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Application of Activated Carbon Fibers for Removal of Iron and Lead Salts from Waste Water

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IN THIS study, the adsorption characteristics and performance of activated carbon fibers (ACF) were prepared from Polyacrylonitrile (PAN) waste, for removal of heavy metals was investigated. The effects of heavy metals concentration, adsorption temperature, pH of adsorption solution and contact time for removal of iron sulfate and lead acetate were studied to determine the best performance properties. The surface of ACF before and after adsorption process was investigated by scanning electron microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDX). The adsorption characteristics were mainly affected by pH of adsorption media and the adsorption temperature. The pH 4.0 was the optimum one for the adsorption processes of iron sulfate and lead acetate. Increasing the adsorption temperature from 30 - 80°C improved the removal efficiency of Fe(II) from 71 % to 94 % and for Pb(II) increased from 57 % to 83 % . The surface of ACF after adsorptions is characterized by the formation of some precipitations on the surface of ACF. These precipitations and granulation are noticed. EDX analysis confirms the presence of Fe(II) and Pb(II) onto ACF after adsorptions.

Keywords: Activated carbon fibers, Waste water treatment, Removal efficiency percentage, Adsorption coefficient, Lead acetate, Iron sulfate.

Introduction

Extreme release of heavy metals into the environment as a result of industrial development increase has gained a great problem worldwide. Unlike organic pollutants, heavy metal ions do not degrade into harmless end products [1-3]. The presence of heavy metal ions is of a major concern due to their toxicity to many life forms. Heavy metal contamination exists in aqueous wastes of many industries, such as metal plating, mining operations, radiator manufacturing, alloy industries and storage batteries industries [4, 5].

The problem of heavy metal pollution in water and aquatic organisms includes fish, which needs continuous monitoring and surveillance as these elements do not degrade and tend to bio-magnify in man through food chain. Heavy metals even at low concentrations can cause toxicity to humans and other forms of life. Many industrial processes, such as smelting, metal plating, mining pigments, cadmium-nickel-batteries, brass manufacture and discharge of aqueous effluents are containing high levels of these heavy metal ions. Various physical and chemical processes have been extensively used to remove heavy metal pollutants from aqueous solutions such as chemical precipitation, ion exchange, bio-adsorption, adsorption, membrane filtration, etc. Adsorption on activated carbons is considered one of the most widely applied techniques for pollutants removal from contaminated media owing to its efficiency especially at low concentrations and process simplicity [6,7].

Some heavy metals, especially copper, zinc and chromium in small quantities are necessary for humans' healthy life, but most of the heavy metals, including iron, lead, nickel and others cause often human poisoning and environmental pollution. Since these metals have the ability to blend into water, they may seep into the groundwater and thus contaminated drinking water and then harm the consumers health as well as increase the environmental pollution. [8-10].

Adsorption process adopted is a promising method for a long-term treatment and economically proved. In the process, heavy metals can be removed and minimized the heavy metals even at a low concentration and enhances the application of adsorption as one practical treatment method [11]. In our previous work, adsorption process showed a great tendency to adsorb heavy metals by using activated carbon fibers as smart filter to produce high quality treated effluent without heavy metals [12]. Also, it was proved that activated carbon fibers prepared from waste acrylic fiber has antimicrobial activity [13].

The parameters which should consider in this treatment include the physical and chemical characteristics of the adsorbents, adsorbate, temperature, contact time, pH and the concentration of adsorbate in the adsorption liquid. There is no specific mechanism in the adsorption process but the adsorption characteristics are used to explain and describe the adsorption occurred between the adsorbate ions and the porous surface of activated carbon fibers.

Activated carbon fibers (ACF) are considered as excellent operative adsorbents for a wide diversity of organic and inorganic pollutants which are mainly found in industrial effluents. The large adsorption capability of ACF is mainly due to the high pore volume and large surface area as well as the presence of different functional groups on the surface [14]. The low cost of activated carbons and easiness of their activation procedures make their application as adsorbents for toxic heavy metals very attractive. Activated carbon fiber was especially known for the effectiveness in removing organic and inorganic heavy metals from wastewater as well as of dye pollutants [15, 16].

ACF prepared from Polyacrylonitrile wastes (PAN) precursor has attracted much attention due to its high adsorption performance as compared to other ACF precursors [17]. The present research work is concerned for the use activated carbon fibers from PAN waste fibers as adsorbent filter and to estimate their ability to remove different types of heavy metals from the same adsorption solution. The main point will be on the removal of iron sulphate and lead acetate salts. The important view was aimed also to study the effect of different adsorption conditions to investigate the adsorptive properties of ACF by varying pH of the solution, adsorbent temperature and initial ion concentration of metal salts.

Experimental

Preparation of Activated Carbon Fiber

Activated carbon fibers were prepared from the waste of polyacrylonitrile fibers (PAN). The fibers were pretreated at temperature range of 200-300 °C. It is followed by a carbonization step at 700-1100°C under inert atmosphere. The final step was the activation at 800-1000°C under mixture of steam and/or CO_2.

Materials and Methods

All the reagents used were of AR grade chemicals. Stock solutions of the test reagents were prepared by dissolving lead acetate, and iron sulfate in distilled water. The pH of the investigated solutions was adjusted using reagent grade diluted hydrochloric acid and sodium hydroxide (0.1mol/L).

Adsorption Procedure

Adsorption experiments were carried out in a batch processed by agitating 0.05g of oven dried nonwoven Activated Carbon Fibers (ACF) samples with the prepared solutions of metal ions at constant pH in a thermostat water bath with a shaker. The effects of pH, contact time, and initial metal ions concentrations on the adsorption of Fe(II) and Pb(II) onto ACF were studied. The nonwoven fabric samples were thoroughly mixed with 50 ml of known amount of investigated metal salts in a 100 ml Erlenmeyer flask and the ACF were shaken in a water bath (200 rpm) at room temperature (30 ± 1°C). Adsorption studies were carried out in a range of initial concentration (30-150 ppm) of metal salts. The agitation time (5-180 min.) at the pH maximum adsorption capacity was found from first experimental run of this study. At the end of each adsorption experiment, the solution was filtered through a filter paper and

the concentration of the investigated metal salts in the filtrate was determined with a Flame Atomic Absorption Spectrometer (Agilent Technologies 200 Series AA).

The Pb (II) and Fe (II) concentration of the samples were measured before and after treatment. The removal percentage was then calculated. In case of the effect of pH studies, the uptake experiments were performed at a controlled pH and at room temperature. The pH of the solutions was adjusted using suitable buffers.

The properties of adsorption process were characterized by calculating the removal efficiency percentage (R %), adsorption capacity (SC, mg/g) and distribution coefficient (D, L /g) using the following equations:

$$R = [(C_o - C_i) / C_o] \times 100 \ \ldots\ldots\ldots\ldots \quad (Eq\ 1)$$

$$SC = [(C_o - C_i) \times V] / W \ \ldots\ldots\ldots\ldots (Eq\ 2)$$

$$D = [R/(100-R)] \times V/W \ \ldots\ldots\ldots\ldots (Eq\ 3)$$

Where: C_o is the initial concentration of the investigated metal ion in the solution, mg /L; C_i is the concentration of metal ion solution after the adsorption onto ACF, mg / L; V is the volume of solution, (L); W is the weight of the sorbent material (ACF) per gram.

Scanning Electron Microscope (SEM) and Energy Dispersive X-ray Spectroscopy (EDX)

The fabric was measured on SEM (Tescan Vega 3 SBU) working at 20 KV. The fabric was coated with carbon double face and fixed with stubs of Quanta holder and examined in low vacuum.

Results and Discussion

Effect of iron and lead metal ions on pH adsorption

The pH of the adsorption medium is an important factor, defining the optimum pH condition. The pH affects not only the surface charge of adsorbent, but also the degree of ionization of adsorbate through reactions. The removal of iron sulfate and lead acetate through the porous structure of ACF depends on the pH of the adsorption process. It is simply due to the change of the ACF surface-active groups. The range of pH was varied from 2 to 12 and the adsorption temperature was kept constant at of

30℃. Also, the initial ions concentrations of metal salts were kept constant at 1000 ppm and the duration of adsorption was 60 min.

pH dependence of iron (II) and lead (II) removal efficiency is shown in Figure 1. It is well known that these metal ions undergo hydrolysis reactions in water and form insoluble complexes with increasing pH. This phenomenon is considered as important for understanding the adsorption behavior of all metal ions onto these activated carbon fibers. It is clear that, increasing the pH from 2-12 led to increase the removal efficiency for both types of metal ions, but it was noticed that there is some salts precipitation for iron sulfate and lead acetate above pH 5, consequently all experimental studies were carried out at pH 4.

The adsorption capacity and distribution coefficient of Pb(II) and Fe(II) were also studied and shown in Figures 2 and 3 respectively. The data represented in Figure2 shows that the maximum adsorption capacity for Pb (II) occurred at pH 12 (72 mg/g), while that of Fe (II) occurred at pH 12 (41 mg/g). As mentioned above, this finding as a result of perception of metal hydroxide (pH >5.0). The distribution coefficient values of lead and iron metal ions between adsorbent and liquid phase were shown in Figure3. Comparing the values of distribution coefficient for Pb(II) and Fe(II) ions in equilibrium conditions, it is clear that, the maximum adsorption occurred at the same adsorption conditions (pH 4.0). This is considered a great economical advantage to adsorb different metal ions in one time [18].

Effect of Pb(II) and Fe(II) metal ions concentrations on the adsorption properties

Figure 4 represents the removal efficiency percentage of Pb(II) and Fe(II) as function of initial metal ions concentrations. The metal concentrations were varied between 200 and 1000 ppm and the weight of ACF used was 0.05 gram. The pH parameters were kept at the optimum conditions for Pb(II)and Fe(II), which was at pH 4. For the other parameters, the temperature was kept at 30ºC and the duration of adsorption is kept at 60 min. Increasing the concentration of lead acetate and iron sulfate solutions led to a gradual decrease in the removal efficiency of both metal salts. The removal efficiency percentage of lead acetate decreased from 57.0% to 14.0 %, while the removal efficiency percentage of iron sulfate decreased from 71.0 % to 25.0 %. This is
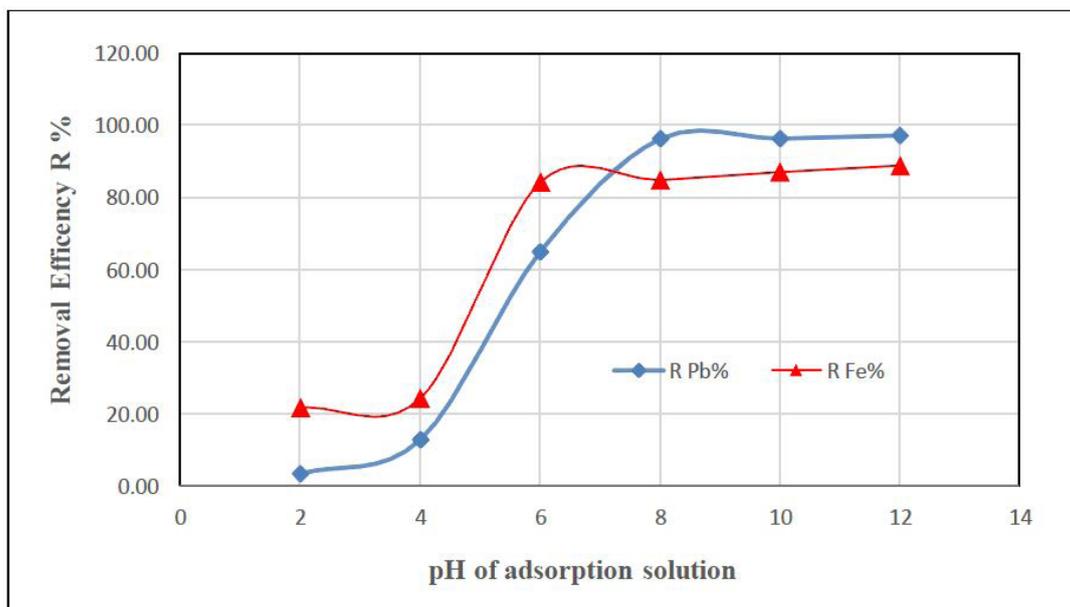
Fig. 1. Effect of pH of adsorption solution on the removal efficiency of Pb (II) and Fe (II)
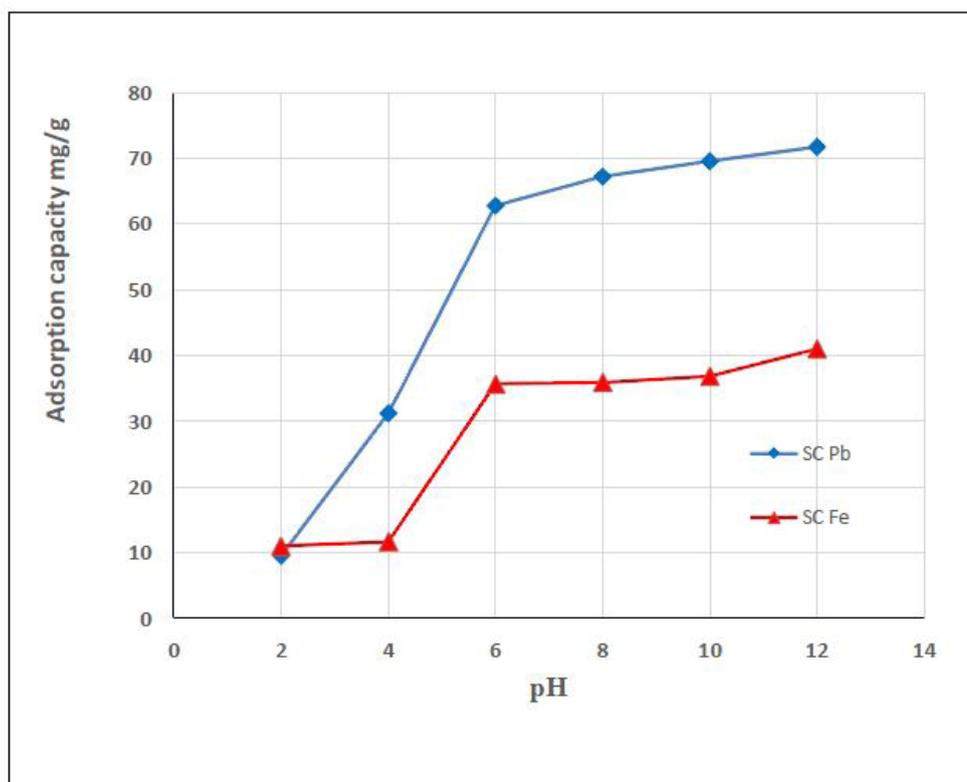

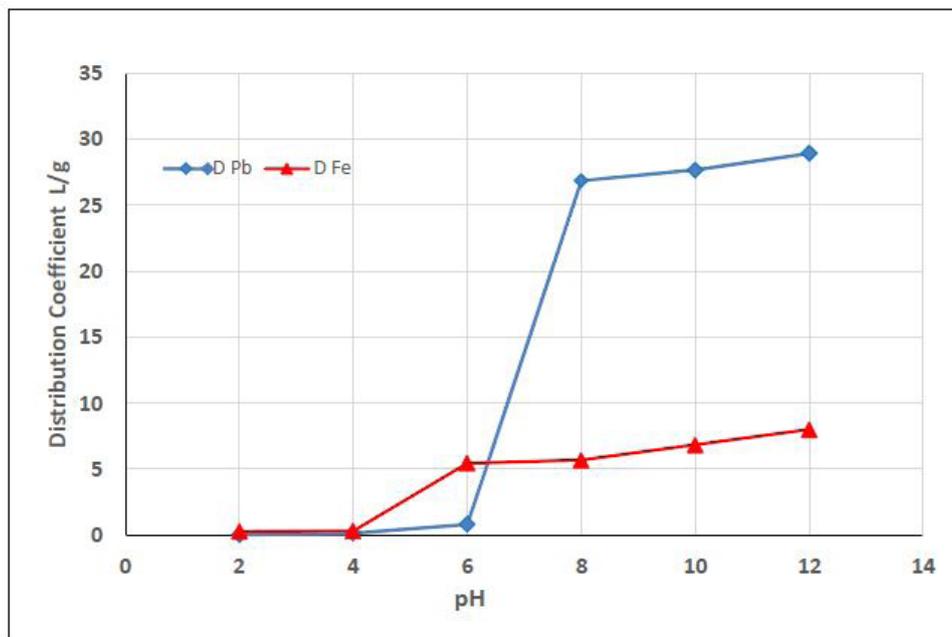**Fig. 2. Effect of pH on the adsorption capacity of Pb (II) and Fe (II)**

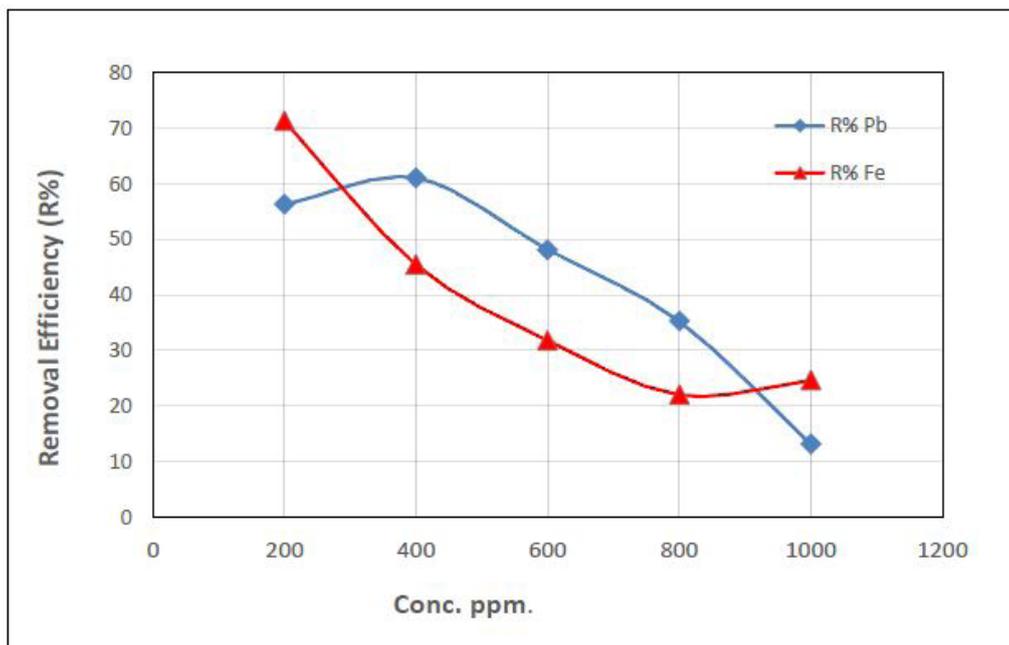**Fig. 3. Effect of pH on the distribution coefficient of Pb (II) and Fe (II)**

Fig. 4. Effect of concentration of Pb(II) and Fe(II) on the removal efficiency

expected for the increase in the number of metal ions in the adsorption solution and increase of the competition between metal ions to be adsorbed on the fixed number of available active groups on the surface of activated carbon fiber. Also, the entrance to the porous structure of ACF became difficult due to the increased accumulation of cations and anions on the surface of ACF.

Figure 5 shows the effect of concentration of lead acetate and iron sulfate on the adsorption capacity of the ACF surface. It was noticed that there is a great difference in the adsorption capacity performance between lead acetate and iron sulfate. The adsorption capacity of lead acetate increased drastically with increasing the lead acetate concentration up to 69.0 mg/g at 600 ppm, followed by a decrease in the adsorption capacity to 31.0 mg/g at 1000 ppm. While, the adsorption capacity of iron sulfate slightly increased 6.0 mg/g at 200 ppm to 11.7 mg/g at 1000 ppm. These effects can be attributed to the effect of anions on the adsorption behavior of ACF. Acetate anions can be easily adsorbed and combined to the active chelating groups on the surface of ACF. These chelating groups can enhance the adsorption of lead ions on the ACF (up to 600 ppm). After 600 ppm concentration the number of available active groups and free pores on the ACF surface drastically decreased. The sulfate anions do not have such ability for the chelating groups on the surface of ACF. Therefore, there is a slightly increase in the adsorption capacity of iron sulfate with increasing the concentration.

Figure 6 shows that the salt concentrations have the same effect on the distribution coefficient of lead acetate and iron sulfate. There is a decrease on the distribution coefficient of Fe(II) and Pb(II) with increasing lead acetate and iron sulfate concentrations. This is expected due to the increase in charge accumulation on the surface of ACF as well as the increase in the repulsion of ions carrying the same charge.

Effect of temperature on the adsorption of Pb(II) and Fe(II) metal ions

The adsorption temperature has a significant effect on the adsorption process of iron sulfate and lead acetate onto the porous surface of ACF as shown in Figure 7-9. The effect of the temperature on the removal efficiency was studied within the range of 30 - 80 ºC. The metal ions concentration was kept at 200 ppm, pH at 4, and the adsorption

time at 60 min. It can be seen from figures 7- 9 that, the increase in the temperature from 30°C up to 80°C has an important role on the removal efficiency and adsorption capacity of Fe(Ⅱ) and Pb(II). The removal efficiency of Fe(II) metal ions increased from 71.0 to 94.0 %, while for Pb ions, it increased from 57.0 to 83.0 % as shown in figure 7.

Also, the adsorption capacity of Pb (Ⅱ) increased from 33.0 to 47.9 mg/g and for Fe (II) it increased from 6 to 9 mg/g. The adsorption capacity of ACF increased with temperature due to the enhancement of the swelling ability of the porous structure of ACF as well as increasing the movement of metal ions as shown in figure 8. Consequently, Pb(II) and Fe(Ⅱ) can easily enter into the pores of ACF and increase the adsorption of Pb(II) and Fe(Ⅱ) into ACF.

The distribution coefficient between the adsorbed Fe (II) and Pb (II) onto ACF is shown in figure 9. It is clearly reflected how extremely the increase in the temperature enforced the metal ions into the porous structure of ACF (i.e. increase the adsorption onto ACF).

It was observed that there is a significant enhancement in the distribution coefficient of iron sulfate compared to that of lead acetate. The distribution coefficient of Fe(II) increased drastically from 2.5 L/g to 15.5 L/g. While the distribution coefficient of Pb(II) slightly increased from 1.4 L/g to 5.0 L/g. This can be explained that there is a different type of adsorption mechanism for the two the metal cations onto the porous surface of ACF. Consequently, the interaction between the Fe(II) and ACF differs from the interaction between Pb(II) and ACF.

Effect of contact time on the adsorption of Pb(II) and Fe(II) metal ions

The adsorption characteristics of both Pb(II) and Fe(II) were also studied as a function of contact time (15 min up to 90 min) as shown in figures 10-12, which were studied at the metal concentration of 200 ppm, pH 4 and the temperature 30°C. Figure 10 shows that the removal efficiency of Pb(II) and Fe(II) increased with increasing the contact time. It was noticed that the removal efficiency Fe(II) increased from 47.5% up to 80 .5%. Also, the removal efficiency Pb(II) increased from 50.5% up to 62 %.
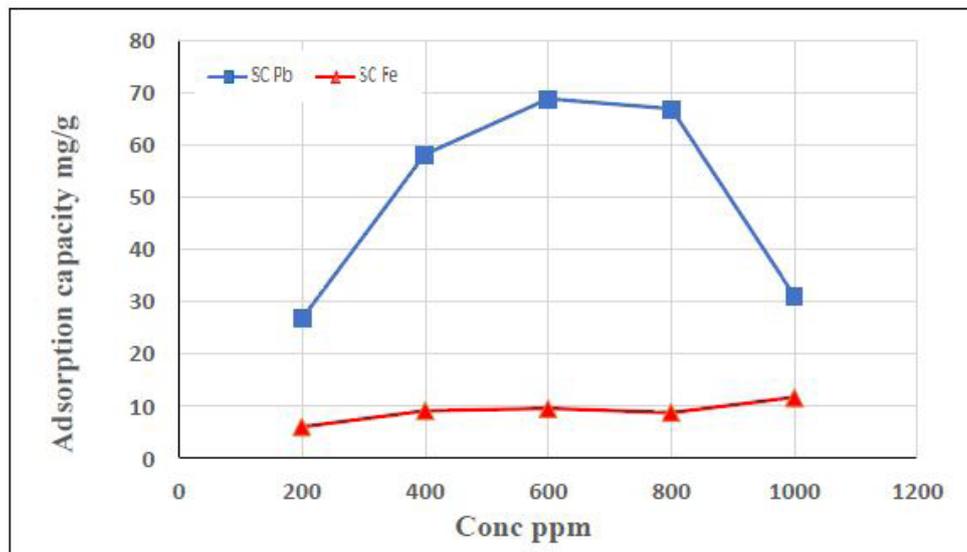
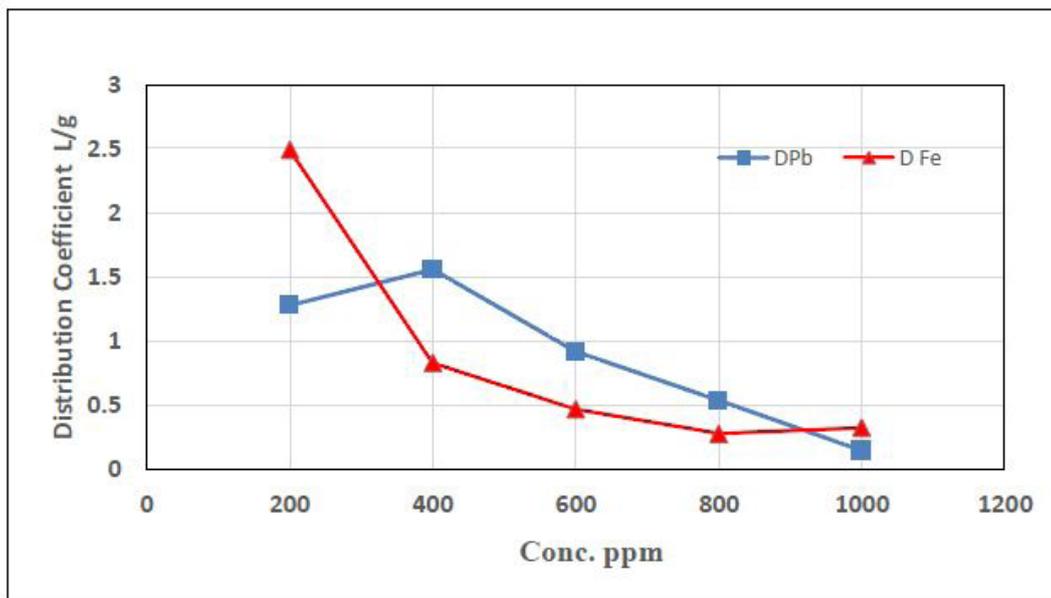**Fig. 5. Effect of concentration of Pb (II) and Fe (II) on the adsorption capacity**

Fig. 6. Effect of concentration of Pb (II) and Fe (II) on the distribution coefficient
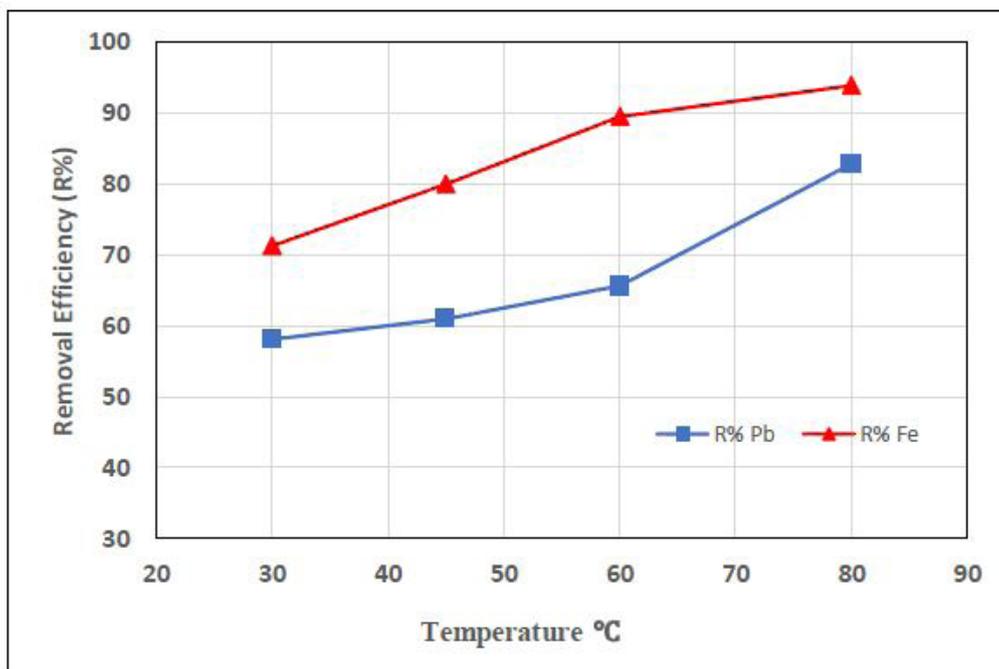
Fig. 7. Effect of temperature on the removal efficiency of Pb (II) and Fe (II)
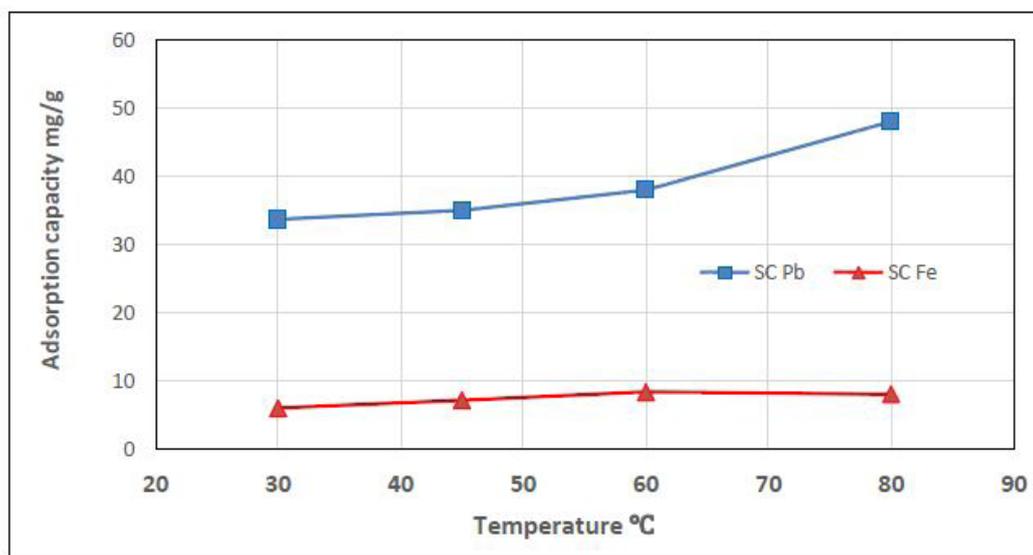

Fig. 8. Effect of temperature on the adsorption capacity of Pb (II) and Fe (II)
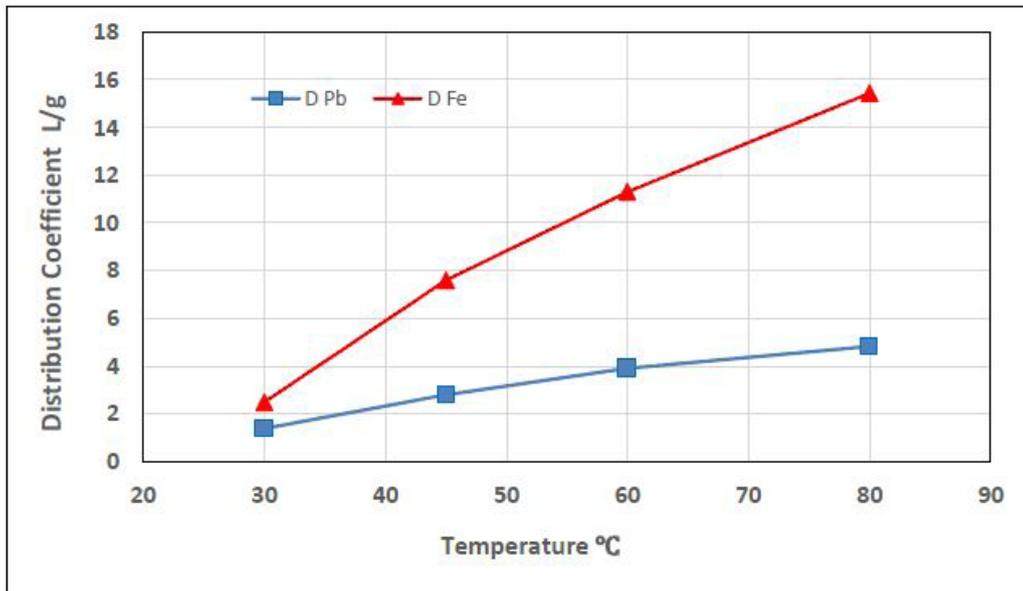
Fig. 9. Effect of temperature on the distribution coefficient of Pb (II) and Fe (II)
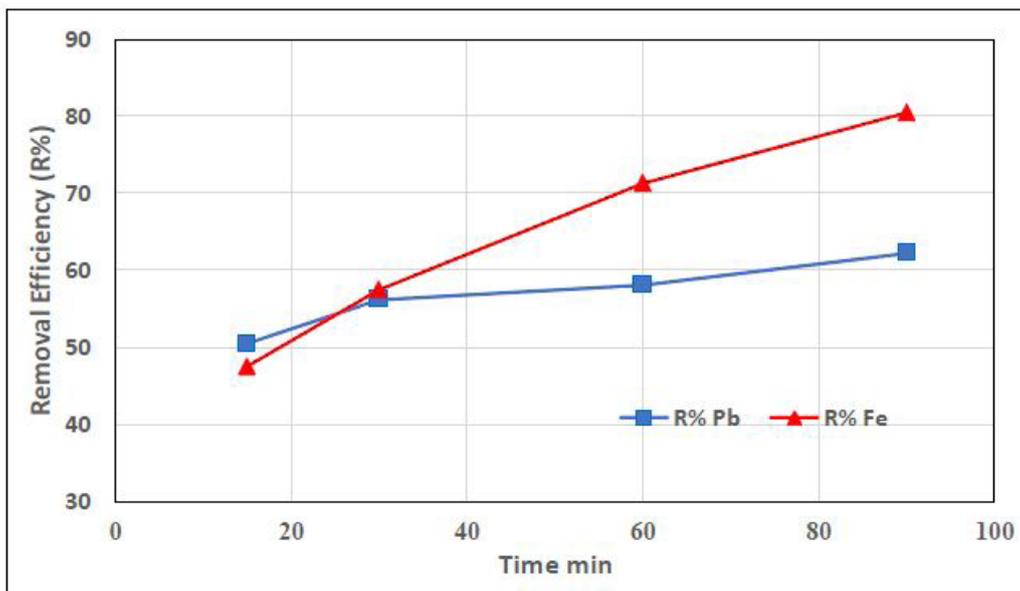

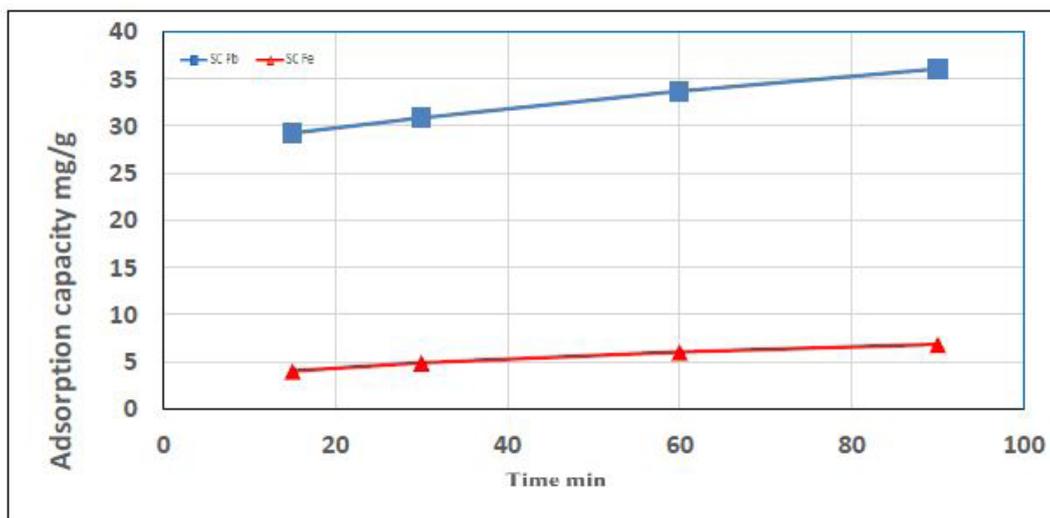**Fig. 10. Effect of contact time on the removal efficiency of Pb (II) and Fe (II)**

Fig. 11. Effect of contact time on the adsorption capacity of Pb (II) and Fe (II)
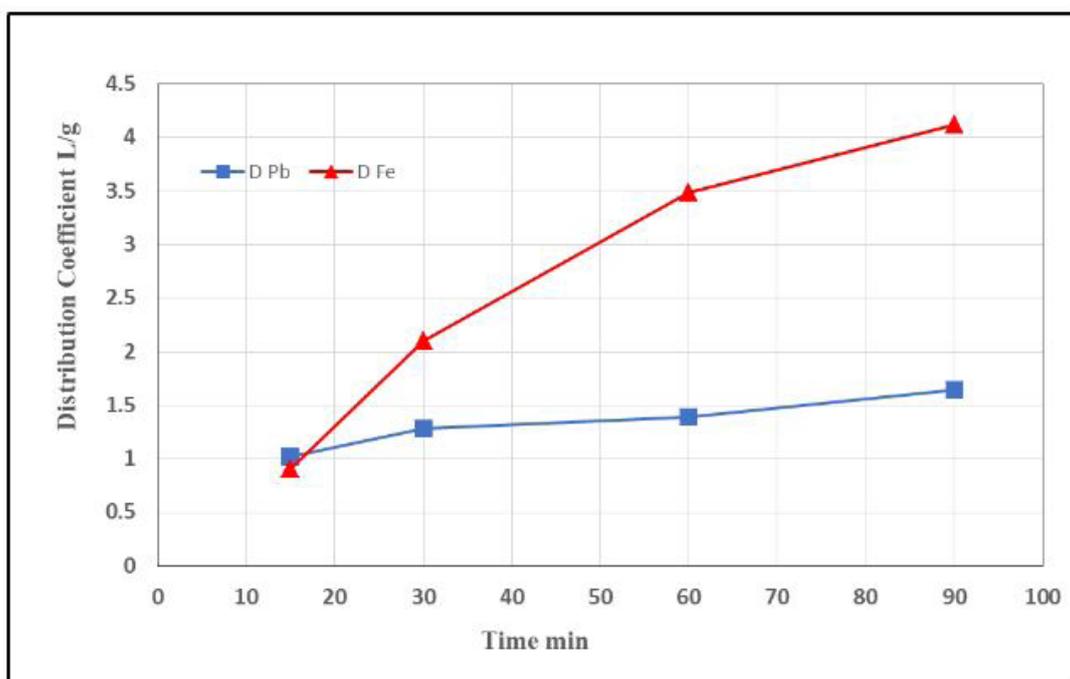

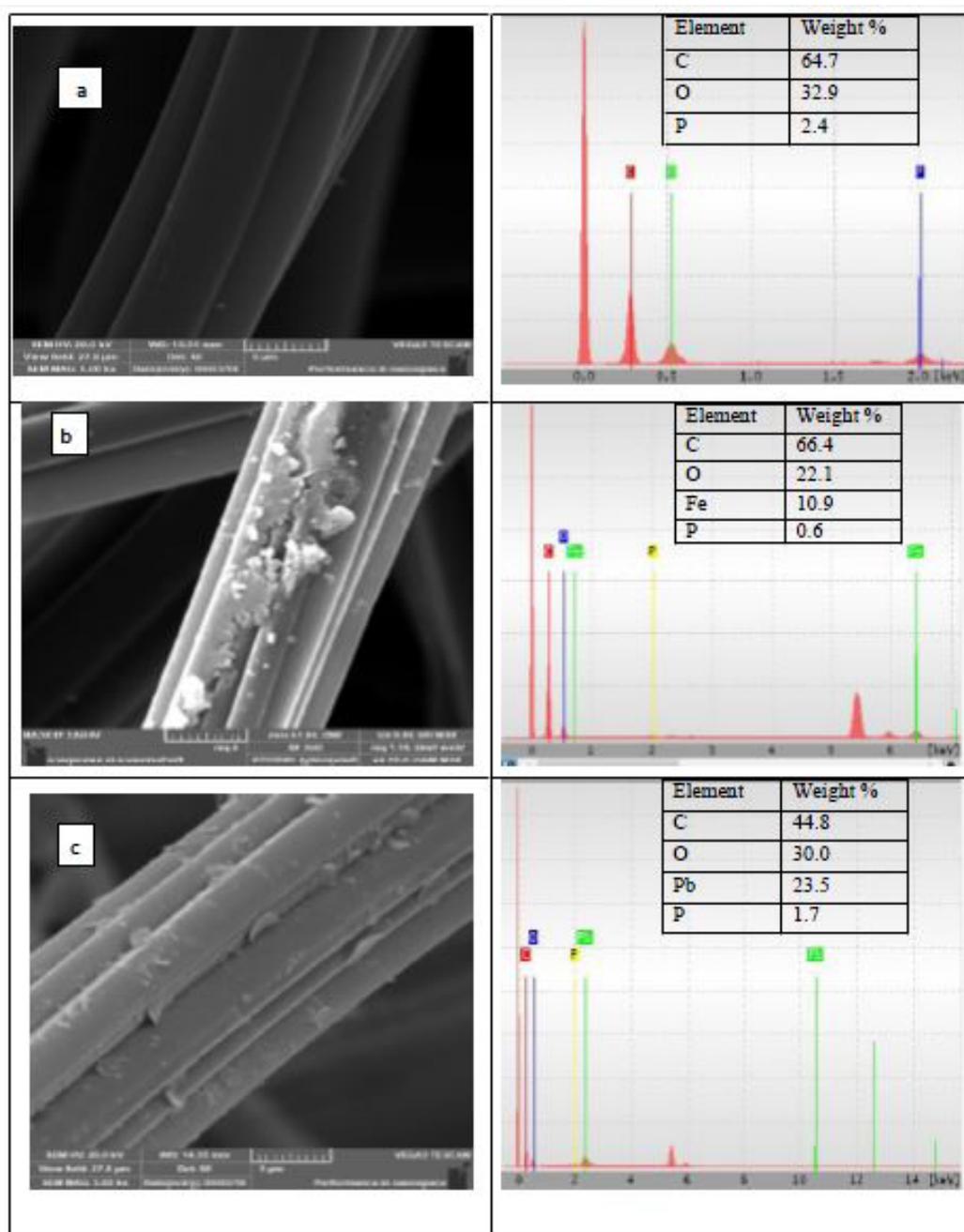**Fig. 12. Effect of time on distribution coefficient of Pb (II) and Fe (II)**

Fig. 13. SEM Micrographs and EDX of ACF. (a) Blank sample of ACF, (b) ACF after Fe(II) adsorption, and (c) ACF after Pb(II) adsorption.

The influence of contact time on the adsorption capacity of ACF is shown in figure 11, which determined the amount of Pb (II) and Fe (II) metal ions adsorbed into the porous structure of ACF. It was observed that the amount of Pb (II) and Fe (II) metal ions retained in ACF increased with increasing the contact time. The maximum value was achieved within 60 min to reach 34 and 7.0 mg/g for Pb(II), and Fe (II) respectively.

Figure 12 demonstrates the effect of contact time on the distribution coefficient. The distribution coefficient of Fe(II) increased from 0.9 L/g to 4.1 L/g. While the distribution coefficient of Pb(II) slightly increased from 1.0 L/g to 1.7 L /g. The competition between the ions increased when the surface coverage increased of the ACF, with increasing the contact times. Therefore, the adsorption capacity of ACF will be reduced [19].

Scanning Electron Microscope (SEM) and Energy Dispersive X-Ray (EDX)

SEM images were used to examine the surface topography of ACF before and after metal adsorption of metal ions as shown in Fig. 13. Blank sample appear as filamentous smooth surfaces. The surface of ACF after adsorptions is characterized by the formation of some precipitations on the surface of ACF. These precipitations and granulation are noticed and indicates the adsorption of metal salts onto the activated carbon fiber porous surface.

ACF was analyzed by EDX before and after metal adsorption. Fig.13 (a) shows the presence of carbon and oxygen elements onto ACF. Figure 13(b) and (c) shows ACF after Fe(II) and Pb(II) adsorption. It confirms the presence of Fe(II) and Pb(II) onto ACF after adsorptions.

Conclusion

The adsorption characteristics and performance of activated carbon fiber, prepared from polyacrylonitrile for the removal of heavy metals were investigated. The effects of heavy metals concentration, adsorption temperature, pH of solution adsorption and contact time on the removal of iron sulfate and lead acetate were studied to determine the best performance conditions. The adsorption characteristics were affected by adsorption medium pH and the adsorption temperature. Increasing the adsorption

temperature from 30°C up to 80°C enhance the removal efficiency of Fe(II) from 71 % to 94 %, while in case of Pb(II) increased from 57 % to 83 % . The amount of Pb (II) and Fe (II) metal ions retained in ACF increased with increasing the contact time. The adsorption capacity of ACF increased with increasing the temperature due to the swelling ability of the ACF porous structure of as well as the increase in the movement of metal ions. Consequently, Fe(II) and Pb(II) can easily penetrate into the pores of ACF and increase the adsorption of Fe(II) and Pb(II) into ACF.

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استخدام ألياف الكربون المنشط لازالة أملاح الحديد و الرصاص من مياه الصرف

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دراسه خصائص عمليه امتزاز وأداء ألياف الكربون النشط و الذي حضرمن مخلفات الياف البولي اكريلك و ذلك من أجل استخدامه في معالجه مياه الصرف الصناعي لازاله الاملاح الثقيلة.تم دراسة تأثير تركيز المعادن الثقيلة ، ودرجة حرارة الامتزاز ، و الاس الهيدروجيني لمحلول الامتزاز و زمن عمليه الامتزازعلى ازالة كبريتات الحديدوز وخلات الرصاص لتحديد أفضل أداء لالياف الكربون النشط. ومن الدراسه تبين أن عمليه الامتزاز تعتمد بشكل رئيسي علي كل من الاس الهيدروجينى ودرجة الحرارة. ولوحظ ان زيادة درجة حرارة الامتزاز من 30 درجة مئوية إلى 80 درجة تؤدى الى زيادة النسبة المئوية لازالة Fe (II) من 71 ٪ إلى 94 ٪بالمقارنه لنسبة المئوية لازالة Pb (II) والتى زادت من 57 ٪ إلى83٪

- تم إستخدام الميكروسكوب الالكتروني الماسح لدراسه خواص سطح الياف الكربون قبل عمليه الامتزاز وبعده.

- قد لوحظ أن مظهريه الالياف بعد عمليه الامتزاز تختلف عن تلك التي قبل العمليه ،علاوه علي إختلاف الالياف التي تم امتزاز أملاح الحديد او الرصاص حيث تبدو ترسبات و جسيمات علي السطح أكثر.

- استخدم جهاز طيف الاشعه المشتته السينيه (EDX) يؤكد تحليل EDX على وجود (Fe (II او (Pb (II على ACF بعد الامتزاز.

- الدراسه وضحت ان الهيكل المسامى لACF يتيح استخدامه كماده ماصه مناسبة لإزالة أيونات المعادن الثقيلة من مياه الصرف الصحي من خلال عملية الامتزاز .