 minutes. Subsequently, 40 ml of acetic anhydride were added in batches and mixed. The mixture was left for 48 hours at a temperature of 80°C . Then the mixture was diluted with glacial acetic acid and slowly decanted into a container supplied with a mixer containing 15 liters of cool distilled water. The product was filtered, dried, and identified[7].

2.4. Samples preparation

Approx. 10 g of cellulose acetate was dried for 48 hours at a temperature of 60°C, then milled using a tumbler mill and sorted with sieves into three groups according to particle size. The particle size of the groups was: (i) lower than 38 μm; (ii) between 38–53 μm; and (iii) between 53–106 μm.

2.5. Columns preparation

1 g from each group of cellulose acetate was placed in a glass column with a diameter of 1 cm and pressed well after being soaked with deionized water. Ionic solutions were passed through from the top of the column. The solution that came out of the end of the column was collected and analyzed. The recovery process was repeated at different particle sizes of adsorbent, different retention times, and various pH of the medium. The efficiency of the ions recovery process using cellulose acetate was evaluated by ion content, which was determined by atomic absorption spectroscopy. The amount of ion adsorbed onto the adsorbent was calculated using Equation 1 [1].

$$X/M = (C_o - C_e) * V/M \quad \dots\dots\dots (Eq. 1)$$

Where X/M is the amount of ion per mass of adsorbent, C_o is initial ion concentration, C_e is the concentration of an ion after equilibrium has been reached, V is the total volume of the solution to which the adsorbent mass is exposed, and M is the mass of the adsorbent.

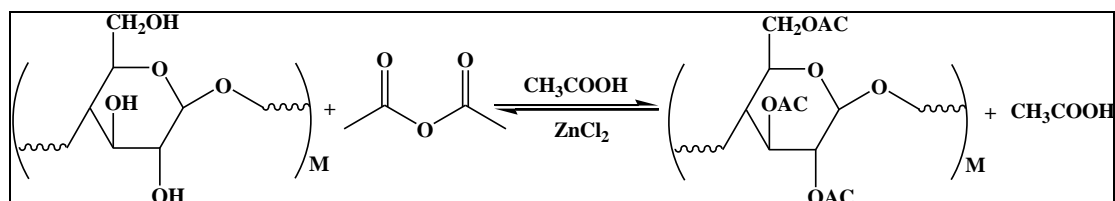
3. RESULTS AND DISCUSSION

3.1. Cellulose extraction

All the raw resources of cellulose are impure, at a best ratio of cellulose less than 80%. So, the purification step is crucial. The major purpose of cellulose extraction was to remove the dissolved parts such as β-cellulose, hemicellulose, and lignin. All of these types of cellulose were dissolved in potassium hydroxide with a concentration of 17.5% except α-cellulose. After the extraction, the extracted cellulose evaluated were found to contain 96.4% of α-cellulose [8].

3.2. Cellulose acetate preparation

The esterification reaction is a reverse endothermic reaction, the contents of which are ester and water so that all chemicals and reagents used in the reaction must be of a high purity. Water molecules must be withdrawn from the reaction to prevent the reverse reaction, through the addition of salts such as zinc chloride anhydrous (see Scheme. 1).



Scheme 1. Reaction of cellulose esterification

In addition, supplying the reaction with heat lead to an increase in the yield. A series of experiments was conducted on the preparation of cellulose acetate according to the method mentioned above. The efficiency of the process was evaluated based on the degree of esterification of cellulose [9,10]. The solubility of cellulose fibers indicates their transformation into cellulose acetate. The experiments show the amount of acetic anhydride and temperature of reaction greatly affected the degree of esterification. When using an excessive amount of acetic anhydride, the content of acetate groups in the products will increase, leading to a higher degree of esterification. Moreover, when the temperature is increased to below 80°C, the cellulose fibers become swollen better, therefore can be adsorbed easily of acetic acid. In contrast, increasing the temperature to over 80°C seems to result in a reduction in the extent of esterification because at high temperatures the phase transition (from liquid to vapor) of acetic acid reduces its activity on cellulose fibers (see Figure 2).

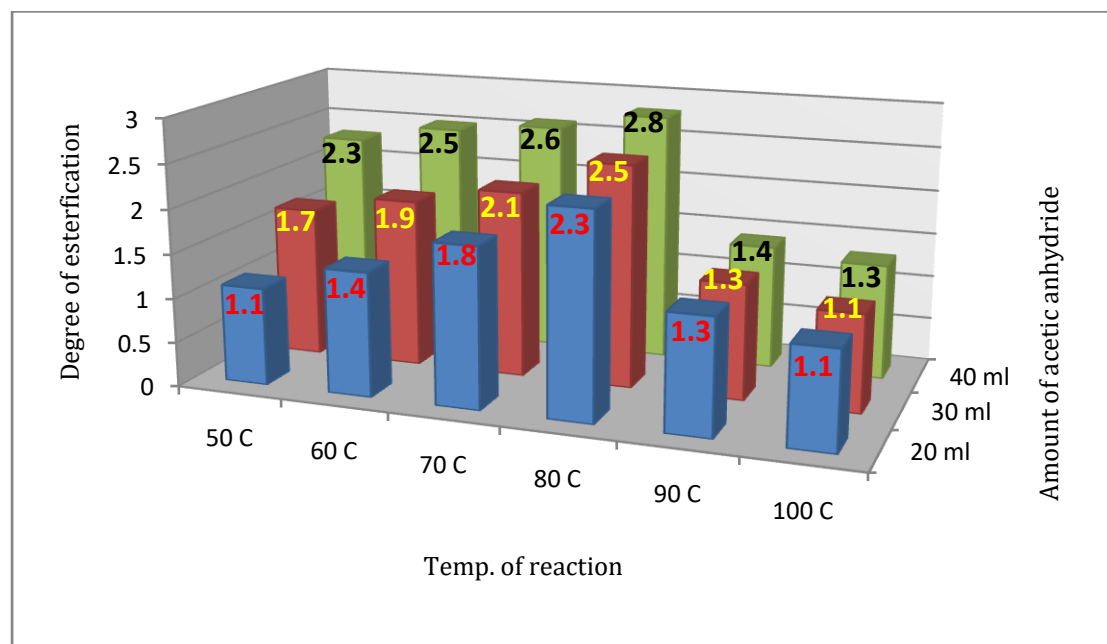


Figure 2. Change of esterification degree with amount of acetic anhydride and temperature of reaction

3.3.(FT-IR) Identification of cellulose acetate

FT-IR spectroscopic inquiries proof about the absorption bands to characterize the prepared cellulose acetate and compared with cellulose bleached. The wavenumbers, ranging from 500-4000 cm^{-1} , show typical peaks of these substances. Broad peaks observed in the area of 3329-3356 cm^{-1} are typical for stretching of hydroxyl groups

intramolecular and intermolecular of cellulose chains. A peak at 1735 cm^{-1} is assigned to stretching of C=O of acetyl groups. Also, peaks appear at 1219 cm^{-1} for cellulose diacetate and at 1217 cm^{-1} for cellulose triacetate. This confirms the presence of $-\text{OCH}_3$ in the structure of cellulose diacetate and cellulose triacetate after esterification. Peaks appearing in the scale of between 1427 cm^{-1} and 1431 cm^{-1} are assigned to scissoring vibration of CH_2 . Stretching of C-O observed at around $1029\text{--}1031\text{ cm}^{-1}$ is typical for glycoside bonds C-O-C in cellulose molecules (Fig. 3)[7].

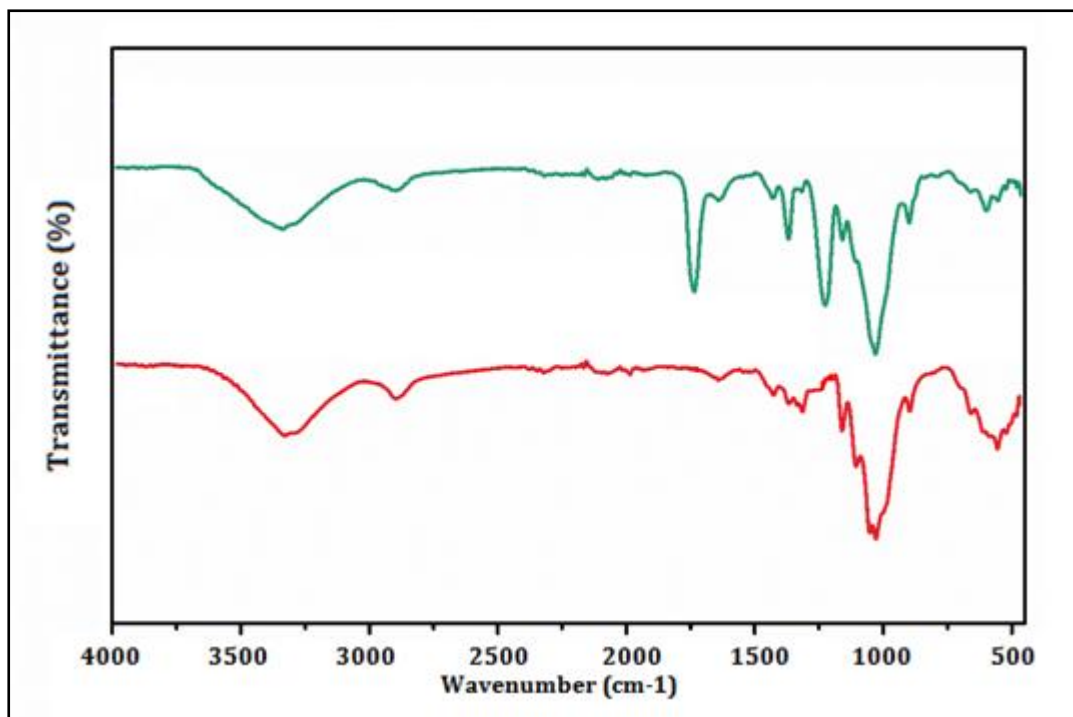


Figure 3. FTIR spectra of bleached cellulose (red) and cellulose acetate (green)

3.4. Optimum conditions for ions recovery

A series of experiments was conducted to select optimum conditions for ions recovery from aqueous solutions according to the method mentioned above. Three factors were identified to study the effects on the recovery process: particle size, retention time, and pH of the medium.

3.4.1. Effect of particles size onto ions recovery

As a preliminary experiment, the recovery operation of these ions was carried out at (pH= 6.7 at room temp.) with 10 min retention time to indicate the best size of these particle groups for removing ions. The results show that at long retention time, ion was removed completely from the aqueous solution by all particle groups. But, at a rapid rate flow with a retention time less than 5 min, the best particle group of absorbent was less than $38\text{ }\mu\text{m}$. The first reason is that the large surface area was available in the smallest size, and the larger surface contained a greater number of channels ready to absorb. In addition, the large surface led to a greater number of functional groups opposed to the solution that can be formed to coordinate bonds with ions (see Figure 4)[11].

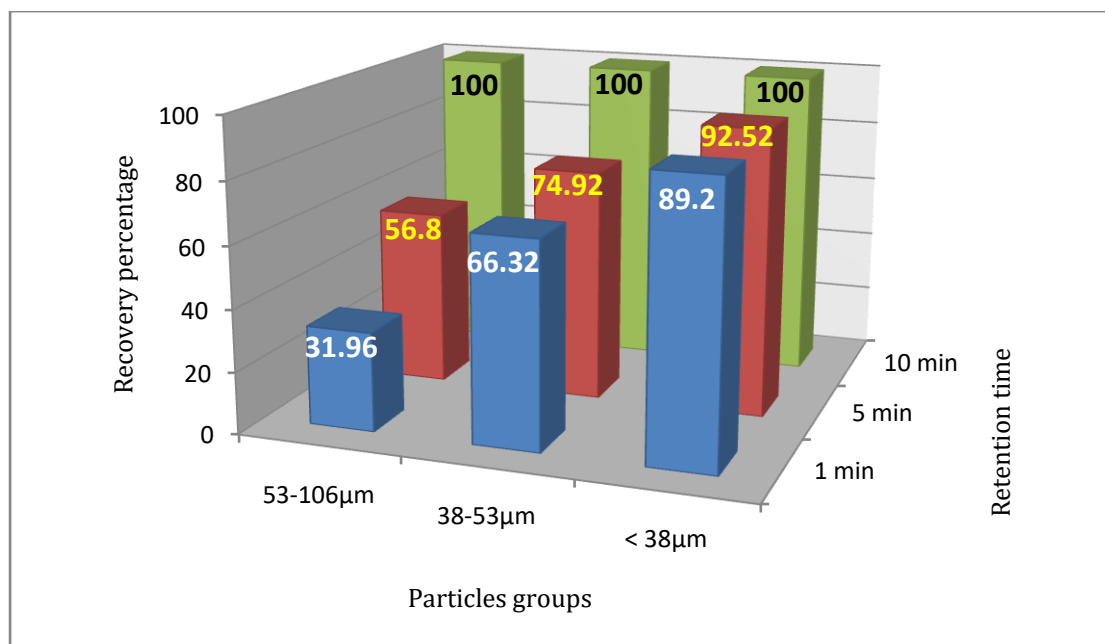


Figure 4. Effects of particles size on ions recovery at pH = 6.7

3.4.2. Effect of retention time onto ions recovery

The increase in retention time has a significant effect on the recovery percentage of ions. The recovery of all ions with an increase in the retention time as the recovery percentage at 1 min was more than 72% for all studied ions. With 2 min retention time, the recovery percentage reached to 80%. At 3 min, the recovery percentage for some ions was more than 90%. According to this, an increase in the contact time of the solution with the adsorbent leads to a greater chance of the ions bonding with active sites in cellulose acetate to reach the equilibrium state (see Figure 5)[12].

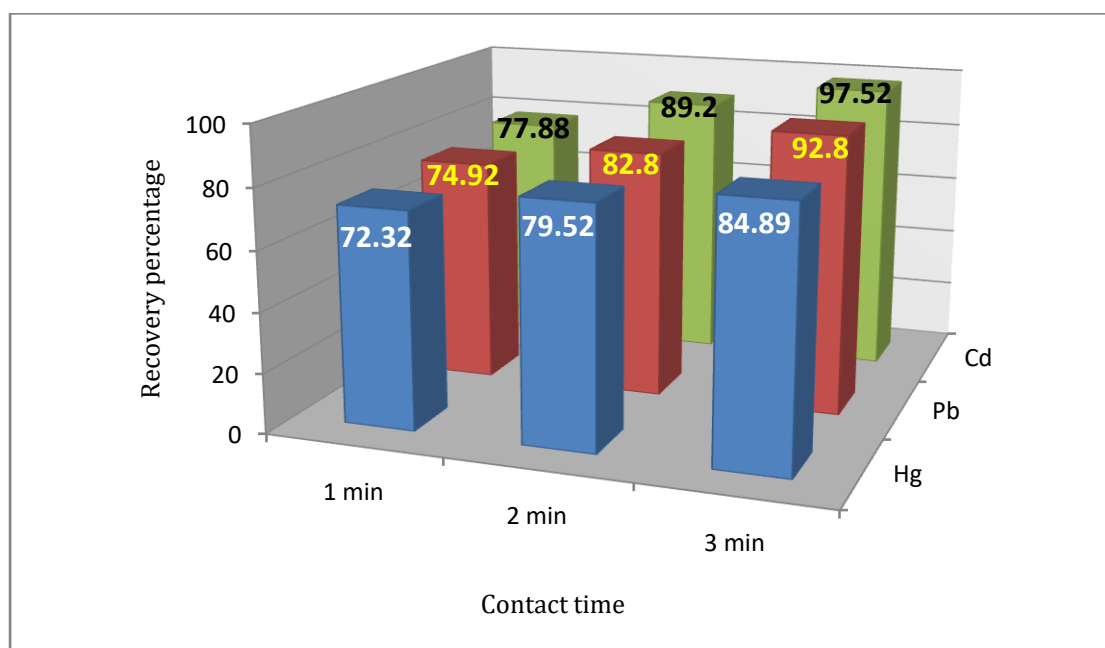


Figure 5. Effects of contact time on ions recovery at pH = 6.7 and particles size < 38 µm

3.4.3. Effect of pH onto ions recovery

The change in the pH of the medium has a significant effect on the recovery percentage of ions, where the recovery percentage of studied ions ranged between 55% and approximately 70% for most ions at pH = 2. The recovery percentage increased to 95% for some ions at pH = 6.7. As for pH = 10, the recovery percentage was reached 80% for all ions. The results indicate that the highest recovery value was recorded in the neutral medium. This means that the chances of adsorption are increased due to the increase in the active sites that are ready for adsorption on the surface of cellulose acetate in the neutral medium. Cellulose acetate is a hydrophilic polymer, and as such it swells to more than 10 times the volume of the dry substance, resulting in a significant increase in the surface area and the number of active sites. Additionally, it has a surface with neutral charges, and increasing the concentration of a negative or positive charge in the medium leads to its shrinking and changing shape, in turn reducing the number of active sites ready to link (see Figure 6)[12].

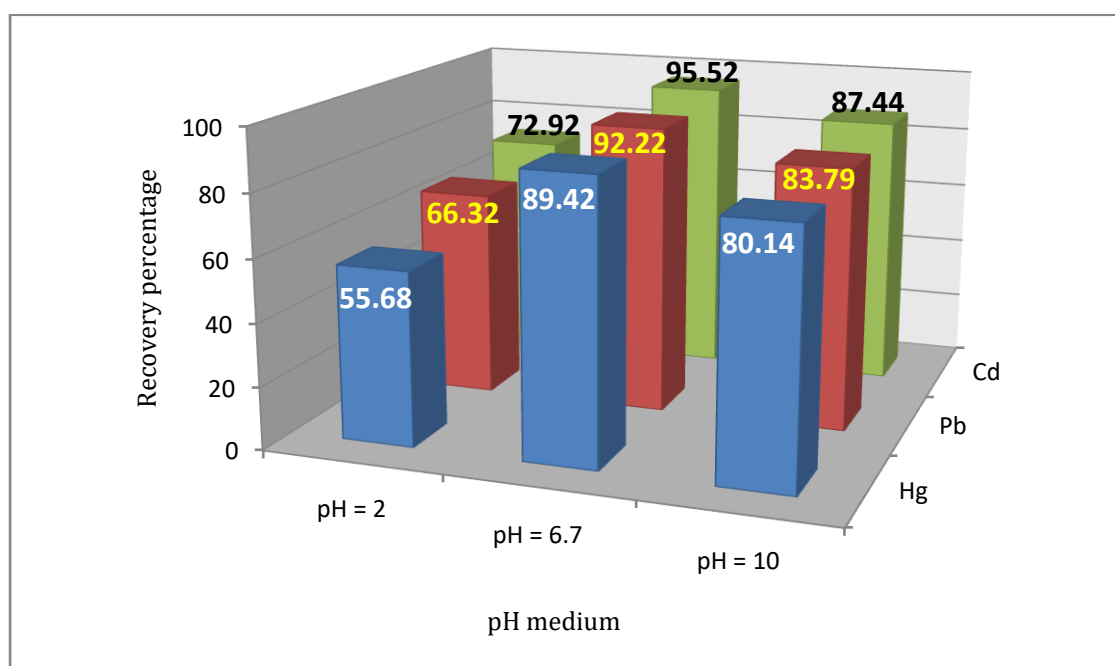


Figure 6. Effects of pH medium on ions recovery at 3 min retention time and particles size < 38 μ m

4. CONCLUSIONS

Cellulose acetate was successfully prepared from bleached Iraqi cotton raw via acetylation. Appropriated conditions for the preparation where: a temperature of 80°C and 40 mL of acetic anhydride. The method produced cellulose acetate with a high degree of esterification, which is typical for cellulose acetate. As for the results of the ions recovery, they revealed that cellulose acetate can be used with high efficiency to recover heavy metal ions from contaminated water, and is considered a good adsorbent surface, ion exchange, and is efficient due to its chemical composition.

5. References

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