

**BIOSORPTIVE-FLOTATION OF MERCURY (II) IONS FROM AQUEOUS SOLUTIONS BY ACTIVATED CARBON PREPARED FROM SUGAR BEET PULP AS A SORBENT AND OLEIC ACID AS A SURFACTANT**

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**ABSTRACT**

The beet pulp, a major low value by-product in sugar industry was used to prepare activated carbon for mercury (II) removal. Bench-scale experiments were conducted in the laboratory, aiming to remove mercury (II) from water. They were based on using activated carbon (AC), which was prepared from sugar beet pulp generated as plant wastes as an effective sorbent and oleic acid (HOL) as a surfactant. The main parameters (namely: initial solution pHs, sorbent, surfactant and mercury (II) concentrations, temperature, shaking time, ionic strength and the presence of foreign ions) that influence the biosorptive-flotation process were examined. Good results were obtained under the optimum conditions, according to which nearly 100% of mercury (II), at pH 7 and at room temperature (~ 25°C), was removed. The procedure was successfully applied to recover mercury (II) spiked to some natural water samples. Moreover, a sorption and flotation mechanism is suggested.

**Keywords:** mercury, biosorptive-flotation, natural water, sugar beet pulp, oleic acid.

**INTRODUCTION**

Mercury is an important and useful industrial material. Mercury and mercury compounds have been used from a long time as pigments in

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inks (cinnabar, red sulphide), as aids to early metallurgy (gilding copper) and instrumentation (thermometers, barometers) and in many industries (recovery of gold from its ores, manufacture of chlorine and sodium hydroxide by electrolysis of brine, etc.), or are present in its wastewaters (**Soé Silva, et al., (2010)**).

Mercury is one of the most toxic metals present in the environment. Once mercury enters the food chain, large concentrations of this element accumulate in humans and animals, causing numerous adverse effects on their health (**Soé Silva, et al., 2010**). Therefore, the removal of this metal from natural water and wastewater is a vitally needed.

During the last few years, increasing attention has been focused on the separation, preconcentration and/or determination of trace-metal ions in the environment. This field of interest is becoming a real challenge due to the specificity, accuracy and sensitivity required by even-more and more stringent regulations (**Havens, et al., 2000 and Brach, et al., 2002**). Numerous techniques are available in this concern and have been reported (**Ghazy, et al., 2001a; Leyden, et al., 1981; Mizuike, et al., 1986; Ghazy, et al., 1994 and Zouboulis, et al., 1994**). These techniques may involve: chemical precipitation, ion exchange, reverse osmosis, electro-deposition, adsorption, solvent extraction and flotation separation processes. Of these, adsorption has proved to be an effective technique.

Activated carbons are unique and versatile adsorbents because of their extended surface area, micro-porous structure, high adsorption capacity and high degree of surface reactivity (**Ghazy, et al., 2001c; Allen, et al., 1995; Youssef, et al., 1996; Ho, et al., 1998 and Samra, 2000**). They find their wide applications in the removal of color, odor, taste and other undesirable organic and inorganic impurities from different aqueous media (**Zouboulis, et al., 1994 and Sharma, et al., 1996**). They are being increasingly used in the field of hydrometallurgy for the recovery of gold, silver, other inorganics and as catalyst support (**Abd El-Rahiem, 1996**). Their use in medicine to combat certain types of bacterial ailment is also well known (**Abd El-Rahiem, 1996**). Moreover, they are usually considered to be adsorbents against which others are assessed (**Sharma, et al., 1996**). However, the adsorption may suffer from economic limitations owing to difficulties encountered in separating the sorbent from the suspension in order for it to be

regenerated (**Zouboulis, et al., 1994**). Therefore, attempts have been made to develop separation techniques.

Flotation as a solid/liquid or liquid/liquid (or both) separation process has recently received considerable interest owing to its simplicity, rapidity, good separation yields ( $R > 95\%$ ) for small impurity concentrations ( $10^{-6} - 10^{-2} \text{ mol.l}^{-1}$ ), a large possibility of applications for species having different nature and structure, flexibility and friability of equipment and processing for recovery purpose (**Stoica, et al., 1998 and Ghazy, et al., 2003**). It is believed that this process will soon be incorporated as a clean technology to treat both water and wastewater (**Rubio, et al., 2002**). For the aforementioned reasons a combination of adsorption and flotation into a unified operation termed sorptive-flotation could be considered as a vital process (**Ghazy, et al., 2001d**).

In developing countries, the pollution control measures frequently need to be based on lower cost technologies. In this context, one area that is being explored is the use of naturally occurring materials that have the potential for adsorbing pollutants (**Sharma, et al., 1996**). Accordingly, this investigation aims to establish a selective, rapid and simple procedure for the removal of mercury ions from aqueous solutions using activated carbon (in the powder form) obtained from sugar beet pulp, as an organic sorbent (which may be inexpensive, readily available and as alternative to existing commercial adsorbents) and oleic acid as a surfactant under the recommended conditions.

## EXPERIMENTAL

### **1. Activated carbon (AC)**

Sugar beet pulp used in preparation of activated carbon was provided from sugar's plant of Belqas, Egypt. The sugar beet pulp was first dried to obtain minimum humidity. Then, the dried sample heated first by boiling in 0.1N  $\text{HNO}_3$  for three hours. The solution was decanted and the residue was treated further by boiling in 0.1N  $\text{NaOH}$ , again for three hours. The treated adsorbent was washed several times with double distilled water. The material was soaked in double distilled water for sufficient amount of time (till it registered neutral pH), as swelling would produce more sites for adsorption. After collecting sufficient quantities, the treated adsorbent was heated in tube furnace at temperature of  $700^\circ\text{C}$  for time 150 min. The activated carbon was ground and sieved to obtain different particle size ranging from (125-750  $\mu\text{m}$ ). Finally, the prepared

activated carbon samples were stored in air tight bottles and placed in a  $\text{CaCl}_2$  desiccator until use in adsorption experiments.

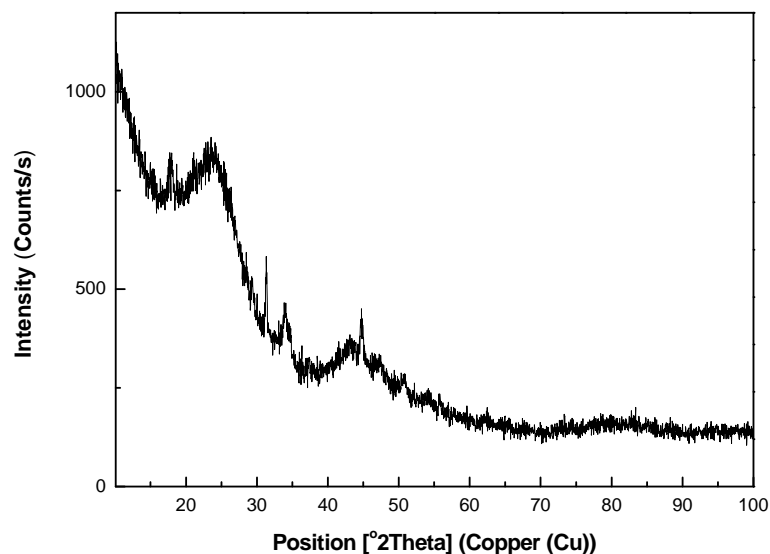
Experimental characterization of the carbon sample under investigation (Table 1) revealed that: Its density was  $0.674 \text{ g.cm}^{-3}$ , its suspension pH after 4 h of stirring (water pH = 6.8) was 8.15, the surface acidic groups were: carboxylic ( $0.25 \text{ mmole.g}^{-1}$ ), lactonic ( $1.375 \text{ mmole.g}^{-1}$ ), phenolic ( $0.625 \text{ mmole.g}^{-1}$ ), the total basic groups were ( $1.4875 \text{ mmole.g}^{-1}$ ), water soluble matter was 13 %, iodine value was  $355.6 \text{ mg.g}^{-1}$ , moisture content was 3.7 %, ash content was 15.738%, volatile matter content was 13.168%, and fixed carbon was 67.394%.

**Table (1)** :Characteristics of activated carbon:

No.	Parameter	Value
1	Particle size	125-250 $\mu\text{m}$
2	Density	$0.674 \text{ g.cm}^{-3}$
3	Suspension pH after 4 h stirring (water pH = 6.8)	8.15
4	Iodine value	$355.6 \text{ mg.g}^{-1}$
5	Moisture content	3.7 %
6	Ash content	15.738%
7	Volatile matter content	13.168%
8	Fixed carbon	67.394%
9	Water soluble matter	13 %
10	Surface acidic groups a- Carboxylic b- Lactonic c- Phenolic Total basic groups	$0.25 \text{ mmole.g}^{-1}$ $1.375 \text{ mmole.g}^{-1}$ $0.625 \text{ mmole.g}^{-1}$ 1.4875 $\text{mmole.g}^{-1}$

### 1.1. XRD analysis

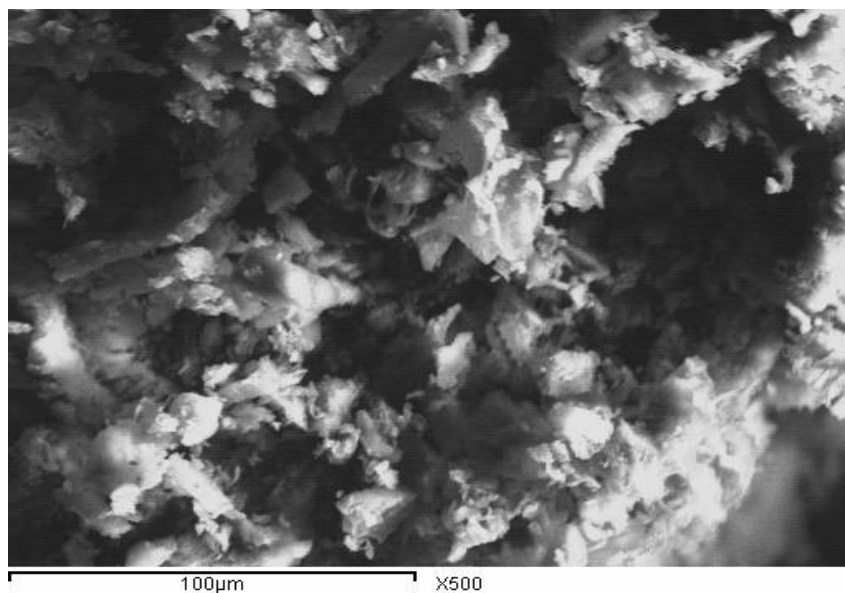
X-ray diffraction pattern of the activated carbon sample is shown in figure 1. It is clearly noticed that, there is a broad diffraction peak at 2 theta (20-27), this is attributed to the amorphous nature of activated carbons. Also, the appearances of other broad peaks are due to the presence of voids within the activated carbons.



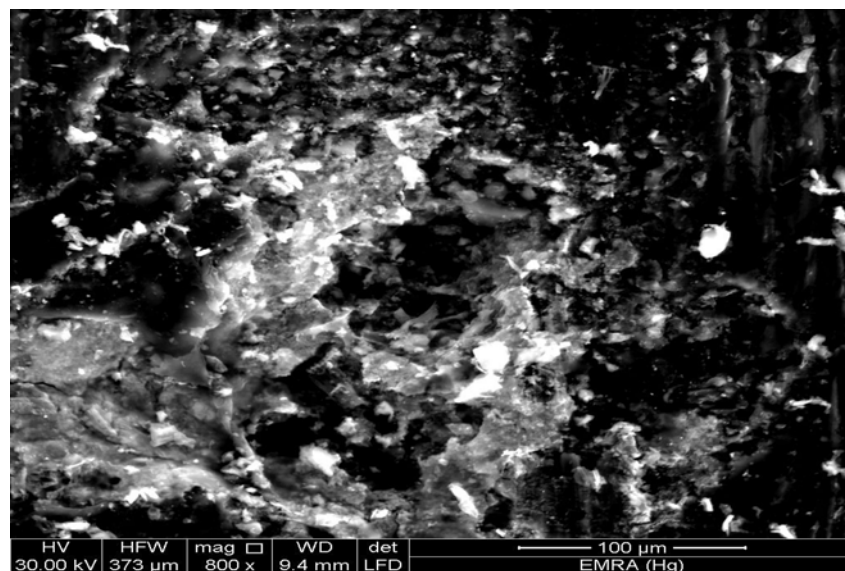
**Fig. (1):** X-ray diffraction of activated carbon sample

### **1.2. Surface morphology:**

A scanning electron microscope (SEM) was used to examine the surface of the activated carbon sample. The SEM images (Figures 2a and 2b) show a highly porous morphology of adsorbent with pores of different sizes and shapes. This was because during carbonization process of raw material at high temperature (700°C), most volatile matter was lost and thus created a system with advanced pore structure. Pores development in an activated carbon is important since pores act as active sites which played the main role in adsorption. Pores formed on surface of adsorbent are sites for metals to be adsorbed onto the adsorbent.



**Fig. (2) a:** SEM image of activated carbon sample free of metal.

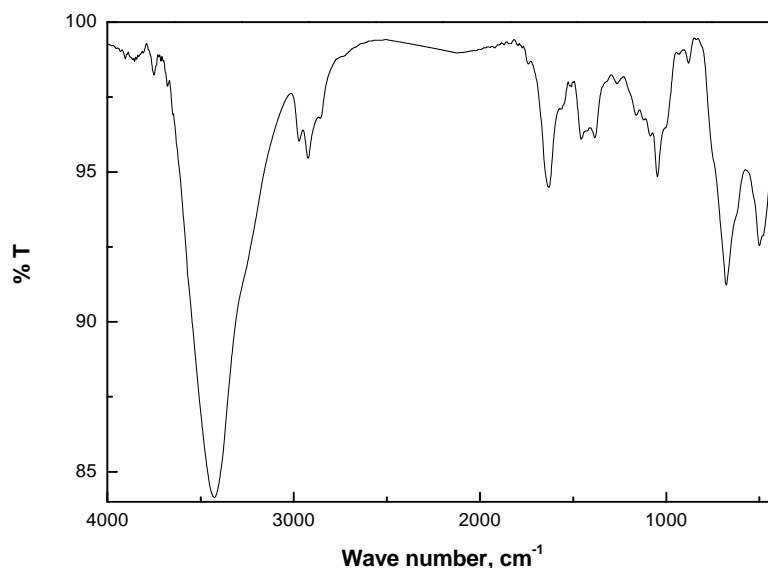


**Fig. (2) b:** SEM image of activated carbon sample loaded with metal.

### **1.3. Fourier Transform-Infrared spectroscopy (FT-IR):**

FT-IR investigates the surface carbon-oxygen groups and used to obtain information about the nature of possible interaction between the functional groups of activated carbon sample with  $\text{Hg}^{2+}$ . The activated

carbon sample was diluted with KBr, compressed into wafer and FT-IR spectrum was recorded by FT/IR-6100 type A spectrophotometer. The result obtained is given in figure 3.



**Fig. (3):** FT-IR spectrum of activated carbon sample.

A variety of C-O (carbon oxygen) surface functional groups were observed in the activated carbon sample:

O-H stretching mode of hydroxyl groups and adsorbed water at  $3424.96\text{ cm}^{-1}$ , asymmetric C-H stretching vibrations of the methyl group at  $2970.8\text{ cm}^{-1}$ , asymmetric C-H stretching vibrations of the methylene group at  $2922.59\text{ cm}^{-1}$ , carbonyl group at  $1628.59\text{ cm}^{-1}$ , in-plane bending vibration of C-H in methyl group at  $1383.68\text{ cm}^{-1}$ , C-O stretching in acids, alcohols, phenols, ethers and esters at ( $1264.11, 1161.9, 1085.73, 1047.16\text{ cm}^{-1}$ ), out of plane deformation mode of C-H in various substituted benzene rings at ( $880.345, 677.856, 500.437\text{ cm}^{-1}$ ).

Not only the C-O of phenolic, carbonyl and carboxylic groups were present in the FT IR spectrum of activated carbon, but also the asymmetric and symmetric stretching of C-H stretching vibrations of methylene group were observed. The presence of such methylene groups induces hydrophobicity into the carbon material.

## **2. Reagents**

All of the solutions were prepared from certified reagent grade chemicals.

### **2.1. Mercury (II) solution**

1.354 g of mercury (II) chloride and 10 g of NaCl were dissolved in water and diluted to 1000 ml. This stock solution ( $1 \text{ mg.ml}^{-1}$ ) was diluted with water to prepare required solutions which were used for further studies. Presence of NaCl provides sufficient chloride ion concentration to hold the mercury (II) in the solution as anionic complex  $[\text{HgCl}_4]^{2-}$  (tetrachloro mercurate (II)) and this prevent the reduction of Hg (II) to Hg (I) by activated carbon sorbent.

### **2.2. Buffer solution of potassium iodide**

5 g of potassium iodide and 5 g of potassium hydrogen phthalate were dissolved in water and a few crystals of sodium thiosulphate was added to it and diluted to 250 ml with water.

### **2.3. Rhodamine 6G solution (0.005 wt.%)**

0.05 g of rhodamine 6G was dissolved in water and diluted to 1 liter.

### **2.4. Other ions stock solutions**

( $10 \text{ g.l}^{-1}$ ) each, was prepared by weighing the requested amount in doubly distilled water. The metal salts were used as their chlorides whereas the anions were used as their sodium or potassium salts. Standard aqueous solutions of HCl, and NaOH were used for pH adjustments with measurements being carried out using HI931401 microprocessor pH meter.

## **3. Method for determination**

The residual Hg (II) concentration in the filtrate was analyzed by monitoring the absorbance at 575 nm (characteristic of  $\text{R}_2\text{HgI}_4$  complex) using rhodamine 6G and buffered potassium iodide as reagents. UV-Vis spectra of the pink colored ( $\text{R}_2\text{HgI}_4$ ) solutions were recorded on a UV-1100 spectrophotometer with 1 cm glass cells.

## **4. Instruments and equipments**

Spectrophotometric measurements were carried out using a UV-1100 spectrophotometer with 1 cm glass cells. A flotation procedure was



carried out in a flotation cell, which was a cylindrical tube of 1.5 cm inner diameter and 29 cm length with a stopcock at the bottom (**Ghazy, et al., 2001b**). The stirring of solutions was performed with a magnetic stirrer Model VEHP, Scientifica, Italy. The shaking of solutions was performed with a nuve SL 350 shaker at 250 rpm. The pH was measured using a HI931401 microprocessor pH meter.

### **5. General procedure**

To study the different parameters affecting the sorptive-flotation process, 10 ml aliquot of suspension containing defined amounts of  $\text{Hg}^{2+}$  ion, sorbent sample, HCl,  $\text{HNO}_3$  or  $\text{H}_2\text{SO}_4$  and/or NaOH (for controlling pH) was introduced into a flotation cell. The flotation cell was shaken for the optimized time, to ensure complete flotation of  $\text{Hg}^{2+}$  ion with sorbents. To this suspension inside the cell, 3 ml of HOL was added. Again, the cell was inverted upside down twenty times by hand and kept standing for 5 min to complete flotation.

The removal percentage ( $R_e$  %) of  $\text{Hg}^{2+}$  calculated from the relationship:

$$R_e \% = (1 - C_f/C_i) \times 100\%,$$

where:  $C_i$  and  $C_f$  denote the initial and residual  $\text{Hg}^{2+}$  ions concentrations.

To study the flotation of sorbent, the previous procedure steps were performed in the absence of  $\text{Hg}^{2+}$  ion. After complete flotation, the float containing sorbent was filtered through a  $G_5$  sintered-glass filter (porosity 1–1.5  $\mu\text{m}$ ) and dried in an oven at  $125^\circ\text{C}$  to a constant weight.

The floatability percentage ( $F$  %) of the sorbent was calculated as following:

$$F \% = C_f/C_i \times 100\%,$$

where:  $C_i$  and  $C_f$  denote the initial and float concentrations of the AC sorbent.

All experiments were carried out at room temperature ( $\sim 25^\circ\text{C}$ ).

Another series of experiments were carried out on 1 L of pre-filtered natural water samples suspension (placed into 2 L glass beaker) containing a definite amount of activated carbon sample, 10 ml of  $1 \times 10^{-3}$   $\text{mol.l}^{-1}$  HOL with initial pH adjusted to the required value and spiked with  $\text{Hg}^{2+}$  ion. The suspension was mechanically stirred at 250 rpm for the recommended time. It was noted that the  $\text{Hg}^{2+}$ -sorbent-HOL system is self-floatable without need for a stream of air bubbles.

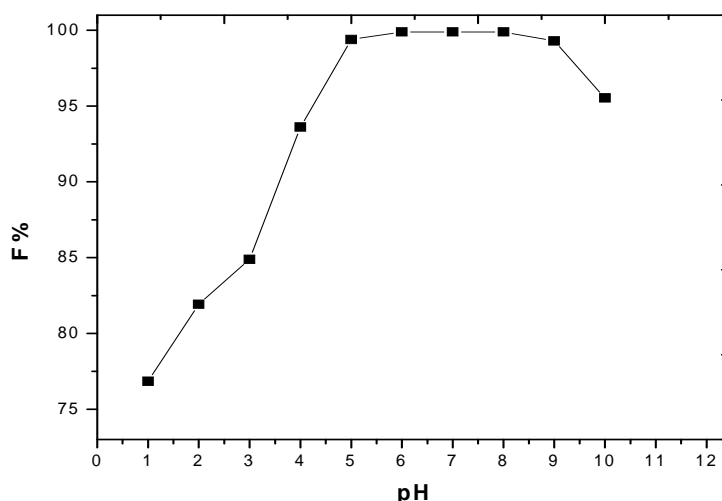
## RESULTS AND DISCUSSION

### 1. Floatability of activated carbon (AC)

The removal of fine particles of carbon sorbent from aqueous solutions (particularly those that passed through a filtration medium) was an obvious economic measure for the undertaken studies.

#### 1.1. Effect of pH

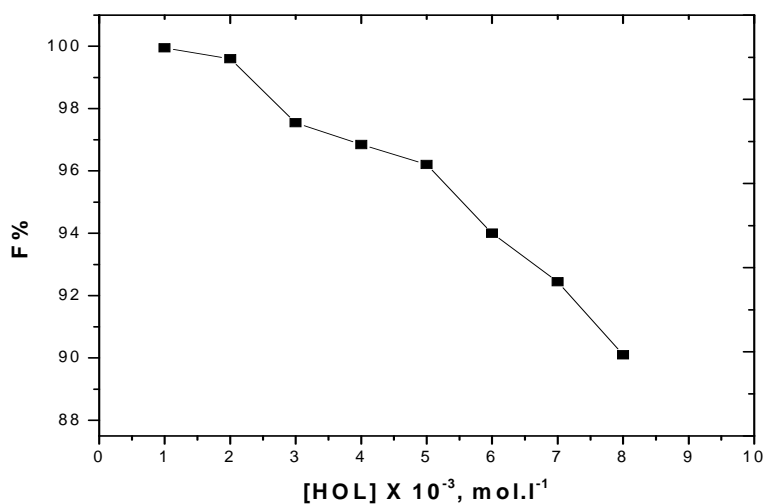
Preliminary series of experiments was conducted to float 1000 mg.l<sup>-1</sup> of AC over a wide range of pH values using 1×10<sup>-3</sup> mol.l<sup>-1</sup> HOL. The obtained results are depicted in figure 4, from which it is clear that a maximum flotation (~ 100 %) for AC was attained over a wide pH range (5-9).



**Fig. (4):** Flotation of 1000 mg.l<sup>-1</sup> of AC using 1×10<sup>-3</sup> mol.l<sup>-1</sup> HOL at different pH values.

#### 1.2. Effect of surfactant concentration

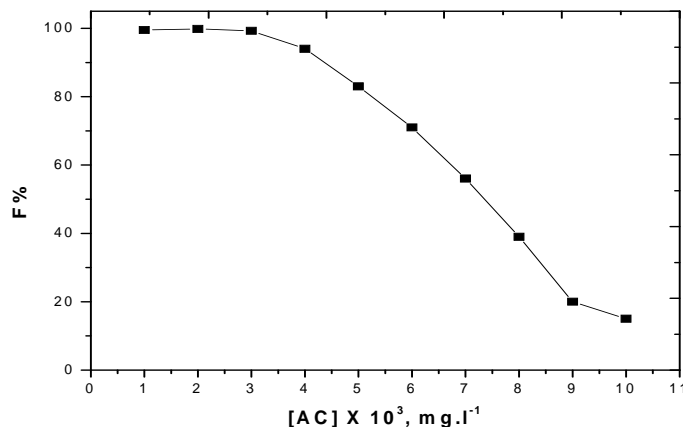
The separation of 1000 mg.l<sup>-1</sup> of activated carbon using different concentrations of oleic acid (HOL) surfactant at pH 7 is presented in figure 5. The results proved that oleic acid is an effective surfactant for a quantitative removal of the sorbent when the concentration is 1×10<sup>-3</sup> mol.l<sup>-1</sup>. In general, it was found that for the undertaken studies the recommended HOL concentration was 1×10<sup>-3</sup> mol.l<sup>-1</sup>.



**Fig. (5):** Flotation of  $1000 \text{ mg.l}^{-1}$  of AC at pH 7 using different concentration of HOL.

### **1.3. Effect of sorbent dosage**

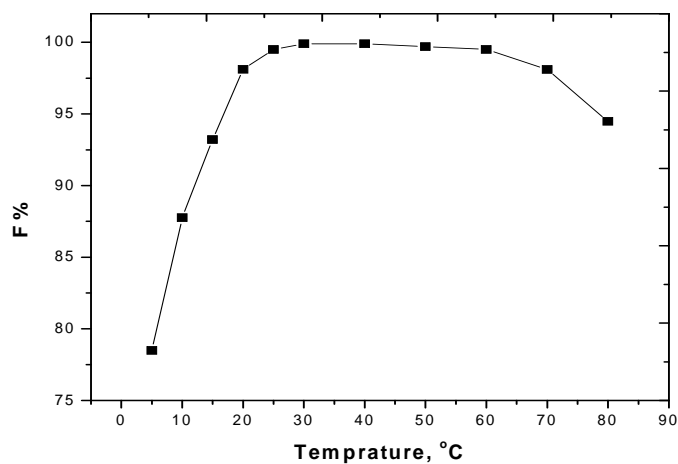
Another series of experiments was carried out to float different concentrations of AC samples using  $1 \times 10^{-3} \text{ mol.l}^{-1}$  of HOL at pH 7. As can be seen from the data recorded in figure 6, quantitative separation of the sorbent was attained over a wide concentration range up to concentration of  $3000 \text{ mg.l}^{-1}$ . Hence, for all experiments the recommended concentration of AC is  $1000 \text{ mg.l}^{-1}$ .



**Fig. (6):** Flotation of different concentrations of AC using  $1 \times 10^{-3}$  mol.l<sup>-1</sup> HOL at pH 7.

#### 1.4. Effect of temperature

In order to find the suitable temperature for complete flotation of 1000 mg.l<sup>-1</sup> of AC at pH 7 using  $1 \times 10^{-3}$  mol.l<sup>-1</sup> HOL, an extensive series of experiments was carried out at different temperatures. The results recorded in figure 7 show that the floatability of sorbent was not affected by increasing the temperature up to 70°C.



**Fig. (7):** Effect of temperature on the flotation of 1000 mg.l<sup>-1</sup> of AC using  $1 \times 10^{-3}$  mol.l<sup>-1</sup> HOL at pH 7.

From the above results it is obvious that the process is economic and effective (F~100%) since it needs small concentration of surfactant ( $1 \times 10^{-3} \text{ mol.l}^{-1}$  HOL) to float high concentrations of AC ( $1000 \text{ mg.l}^{-1}$ ) and acting at a wide range of pH (5-9) and temperature range of (10-70°C).

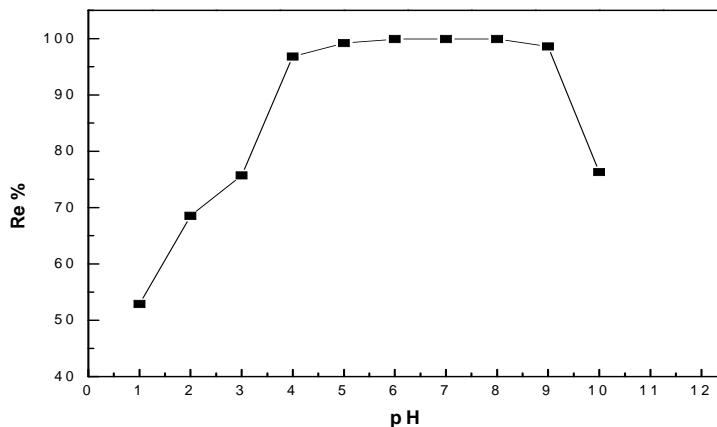
## **2. Removal of mercury ions**

### **2.1. Effect of pH**

The concentrating tendency of hydroxyl ion in the float is sensitive to variations in the solution pH. In order to find the optimal pH value for the biosorptive-flotation process, the removal efficiency of  $\text{Hg}^{2+}$  ions over the pH range (1 – 10) was studied. Figure 8 illustrates the influence of the pH on the combined process of sorption and flotation for the removal of  $15 \text{ mg.l}^{-1}$  of  $\text{Hg}^{2+}$  ions using  $1000 \text{ mg.l}^{-1}$  of AC and  $1 \times 10^{-3} \text{ mol.l}^{-1}$  of HOL. It should be noted that the removal of  $\text{Hg}^{2+}$  ions was diminished at  $\text{pH} < 4.0$ , which may be attributed to the fact that at strong acidic medium i.e. at higher  $\text{H}^+$  ion concentration, the adsorbent surface becomes more positively charged, thus reducing the attraction between adsorbent and metal ions, also the oxo groups ( $\text{C}_x\text{O}$  and  $\text{C}_x\text{O}_2$ ) formed on the carbon surface during activation react with water according to  $\text{C}_x\text{O}_2 + \text{H}_2\text{O} = \text{C}_x\text{O}^{2+} + 2\text{OH}^-$  to form a positively charged surface group (Sharma, et al., 1996), thereby hindering the adsorption of  $\text{Hg}^{2+}$  ions.

When the pH increases, the concentration of hydronium ion ( $\text{H}_3\text{O}^+$ ) is very low, biosorbent surface was more negatively charged, and functional groups of biomass such as carboxylic groups were more deprotonated in a wide range of pH from (4 – 9), thus the sites are easily available for metal ion binding. So, the proton competition was decreased, and the removal percentage of metal ions is increased.

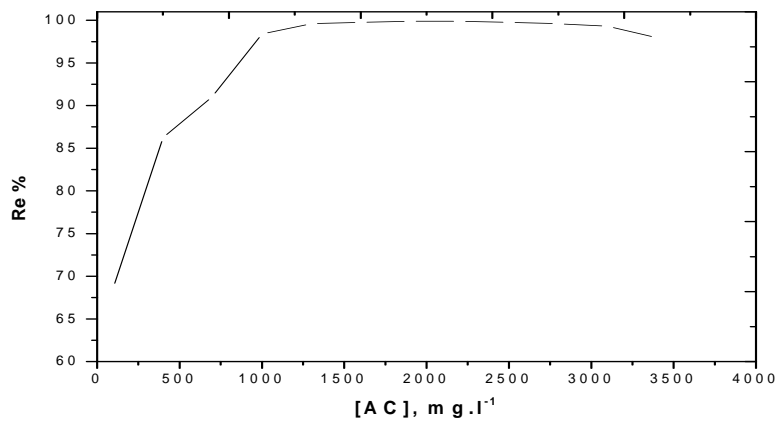
The decrease in the removal rate at high pH values ( $> 9$ ) may be attributed to the fact that oleate anions are not capable of combination with the negative surface of AC. Therefore, pH 7 was recommended throughout all other experiments.



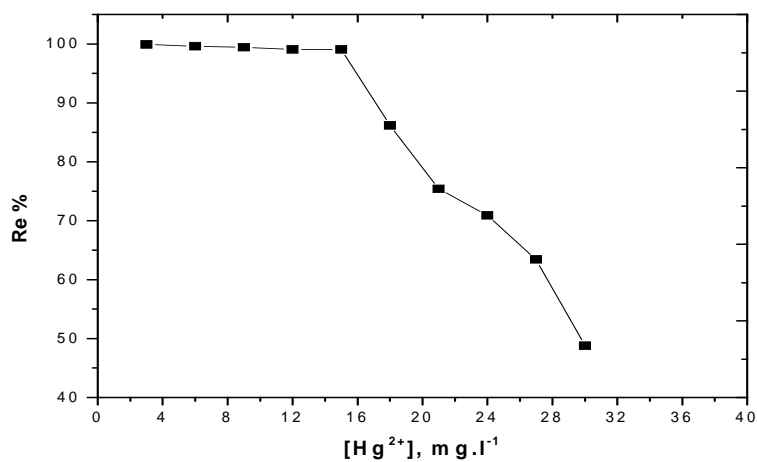
**Fig. (8):** Removal (%) of  $15 \text{ mg.l}^{-1}$  of  $\text{Hg}^{2+}$  ions from aqueous solutions as a function of the pH using  $1000 \text{ mg.l}^{-1}$  of AC and  $1 \times 10^{-3} \text{ mol.l}^{-1}$  of HOL.

## **2.2. Effect of sorbent and metal ion concentrations**

Two parallel series of experiments were performed to study the influence of the activated carbon dose (Figure 9) and changing mercury concentrations (Figure 10) on the removal percentage of  $\text{Hg}^{2+}$  ions from aqueous solutions at pH 7 using  $1 \times 10^{-3} \text{ mol.l}^{-1}$  of HOL. As can be seen from figure 9, the removal percentage of  $\text{Hg}^{2+}$  ions increased as the AC dose increased, while it decreased as the concentration of the metal ion increased (Figure 10). The reason for attaining a maximum removal of  $\text{Hg}^{2+}$  ions (~100%) at a higher AC dose may be due to an increase in the number of binding sites on the adsorbent available to  $\text{Hg}^{2+}$  ions. Hence,  $1000 \text{ mg.l}^{-1}$  of AC may be a suitable dose for the removal of  $\text{Hg}^{2+}$  ions having a concentration of  $\leq 15 \text{ mg.l}^{-1}$ .



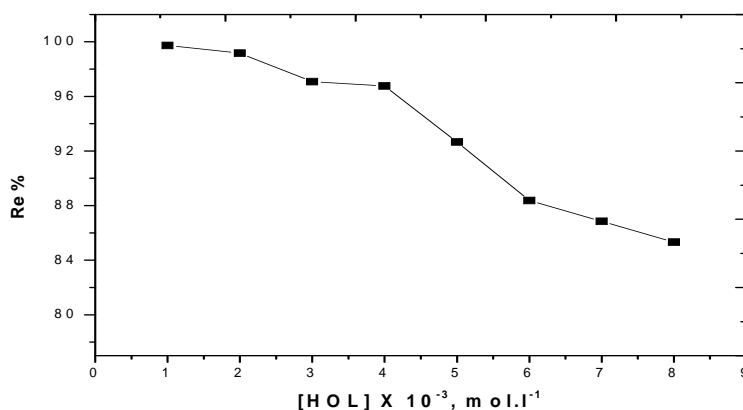
**Fig. (9):** Removal (%) of 15 mg.l<sup>-1</sup> of Hg<sup>2+</sup> ions from aqueous solutions using different concentrations of AC and 1×10<sup>-3</sup> mol.l<sup>-1</sup> of HOL at pH 7.



**Fig. (10):** Removal (%) of different concentrations of Hg<sup>2+</sup> ions from aqueous solutions using 1000 mg.l<sup>-1</sup> of AC and 1×10<sup>-3</sup> mol.l<sup>-1</sup> of HOL at pH 7.

### 2.3. Effect of surfactant concentration

A series of experiments was undertaken to float  $15 \text{ mg.l}^{-1}$  of  $\text{Hg}^{2+}$  ions from aqueous solutions at pH 7, in the presence of  $1000 \text{ mg.l}^{-1}$  of AC sorbent, using different concentrations of HOL. The obtained results (Figure 11) showed that a complete removal of  $\text{Hg}^{2+}$  ions ( $\sim 100\%$ ) was attained at the HOL concentration of  $1 \times 10^{-3} \text{ mol.l}^{-1}$ . The removal of  $\text{Hg}^{2+}$  ions decreased at concentrations above this concentration, a phenomenon that may be attributed to the formation on the air bubble surface of a stable, hydrated envelop of surfactant, or alternatively to the formation of a hydrated micellar coating on the solid surface. In either case, the hydrophobicity of the surface would then not be satisfactory for flotation (Ghazy, et al., 2001c) and (Klassen, et al., 1963). Consequently, the concentration of HOL was fixed at  $1 \times 10^{-3} \text{ mol.l}^{-1}$  throughout all other experiments.



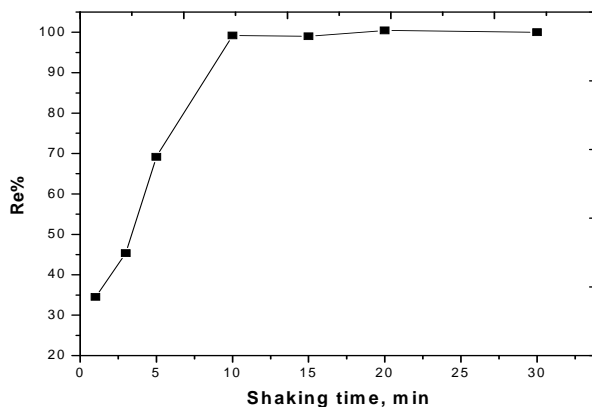
**Fig. (11):** Removal (%) of  $15 \text{ mg.l}^{-1}$  of  $\text{Hg}^{2+}$  ions from aqueous solutions using  $1000 \text{ mg.l}^{-1}$  of AC and different concentrations of HOL at pH 7.

### 2.4. Effect of shaking time

The variation in the removal percentage of  $\text{Hg}^{2+}$  ions with the shaking time was also studied using  $15 \text{ mg.l}^{-1}$  of  $\text{Hg}^{2+}$  ions,  $1000 \text{ mg.l}^{-1}$  of AC and  $1 \times 10^{-3} \text{ mol.l}^{-1}$  of HOL at pH 7. The shaking time was varied from (1-30) min. The obtained results (Figure 12) showed that the percentage removal increased to its maximum value ( $\sim 100\%$ ) after shaking time of 10 min for  $15 \text{ mg.l}^{-1}$  of  $\text{Hg}^{2+}$  ions. Therefore, 10 min of



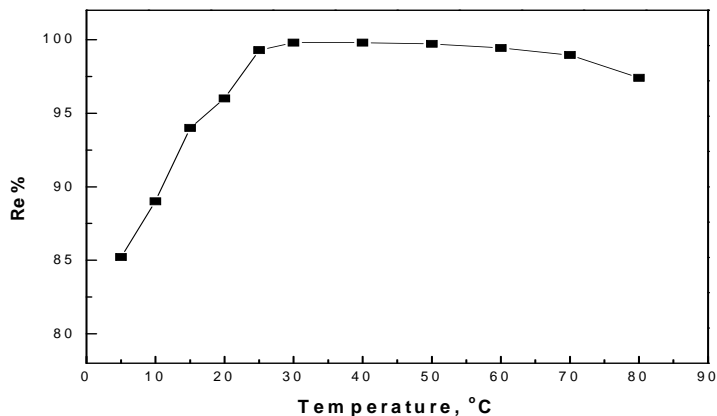
shaking was considered to be sufficient for the removal of  $\text{Hg}^{2+}$  ions having a concentration of  $15 \text{ mg.l}^{-1}$ . Thus, 10 min of shaking was recommended for all experiments in this investigation.



**Fig. (12):** Effect of shaking time on the removal (%) of  $15 \text{ mg.l}^{-1}$   $\text{Hg}^{2+}$  ions using  $1000 \text{ mg.l}^{-1}$  of AC and  $1 \times 10^{-3} \text{ mol.l}^{-1}$  of HOL at pH 7.

### **2.5. Effect of temperature**

Studies of the influence of temperature on the separation process seemed to be important from a practical viewpoint, especially in the case of hot industrial effluents. For such studies, one solution containing  $15 \text{ mg.l}^{-1}$  of  $\text{Hg}^{2+}$  ions and  $1000 \text{ mg.l}^{-1}$  of AC and a second solution containing  $1 \times 10^{-3} \text{ mol.l}^{-1}$  of HOL were either heated or cooled to the same temperature using a water bath. The surfactant solution was quickly poured onto the  $\text{Hg}^{2+}$  solution contained within a flotation cell jacketed with 1-cm thick fiberglass insulation. The mixture was then floated using the previously described procedure. The obtained results (Figure 13) indicated that the removal percentage of  $\text{Hg}^{2+}$  ions increased as the temperature increased. Such data indicate that the adsorption of  $\text{Hg}^{2+}$  ions may proceed through chemical bond formation, which is in good agreement with literature data (Yubin, et al., 1998). Such results suggest the creation of new active sites on the surface of AC available for  $\text{Hg}^{2+}$  ions adsorption.



**Fig. (13):** Effect of temperature on the removal (%) of  $15 \text{ mg.l}^{-1} \text{ Hg}^{2+}$  ions using  $1000 \text{ mg.l}^{-1}$  of AC and  $1 \times 10^{-3} \text{ mol.l}^{-1}$  of HOL at pH 7.

### **2.6. Effect of ionic strength**

Table 2 shows the effect of the ionic strength on the floatability of  $15 \text{ mg.l}^{-1}$  of  $\text{Hg}^{2+}$  ions using  $1000 \text{ mg.l}^{-1}$  of AC and  $1 \times 10^{-3} \text{ mol.l}^{-1}$  of HOL at pH 7. The cations and anions nearly present in natural water samples were taken into consideration. As can be seen, all of the salts added to the floating medium had no effect on the percentage removal of  $\text{Hg}^{2+}$  ions. Although  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions may form magnesium and calcium oleates, their expected harmful effect on the recovery of  $\text{Hg}^{2+}$  ions was not observed. This situation may be due to the fact that  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions may be used as activators for this process (Ghazy, et al., 2001d). Therefore, this simple biosorptive-flotation procedure may find its application for the recovery of  $\text{Hg}^{2+}$  ions from sea-water samples.

**Table (2):** Effect of ionic strength:

Salt	Concentration, mol.l <sup>-1</sup>	Re %
NaCl	0.1	100
	0.5	100
CaCl <sub>2</sub>	0.1	100
	0.5	99.7
KCl	0.1	100
	0.5	98.8
MgCl <sub>2</sub>	0.1	100
	0.5	99.3
NH <sub>4</sub> Cl	0.1	100
	0.5	99.9

### **2.7. Effect of foreign ions**

Under the optimized conditions determined for this investigation, the removal percentage of 15 mg.l<sup>-1</sup> of Hg<sup>2+</sup> ions from a solution of pH 7 containing 1000 mg.l<sup>-1</sup> of AC sorbent and 1×10<sup>-3</sup> mol.l<sup>-1</sup> of HOL was studied in the presence of high concentrations of various cations and anions, usually present in some water samples. The corresponding results obtained are listed in table 3. All of the cations were used as their chlorides or sulfates, whereas the anions were used as the corresponding sodium salts. An inspection of the data in table 3 indicates that the removal of Hg<sup>2+</sup> ions was quantitative in all cases.

### **2.8. Application**

To investigate the applicability of the recommended procedure, a series of experiments was performed to recover 10, 15 and 20 mg.l<sup>-1</sup> of Hg<sup>2+</sup> ions added to aqueous and some natural water samples. The biosorptive-flotation experiments were carried out using 1 L of clear, filtered, uncontaminated sample solutions after adjusting their pH values to 7.0. The obtained results are listed in table 4, and show that the recovery was satisfactory and quantitative (~100%) in most cases. Moreover, the recovery of Hg<sup>2+</sup> ions from brackish water samples are good, compared with other fresh-water samples, which may be attributed to the presence of Na<sup>+</sup>, Mg<sup>2+</sup> and Ca<sup>2+</sup> ions in the former ones, acting as activators (Ghazy, et al., 2001b).

Table( 3): Effect of foreign ions:

Foreign ion	Tolerance limit, $\text{mg.l}^{-1} \times 10^3$	Re %
$\text{Na}^+$	11.1	100
$\text{Co}^{2+}$	2.9	99.8
$\text{Mg}^{2+}$	6.9	99.9
$\text{Ca}^{2+}$	7.9	100
$\text{Cu}^{2+}$	0.005	99.5
$\text{Zn}^{2+}$	0.8	99.9
$\text{Ba}^{2+}$	7.2	100
$\text{NH}_4^+$	9.1	100
$\text{Al}^{3+}$	3.8	99.5
$\text{Mn}^{2+}$	6.1	99.7
$\text{Cd}^{2+}$	0.7	99.5
$\text{K}^+$	19.5	100
$\text{Cl}^-$	17.3	99.8
$\text{HCO}_3^-$	0.7	99.5
$\text{S}_2\text{O}_3^{2-}$	5.8	100
$\text{SO}_4^{2-}$	49	99.9
$\text{CH}_3\text{COO}^-$	29.7	100
$\text{NO}_3^-$	31.9	99.1
$\text{C}_2\text{O}_4^{2-}$	22.3	99.7
$\text{HCOO}^-$	29.5	100
$\text{CO}_3^{2-}$	0.05	99.9

### Adsorption and flotation mechanism

Before discussing the possible sorptive-flotation mechanism involved, the following points need to be taken into consideration:

1. Most metal cations are removed by: (i) adsorption onto solid phases via coprecipitation of their insoluble hydroxides; (ii) flocculation by the adsorption of hydrolytic products or (iii) complexation with specific surface sites, provided that the appropriate conditions prevail (Apak, et al., 1998 and Zouboulis, et al., 1995).
2. Most activated carbon surfaces are negatively charged (Ghazy, et al., 2001b) and are characterized by the presence of oxo groups (Sharma, et al., 1996),  $\text{C}_x\text{O}$  and  $\text{C}_x\text{O}_2$ , which react in aqueous suspensions as organic carboxylic and phenolic groups (Donnet, 1982).

3. An experimental characterization of the surfaces of activated carbon was carried out and the obtained results reveal that:
  - i. Carboxylic, lactonic and phenolic functional groups were present on the surfaces of the carbon samples.
  - ii. The increase in the solution pH observed after stirring the AC sorbent with distilled water for 4 h may be attributed to the adsorption of  $H^+$  ions from the solution or the desorption of  $OH^-$  ions from the sorbent surface, which agrees well with the literature data that most activated carbon surfaces are negatively charged (**Zouboulis, et al., 1994**).
4. Oleic acid (HOL) surfactant begins to dissociate at  $pH \geq 5.2$  (**Ghazy, et al., 2001c**).

**Therefore, the proposed mechanism may occur as follows:**

- A. At  $pH < 6$ , the mercury ions may be adsorbed on sites of the AC sorbent. The adsorbent-adsorbate system is made hydrophobic by combining with undissociated oleic acid molecules. Such a combination may occur through hydrogen bonding of the hydroxide group of HOL.
- B. In the pH range (6 – 9), adsorption may be electrostatically in nature. The adsorbent-adsorbate system is made hydrophobic by combination with undissociated oleic acid through hydrogen bonding and/or chemically with oleate anions. These hydrophobic aggregates are floated to the solution surface with the aid of air bubbles.
- C. In an alkaline medium, at  $pH > 9$ , the removal of mercury ions decreases, which may be attributed to the incapability of adsorption of the negative oleate ions on the negative surface of activated carbon.

**Table(4):** Recovery of mercury:

<b>Sample location</b>	<b>Added Hg<sup>2+</sup> ions, mg.l<sup>-1</sup></b>	<b>Re %</b>
<b>Distilled water</b>	10	99.9
	15	99.9
	20	98.7
<b>Tap water (our lab.)</b>	10	98.4
	15	98.1
	20	97.8
<b>Nile water (Mansoura)</b>	10	98.9
	15	98.2
	20	97.7
<b>Sea water a-Gamasah</b>	10	99.4
	15	98.7
	20	97.8
<b>b-Ras El-Bar</b>	10	98.2
	15	97.9
	20	96.4
<b>c-New Damietta</b>	10	97.3
	15	97.1
	20	96.2
<b>d-Sharm El-Sheikh</b>	10	98.7
	15	98.5
	20	98.1
<b>Lake water (Manzalah)</b>	10	98.8
	15	98.3
	20	97.2
<b>Under ground water (Awish El-Hagar village)</b>	10	98.1
	15	97.6
	20	97.2

## CONCLUSION

The sugar beet pulp (which an agricultural plant waste) was used in the preparation of activated carbon in powder form (which is an effective and inexpensive sorbent) for the removal of  $\text{Hg}^{2+}$  ions from aqueous solutions. Flotation technique which has advantages (compared with other separation methods) of being simple, inexpensive, less time consuming and expected to be soon incorporated as a clean technology to treat water and wastewater has been applied in this investigation. Moreover, the removal of Hg (II) attained ~100% in the presence of oleic acid as a cheap surfactant. The experimental results revealed the following:

- (i) The biosorptive-flotation process was endothermic in nature and therefore  $\text{Hg}^{2+}$  ions were to some extent adsorbed chemically on the activated carbon.
- (ii) Carboxylic, phenolic and lactonic groups present on the surface of the activated carbon play a great role in the biosorption of  $\text{Hg}^{2+}$  ions.
- (iii) Biosorption could occur through adsorption of  $\text{Hg}^{2+}$  ions and/or its hydrolytic species.
- (iv) The procedure was successfully applied for the removal of about 100%  $\text{Hg}^{2+}$  ions spiked to aqueous and natural water samples under the optimum conditions, ca. at pH 7 and at room temperature (~ 25°C).

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التعويم الإمتزازي لأيونات الزئبق الثنائي من محاليل مائيه بواسطه الكربون النشط المحضر من مخلفات بنجر السكر كسطح إمتزاز و حمض الأوليك كعامل سطحي نشط.

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تم إستخدام مخلفات البنجر (النااتجه من تصنيع السكر) في تحضير كربون نشط تم استغلاله في إزاله الزئبق الثنائي. نم عمل تجارب معملية بهدف إزاله الزئبق الثنائي من الوسط المائي. إعتمدت التجارب على إستخدام كربون نشط (تم تحضيره من مخلفات البنجر الناتجه من تصنيع السكر) كسطح إمتزاز فعال وتم إستخدام حمض الأوليك كعامل سطحي نشط. تم دراسة تأثير العوامل المختلفه والتي تؤثر تأثيرا مباشرا على عملية التعويم الإمتزازي مثل: الأس الهيدروجيني، تركيزات كل من الزئبق الثنائي ، سطح الإمتزاز (الكربون النشط المحضر من مخلفات بنجر السكر)، العامل السطحي النشط، القوه الأيونية للمحلول، درجة الحرارة، وقت الرج، وتداخل الأيونات الغريبة. تم الحصول على نتائج جيدة وذلك عند أس هيدروجيني ٧ وعند درجة حرارة الغرفه ( $25 \pm 2^\circ\text{C}$ ) ويقترّب الفصل من ١٠٠٪. تم تطبيق هذه الطريقه في فصل ايونات الزئبق من عينات مائيه طبيعيه. أخيرا تم إقتراح ميكانيكيه لعملية التعويم الإمتزازي.