Modified Poly(ethylene terephthalate) Nano Fibers for Removal of Copper(II) Ions

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Abstract: In this research, the adsorption of Cu^{2+} ions from aqueous solution was investigated by the modified poly (ethylene terephthalate) fibers as a new adsorbent. The best condition of electrospinning was recorded (voltage= 10 kV – distance from nozzle= 12.5 cm – solution convcentration= 0.2 g/mL). The optimum condition for removal of Cu^{2+} ions were determined (pH=10 – time= 60 min - C= 120 mg/L, q_m = 62.4 mg/g). The adsorption data were best fitted by dubinin-radushkevich isotherm and pseudo-second order kinetic models, as well. Structure of the nanofibers were emphasized by scanning electron microscpy (SEM) and thermo gravimetric analysis (TGA).

Keywords: Nanofibers, Adsorption, Isotherm, Kinetics.

1. INTRODUCTION

In 1971, baumgarten [1] performed studies on electrospinning of acrylic nanofibers; he succeeded in obtaining fibers ranging in diameter from 500nm to 1000nm. Since the 1990s, Renker, Doshi, Chun and Norris's and other research groups conducted detailed exploratory investigations on electrospinning. During the past decade, extensive research has been undertaken regarding the electrospinning process from the various perspectives like theoretical simulation, fiber formation mechanism, factors influencing the size and morphology of the particles and fibers and their applications. A vast spectrum of polymers (natural, artificial, organic and inorganic) has been electro-spun from solution or molten phases enabling the production of nanofibers set up for various areas like refinement, strengthening of composites, protective fabric or biomedical uses. Electrospinning of the polymeric melts needs no solvent hence there would be also needed for the evaporation to separate them. However, the polymers' melting temperature is an effective and important factor for the applicability of this method for the production of the nanofibers. Generally speaking, the nanofiber that is generated by the electrospinning of the melts features a higher delicacy in contrast to the dissolved mode but it is not an easy task to obtain nano dimensions through melts electrospinning [2-7].

2. MATERIALS AND METHODS

In the present study, poly)ethylene terephthalate) fiber (30 filaments) was procured from Amir Kabir Textiles Department and it was put into use after being washed by acetone in soxhlet system for six hours for removing its possible impurities and being dried in 50°C in autoclave. 2-hydroxy propyle methacrylate (2-HPMA) and acrylic acid (AA) were bought from the German Merck Company and they were utilized after purification. To do so, the distillation operation was carried out in vacuum in both of the cases. Benzoyl peroxide (Bz_2O_2) was also purchased as an initiator from the German Merck Company and it was used after two times of recrystallization in the presence of the methanol-chloroform and it was always kept in the darkness during the experiments. All of the solvents, including toluene, acetone, chloroform, TFA (trifluoroacetic acid) and DMSO (dimethyl sulfoxide), were procured from Merck.Co and the grafting and adsorption experiments were conducted using twice distilled water.

2.1. Graft Copolymerization and Electrospinning

PET fiber's grafting was conducted in a water bath inside 100-milliliter abrasive-head Pyrex tubes. To do so, 0.4g of fiber and 0.06M of benzoyl peroxide (Bz_2O_2) were dissolved in a mixture comprised of acetone (5ml) and distilled water (45ml) for a total volume of 50ml in the fixed temperature of 85°C [8].

To obtain a product with a high degree of grafting, the reaction was allowed to happen within a period of sixty minutes. After the elapse of the intended time, the fiber was carefully pulled out of the tube and firstly washed in distilled water for the removal of the 2-hydroxypropyl methacrylate homopolymers; then, it was purified by a mixture of acetone-benzene and dimethyl formaldehyde respectively for eight and six hours in the soxhlet and the grafting percentage was calculated using the gravimetric method.

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$$G(\%) = \frac{(W_g - W_0)}{W_0} \times 100 \qquad (1)$$

Where, W_0 and W_g are respectively the weights of the initial and grafted fiber.

Various conditions of electrospinning were investigated in terms of the solution type and concentration, the electrical voltage of the device, distance from the (collector) nozzle and the discharge rate of the product and the optimal conditions were stabilized.

2.2. Adsorption Experiment

The experiment for the determination of the amount of the adsorbed copper was carried out in the presence of 0.01g adsorbent (copolymerized nano fiber) and 10ml of the copper solution reaching a concentration of 20mg/l inside 100-milliliter Erlenmeyer flask that was stirring in a fixed round (150rpm) in a constant temperature of 298K as a function of pH, concentration of the adsorbate and time. After filtering the fiber using whatman filter paper (grade 40) and Ultra-Centrifuging in 3000 rpm, the copper concentration was read in an AAS (AAS, PG990) device in 324nm and it was computed based on the solution's concentration reduction in comparison to the initial copper concentration. The calculations were carried out based on the following formula:

$$q = \frac{(C_0 - C_e)}{m} \qquad (2)$$

Where, C_0 and C_e respectively designate the copper's initial and equilibrium concentrations (mg/L), V is the total solution volume (L), m is the adsorbent's weight (g) and q is measured based on mg/g of the amount of adsorbed copper in a given time.

According to the fact that the raw (unmodified) fiber possesses a low adsorption capacity due to its lack of active functional groups, non-copolymerized fiber was utilized in the experiments for comparison.

2.3. Determination of the Adsorption Isotherms

The adsorption isotherms were read in 25ºC (298K) in the presence of 0.01 g of the fiber, in a 10-milliliter volume of the solution for a fixed stirrer revolution of 150rpm in a fixed pH of 10 and an optimum time of 60 minutes. The results obtained from the atomic absorption spectroscopy were investigated according to Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Harkins-Jura's isotherm models.

2.4. Determination of the Adsorption Kinetics

Three well-known and important kinetic models, namely pseudo-first order, pseudo-second order and intraparticle diffusion, were utilized for the investigation of the adsorption kinetics. The fixed conditions of the experiments were stirrer speed: 0 rpm and 5, 10, 20, 40 and 50-minute periods of time.

3. RESULTS AND DISCUSSION

3.1. Determination of the Optimal Electrospinning Conditions

To determine the best solvents for electrospinning, trifluoroacetic acid, dimethyl sulfoxide, dichloromethane, toluene and acetone were utilized and the effects of the solution's concentration, voltage, needle's distance to the collector and discharge rate of the current were investigated. The experiments indicated that TFA is the best solvent for electrospinning and that 20% (0.2ml) is the best concentration of the solution. It was observed that the increase in the solution's concentration causes an increase in the diameter of the fiber and the physical entanglement [9]. The best voltage was recorded at 10kV. The increase in the voltage caused the transmission of a higher rate of current per every surface area at a unit time due to the increase in the number of the like charges as a result of which the surface charge density is increased [10]. The best distance for electrospinning was observed within 12.5cm from the nozzle. The increase in the distance brings about an increase in the drag and the electric field's intensity is reduced and the jet's velocity is reduced towards the collector. Therefore, the flight time is increased and the fiber diameter is reduced but the electric field and drag are decreased if the distance is enlarged extremely as a result of which the fiber's intermediate diameter is increased. It is with the increase in the discharge up to 1ml/hr that the fiber's medium diameter is increased and then decreased [11].

3.2. TGA and SEM Results

The results obtained from the thermo gravimetric analysis are well indicative of the idea that the thermal stability is decreased after adsorption from 350ºC to about 250ºC; the comparison of the images obtained in scanning electron microscopy clearly confirms the adsorption of copper ions on nanofiber (Figures **1-5**).
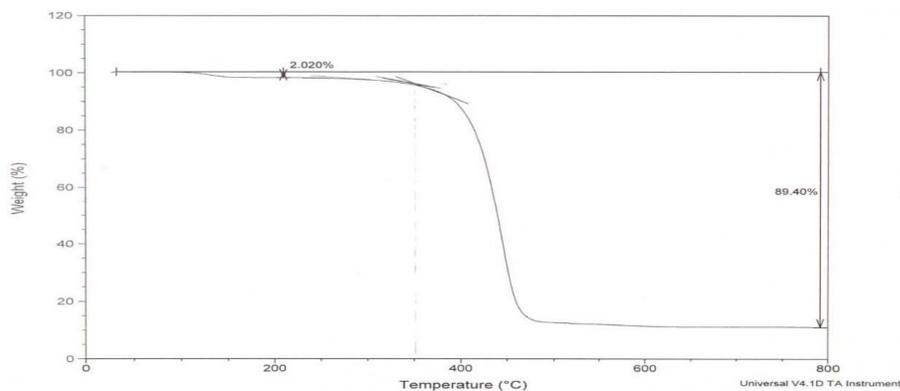
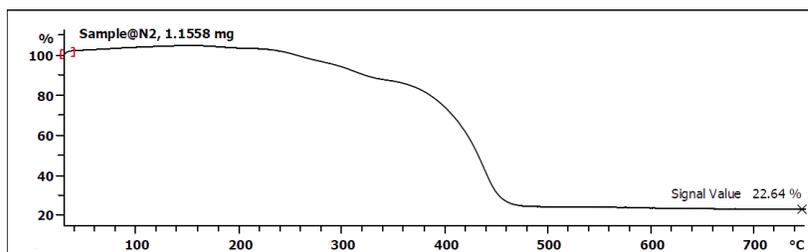**Figure 1:** PET fibers thermogram (42% grafted).

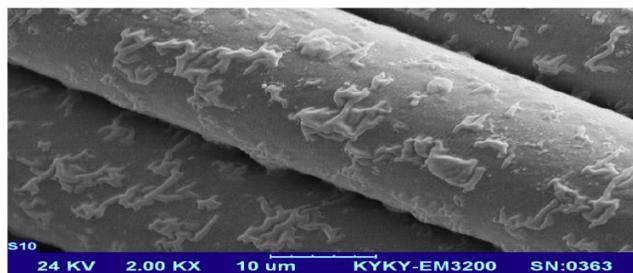**Figure 2:** PET nanofibers thermogram (42% grafted).

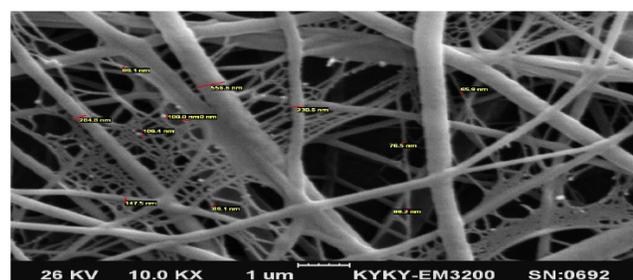**Figure 3:** The SEM of grafted fiber (42%).

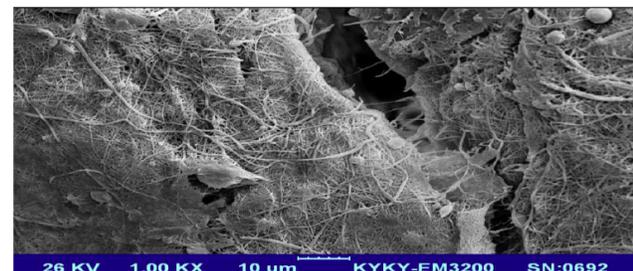**Figure 4:** The SEM of grafted nanofiber(42%).

Figure 5: The SEM of grafted nanofiber(42%)after adsorption.

3.3. pH Effect

The effect of pH on the adsorption of copper ions was investigated in a range from 3.0 to 10.0 under the fixed variable conditions as follow: 0.01g of the adsorbent, 20mg/l of copper; 60-minute period of time; stirrer's speed of 150rpm; temperature of 25ºC and solution volume of 10ml. The best pH and the highest amount of copper adsorption were recorded at 10.0. In acidic environments, the H^+ ions compete with copper ions in being adsorbed to the active fiber sites and they can be more easily adsorbed by the adsorbent due to their higher motility. However, due to the interaction and formation of hydrogen bonds in acrylic acid between OH^- ions, the COO^- anion can adsorb the Cu^{2+} ions (Figure **6**).
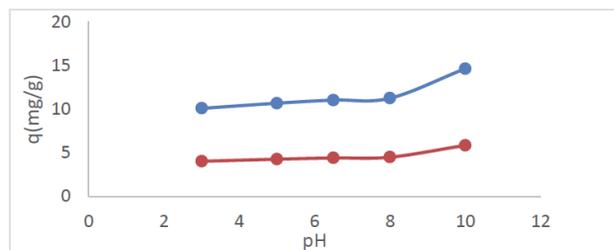

Figure 6: Effect of pH.

3.4. Time Effect

To determine the best adsorption time, the adsorption experiments were carried out in a period of

time between 10min to 90min under the fixed variable conditions (0.01g of the adsorbent, 20ml of Cu^{2+}, temperature of 298K, stirrer's speed of 150rpm and pH of 10). The adsorption process was measured once every 20 minutes and the adsorption rate was completed after 60 minutes. The equilibrium adsorption capacity of copper ions was recorded equal to 5.35mg/g after 60 minutes. It was found 14.65mg/g for the modified nanofiber (Figure **7**).
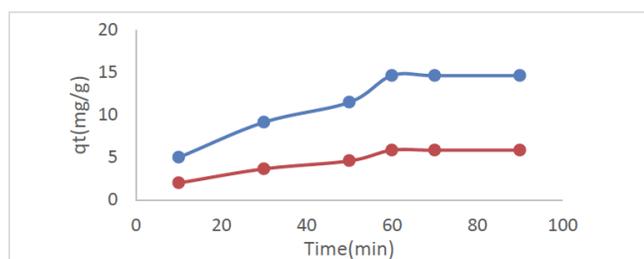

Figure 7: Effect of time.

3.5. The Effect of the Adsorbate Concentration

To determine the maximum capacity of the adsorbent, the concentration of Cu^{2+} as the adsorbate was changed between 20mg/L and 140mg/L. The maximum capacity and efficiency of the adsorbent for a 120-mg/L solution was recorded equal to 64.2mg/g. The results have been demonstrated in the Figure **8**. These values indicate the maximum adsorption capacity and adsorbent's efficiency in the process of adsorption in the solution.
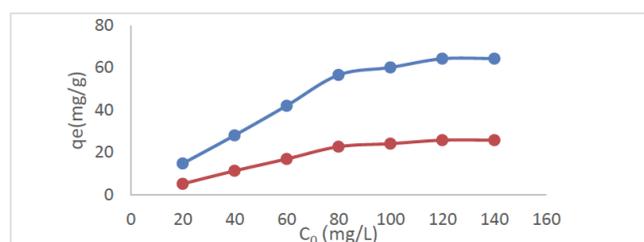

Figure 8: Effect of adsorbate.

3.6. Adsorption Isotherms

The experimental results were investigated through comparison with the various well-known and well-established isotherm models proposed by Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Harkins-Jura.

$$\frac{C_e}{q_e} = \frac{1}{q_m} K + \frac{C_e}{q_m} \qquad \text{langmuir model (1) (3)}$$

$$\frac{1}{q_e} = \frac{1}{K_a} q_m \cdot \frac{1}{C_e} + \frac{1}{q_m} \qquad \text{langmuir model (2) (4)}$$

$$\ln q_e = \ln k_f + \frac{1}{n} . \ln C \qquad \text{Freundlich (5)}$$

$$q_e = a_t + B_0 \ln C_e \qquad \text{Temkin (6)}$$

$$\ln q_e = \ln q_m - 2BRT \ln(1 + \frac{1}{C_e}) \qquad \text{Dubinin-Radushkevich (7)}$$

$$\frac{1}{q_e^2} = (B/A) - (1/A \log C_e) \qquad \text{Harkins-Jura (8)}$$

In the above equations, C_e is the equilibrium concentration in mg/L; q_e is the amount of the adsorbed materials in equilibrium in mg/g; q_m and K_a are the constants in Langmuir equations and specify the process's efficiency; K_f determines the adsorbent's capacity and n shows the intensity (power) of the adsorption and a_t and B_0 are respectively measured in mg/L and mg/g based on the empirical results following the depiction of q_e-$\ln C_e$ curve. Dubinin-Radushkevich model is more popular than Langmuir's because there is no requirement for the homogeneousness of the surface in this model and it does not offer a fixed adsorption potential. In this model, q_e and q_m are respectively the amounts of the adsorbed materials in the equilibrium and specify the maximum theoretical capacity. Harkins-Jura model justifies the presence of inhomogeneous pores and can also come up with notions in multilayer calculations of the adsorption.

As it is clear from the Figures **9-14**, the most consistent isothermal models have been obtained for Dubinin-Radushkevich models based on correlation coefficients.
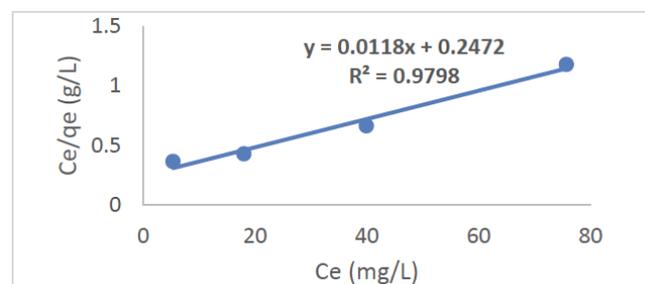

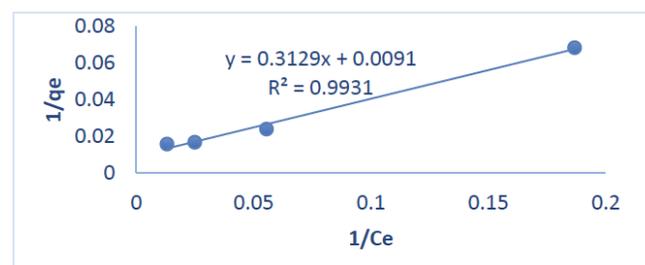**Figure 9:** Langmuir (first model) isotherm (298K).
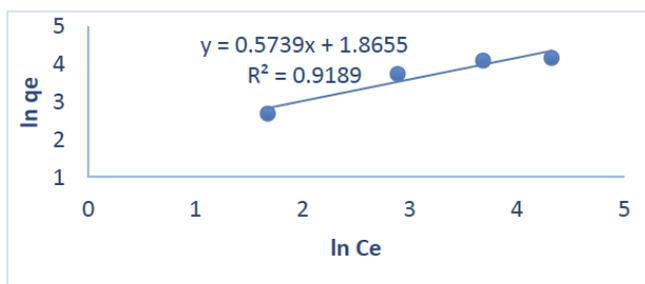

Figure 10: Langmuir (second model) isotherm (298K).
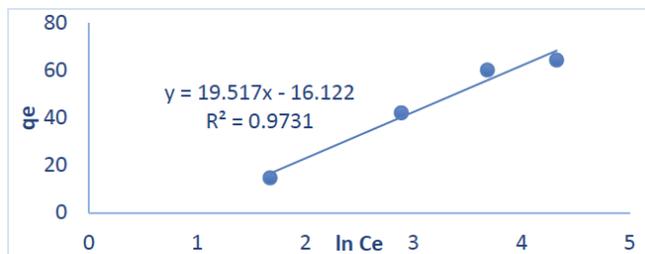
Figure 11: Freundlich isotherm (298K).

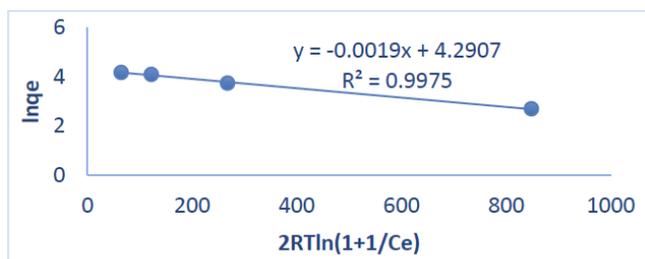**Figure 12:** Temkin isotherm (298 K).
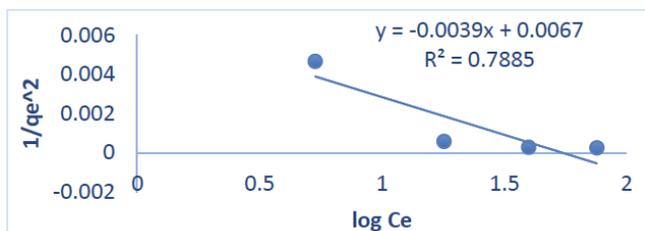

Figure 13: D-R isotherm (298 K).

Figure 14: H-J isotherm (298 K).

3.7. Adsorption Kinetics

The kinetic results of the adsorption were investigated and analyzed based on three kinetic models.

$$\ln(q_e - q_t) = \ln q_e - k_a t \qquad \text{pseudo-first order (9)}$$

$$\frac{t}{q_t} = \frac{1}{K_2 \cdot q_e^2} + \frac{t}{q_e} \qquad \text{pseudo-second order (10)}$$

$$q = K_d \cdot t^{1/2} + I \qquad \text{intraparticle diffusion (11)}$$

Figures **15-17** indicate that the pseudo-second order kinetic model gives the best consistency in justifying the adsorption kinetics of copper on the fiber; C_0 was set herein at 20mg/L.
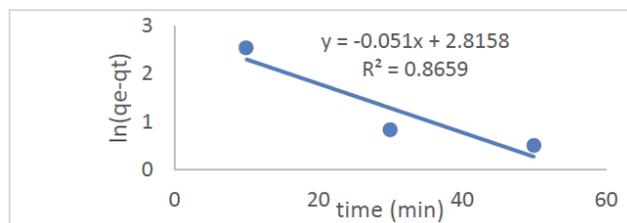
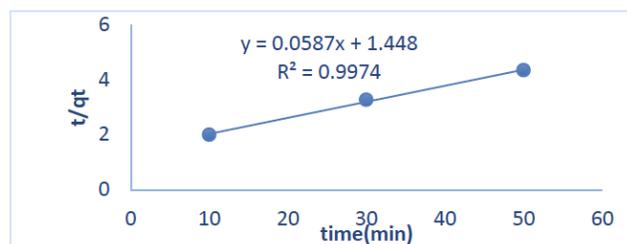

Figure 15: Pseudo-first order kinetics.

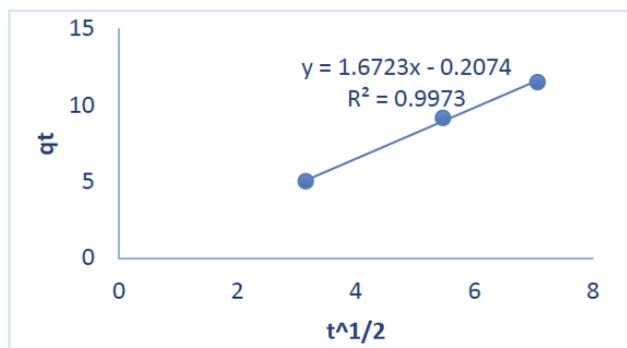**Figure 16:** Pseudo-second order kinetics.

Figure 17: Intra-particle diffusion kinetics.

4. CONCLUSION

In the present study, the electrospinning of the poly (ethylene terephthalate) fiber modified with the monomer mixtures of 2-hydroxypropyl methacrylate and acrylic acid was carried out and the best electrospinning conditions were a 12.5 cm distance from nozzle, a 10-kV voltage of the apparatus, 0.2g/l concentration of the TFA in the solution and a current discharge of 1mL/h.

The nanofiber prepared for the elimination of Cu^{2+} ions from the aqueous solutions based on batch technique was found having a high adsorption power in comparison to the non-nanofibers and an increase by about 2.5 to 3 times was increased for adsorption rate in nano mode.

Nanofiber was investigated before and after adsorption using SEM and TGA techniques and the nanofiber production and ion adsorption by them was examined.

The best adsorption conditions were as follow: pH=10 and time=60 min with the maximum adsorption capacity in the presence of 0.01g of the modified nanofiber.

The data processing for the specification of the best isothermal model and adsorption kinetics was carried out based on first and second order Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Harkins-Jura's isothermal models as well as the pseudo first order, pseudo second order and intraparticle diffusion kinetic models; Dubinin-Radushkevich was the best isothermal model and the pseudo second order was the best kinetic model.

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