Preparation and Adsorption Property of Imido-acetic Acid Type Chelating Nano-fibers by Electro-spinning Technique

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Abstract: A novel nano-fibrous adsorbent from imino-acetic acid (IDA) and polyvinyl alcohol (PVA) mixture solution was prepared by electro-spinning technique. The nano-fibrous adsorbents with imino-acetic acid functional groups were characterized and demonstrated by fourier transform infrared spectrometry (FT-IR) and the scanning electron microscopy (SEM). The effect of the adsorbents to remove heavy metals such as lead (Pb) and copper (Cu) ions from the aqueous solution was studied. The maximum adsorption percentage (SP) of the metal ions can reach 93.08% for Cu (II) and 96.69% for Pb(II), respectively. Furthermore, it shows that the adsorption procedure of the adsorbents is spontaneous and endothermic, and adsorption rate fits well with pseudo-second-order kinetic model. Most importantly, the reusability of the nanofibers for removal of metal ions was also demonstrated to be used at least five times.

1. Introduction

Heavy metal pollution growing rapidly with industrial growth and development has seriously threatened the public health and safety in recent years [1-4]. Therefore, many techniques (such as precipitation, ion exchange, membrane separation and adsorption) have been applied to deal with heavy metal ions in the waste water. Among them, the adsorption technique has been considered as the effective and promising method due to its low-cost and application convenience [5-8]. The properties of adsorbents (such as surface area, functional group type and density on the adsorbent surface) have significant effect on the adsorption efficiency. Hence, the morphology and the functional group type are the two key factors of adsorbents. Therefore, adsorbents of chelating nano-fibers have been widely studied, such as the adsorption of heavy metal ions from the polluted water. Great surface area, high porosity, and small pore size would have the influence on this efficiency [9,10]. Electrospinning is an efficient method of preparing chelating nano-fibers, which could even yield desirable sub-100-nm spinning fibers [11]. Regarding to types of functional groups, imino-acetic acid (IDA) has been widely used for the removal of metal ions as it could simultaneously complex with many kinds of metal ions [12-15]. Unfortunately, most reported IDA type adsorbents were in the form of granule or fiber in micro-meter [16,17], so the applications were limited owing to some disadvantages from adsorbent’s dimension. So far, there is no report on IDA type adsorbents in the form of nano-fibers.

The functionalized polymer with imino-acetic acid (IDA) functional group was synthesized in this study. It was applied to prepare IDA type chelating nano-fibers through electro-spinning [18-20]. In order to get nano-fibers with better morphology and more IDA functional groups available, the effects of spinning solution composition, the spinning parameters and the cross-linking conditions on nano-fibers have been investigated and optimized. In addition, the influence of nano-fibers on adsorption of
copper and lead ions from the aqueous solutions were investigated and analyzed by the kinetic and thermodynamic models.

2. Experimental

2.1. Materials
PVA polymers (99% hydrolyzed; 87-89% hydrolyzed) were purchased from Shanghai Aladdin Reagent Co. Ltd. (China). Polymer with imino-acetic acid as functional group (IDA) was synthesized in our lab. The other chemicals such as glutaraldehyde (GA), epichlorohydrin (ECH), copper nitrate (Cu(NO3)2·3H2O) and lead nitrate (Pb(NO3)2) were all analytical grade.

2.2. Synthesis of IDA Type Polymer
IDA type polymer was synthesized from polyethyleneimine (PEI) according to the method described previously [15]. Mixing PEI (average Mw 70000), sodium chloroacetate and sodium hydroxide (NaOH) solutions in the molar ratios of 1:1.1:1.1 in 100 mL three-necked flask, and then, it was stirred at 60°C for 12 h. After it was cooled to the room temperature, the solution pH was adjusted to 2, and then it was washed by methanol and dried in the vacuum oven.

2.3. Preparation of IDA Type Chelating Nano-fibers
10 wt% PVA99 solution was prepared at 90°C (solution a). 15 wt% PVA88 solution was provided by dissolving 4.5 g of PVA88 in 30 mL deionized water at 45°C for 4 h (solution b). IDA type polymer was dissolved in sodium hydroxide solution (2mol/L) and it was stirred at 30°C for 2 h to obtain 30wt% homogeneous solution (solution c). The spinning solution was consisted of three solutions mentioned above, and the volume ratio of a:b:c= 3:4:2. The mixture solution was stirred at the room temperature for more than 1 h, and then it was spun under the optimized conditions of voltage 24 kV, and its working distance remained 8 cm, and its feeding rate was 0.5 mL/h. The nano-fibers (pristine nano-fibers) were collected finally.

The pristine nano-fiber was pre-cross-linked in GA vapor at 35°C for 18 h (pre-cross-linked nano-fibers), and then it was cross-linked with 20% (mass fraction) ECH solution (pH = 3) for 4 h [20-22], then it was washed with the distilled water, and then it was dried in the vacuum oven at the room temperature. The harvest cross-linked nano-fibers (IDA type chelating nano-fibers) was got.

2.4. Analysis and Characterization
The functional groups of nano-fibers (pristine, pre-cross-linked and cross-linked nano-fibers) were determined in the range of 400-4000 cm⁻¹ by FT-IR (Fourier Transform Infrared Spectrometry, IR Affinity-1, SHIMADZU, Japan). The morphology of the nano-fibers was observed by SEM (scanning electron microscope, JSM-7800F, Japan).

To investigate the stability of IDA type chelating nano-fibers in the aqueous solution, the dissolve-loss studies were carried out by the immersion of nano-fibers in the distilled water for 6 h. All experiments were repeated for three times. The dissolve-loss percentage can be calculated by the following equation [23].

\[
\text{Dissolve-loss percentage (\%)} = \left(\frac{m_1 - m_2}{m_1}\right) \times 100\% \tag{1}
\]

Where \(m_1\) and \(m_2\) are the masses of the dry nano-fibers before and after being soaked, respectively.

2.5. Adsorption Experiments

2.5.1. Batch Adsorption Experiments. The effects of adsorption experimental parameters, pH (2-6), time (0-150 mins.), the initial metal ion concentration (50-250 mg/L), and temperature (298-318 K) were studied in the batch mode. In which 0.1 g cross-linked nano-fibers was immersed into 50 mL of
copper or lead ion solution with stirring for 2.5 h (Fibrous adsorbents loaded Cu(II) or Pb(II) ions). The concentration of metal ions in the solution was determined by atomic absorption spectrometry (AAS, Hitachi, Japan).

The adsorption percentage (SP) and adsorption capacity of metal ions (qe (mg/g)) can be calculated by the following equations [8].

\[
SP = \left(\frac{C_0 - C_e}{C_0}\right) \times 100\% \quad (2)
\]

\[
q_e = \frac{(C_0 - C_e)V}{m} \quad (3)
\]

Where C0 and Ce are the concentration of metal ions in the solution before and after the adsorption (mg/L), respectively. And V (L) is the volume of the solution, m(g) is the mass of nanofibers.

2.5.2. Adsorption/desorption Experiments. Fibrous adsorbents loaded Cu(II) or Pb(II) ions were immersed into HCl solution (0.1 mol/L) at the room temperature with stirring. Then, the fibers were filtrated out, and they were washed with the distilled water for three times, and then they were dried in the vacuum oven at the room temperature. The regenerated nanofibers were reused in the next cycle utilization of the adsorption experiments in the same conditions (50 mg/L, pH value of 3 and pH value of 5.5 for Cu(II) and Pb(II) ions solutions, respectively.). Residual ions in solution were determined by AAS. The relative adsorption percentage (RSP) of metal ions on nano-fibers can be calculated by the following equation.

\[
RSP = \frac{SP(n)}{SP(1)} \times 100\% \quad (4)
\]

Where SP (1) and SP(n) denote the sorption percentage (%) of adsorption/desorption cycle one and cycle n, respectively.

3. Result and Discussion

3.1. Characterization of Nano-fibers

The functional groups of nano-fibers were characterized by FT-IR (Fig. 1). A broad band at 3300-3500 cm\(^{-1}\) was assigned to N-H and O-H stretching vibrations of IDA type polymer and PVA, the carboxyl group peaked at 1720 cm\(^{-1}\) was attributed to the type of amino acetic acid functional groups. The results showed that the IDA type polymer was successfully synthesized and introduced into the composite nano-fibers. Compared with spectrum (a) and (b), the intensity of peaks at 1096 cm\(^{-1}\) and 1250 cm\(^{-1}\) corresponding to the stretching motions of C-O-C and C-O in spectrum (b) was increased as the part of hydroxyl groups of pristine nano-fibers cross-linking with GA. In spectrum (c), the sharp peak at 1399 cm\(^{-1}\) was typical stretching vibration of epichlorohydrin. It is observed that the intensity of peak at 1630 cm\(^{-1}\) corresponding to N-H bond was decreased with epichlorohydrin as the cross-linking of imino group, which indicated that N-H bond has not been converted into the type of IDA functional group completely, and the remaining imino group has been successfully crosslinked with ECH [8,21].
Figure 1. FTIR spectra of IDA type composite chelating nano-fibers: (a) pristine nano-fibers; (b) pre-cross-linked nano-fibers; (c) cross-linked nano-fibers.

Generally, there are two methods to prepare the chelating nano-fibers, one is the modification, namely, the functional group is immobilized onto the nano-fibers surfaces through chemical reaction. And the other method is the employment of the mixture solution which is composed of the functionalized polymers and materials with good spinnability. However, the morphology of the nano-fibers could be destroyed as the functional group is immobilized to nano-fibers surface through chemical reaction [24]. Therefore, electro-spinning mixture solution was used to prepare nano-fibers. The SEM images of pristine, pre-crosslinked and cross-linked nano-fibers were presented in Fig. 2.

Figure 2. The SEM image of nano-fibers: (A) pristine nano-fibers; (B) pre-cross-linked nano-fibers; (C) cross-linked nano-fibers.

Fig.2 (A) showed that the surface of pristine nano-fibers was very smooth. The diameter of the pristine fibers was quite uniform with average value of (150±77) nm. Fig.2 (B) showed that the morphology of nano-fibers pre-crosslinked
Figure 3. The fiber diameter distribution of nano-fibers: (a) pristine nano-fibers; (b) pre-cross-linked nano-fibers; (c) cross-linked nano-fibers.

With GA vapor, and the diameter of the pre-cross-linked nano-fibers was (190±72) nm. As shown in Fig.2(C), the nano-fibrous morphology almost was the stable, and it still showed the fluffy porous network structure, although the diameter of crosslinked IDA type chelating nano-fibers increased to (250±98 nm) nm. It meant that the chelating nano-fibers were successfully formed without remarkable variation in morphology no matter after pre-cross-linking or cross-linking.

Figure 4. Degree of dissolve-loss percentage of nano-fibers (pristine and cross-linked IDA type composite chelating nano-fibers).

Fig. 4 showed that the dissolve-loss percentage (%) of nano-fibers (pristine and cross-linked with ECH) in the distilled water was more than 6 h. As it can be seen, the dissolve-loss percentage of the cross-linked nano-fibers was considerably decreased. The results suggests that the IDA type composite chelating nano-fiber has been cross-linked effectively, which can increase the water diffusivity resistance and improve the stability of nano-fiber membranes in solution.

3.2. Effect of pH on Adsorption Ability

PH was the important factor which could affect the interaction between adsorbents and metal ions. Since hydroxide would be formed and precipitated as the pH value of copper and lead ion solution was
above 6, the experiments were conducted while pH value was 2-5 for Cu(II) and pH value was 2-6 for Pb(II), respectively. Fig. 5 showed that the adsorption rate (AR) (%) of metal ions on nano-fibers was as the function of the pH. For Cu(II), as pH was 3.0, AR value was the maximum. While for Pb(II), only as pH was 5.5, AR value was the maximum. The adsorption percentage increased gradually, for Cu(II) as pH from 2.0 to 3.0 and for Pb(II) only as pH from 2.0 to 5.5. This phenomenon was resulted from the competitive interaction between H+ and the metal ion for the active sites on the adsorbent. As pH value increased, the concentration of H+ in the solution was reduced, and which resulted in that there was more chance of interaction with the binding sites and metal ions [25]. However, as the pH value further increased, the adsorption percentage decreased rapidly for Cu(II). While as the pH value increased to 6.0 for Pb(II), the SR also showed the reduction, which would probably due to the interaction of OH- ion with Cu(II) and Pb(II), and the free target metal ions available was reduced. To exclude the influence of the hydrolysis of metal ions, the optimal pH value was selected as pH = 3.0 for Cu(II), pH = 5.5 for Pb(II) for the subsequent adsorption experiments.

![Figure 5. The effect of solution pH on adsorption percentage. (Initial metal ion concentration of 50 mg/L; Temperature of 293 K)](image)

3.3. Effect of Contact Time on Adsorption

The effect of contact time on adsorption percentage was given in Fig. 6. The results showed that the AR(%) increased sharply within 10 mins., as more than 70% of total sorption of metal ions was adsorbed, then the AR(%) increased slowly till 80 mins., when the adsorption equilibrium was reached. This trend might be explained by the presence of free sites and available metal ions at first. As the adsorption increased, the available sites of Cu(II) and Pb(II) in the aqueous solution were depleted.
Figure 6. The effect of contact time on adsorption percentage (pH 3.0 for Cu(II) and pH 5.5 for Pb(II); Initial concentration of 50 mg/L; Temperature of 293 K).

To describe the kinetic mechanism of the adsorption process more accurately, the experimental data fitted well with two common models, namely pseudo-first-order (Eq. (5)) and pseudo-second order (Eq. (6)) kinetic models respectively [26]. The fitted parameters were shown in Table 1.

\[
\ln(q_e - q_t) = \ln q_e - \frac{k_1}{2.303} t
\]

(5)

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

(6)

Where \( q_e \) (mg/g) and \( q_t \) (mg/g) are the adsorption capacity of metal ions adsorbed at equilibrium and time \( t \) (min), respectively. \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g/mg min) are the rate constants of pseudo-first-order and pseudo-second-order models, respectively.

Table 1. Kinetic Parameters Of Fibrous Adsorbents For Cu(II) And Pb(II) Adsorption (pH=3 For Cu(II), pH=5.5 For Pb(II); Initial Metal Ion Concentration Of 50 Mg/L; Temperature Of 293 K)

| Metal ion | \( q_{exp} \) (mg/g) | Pseudo-first-order model | Pseudo-second-order model |
|-----------|-------------------|--------------------------|---------------------------|
|           | \( k_1 \) (min\(^{-1}\)) | \( q_{cal} \) (mg/g) | \( R^2 \) | \( k_2 \) (g/mg min) | \( q_{cal} \) (mg/g) | \( R^2 \) |
| Cu(II)    | 21.64             | 0.1303                   | 15.12                     | 0.919 | 0.0124 | 22.17 | 0.999 |
| Pb(II)    | 23.71             | 0.0925                   | 15.72                     | 0.916 | 0.0084 | 24.51 | 0.998 |

By comparing the values of correlation coefficient for pseudo-first-order and pseudo-second-order as shown in Table 1. It was found that the kinetic data of both metal ions fitted with pseudo-second-order model more greatly. The results suggested that both concentration of metal ions and unoccupied adsorptive sites were the key factors which influenced on the adsorption performance of the chelated nano-fibers.

3.4. Adsorption Isotherms

The effect of the initial concentration (\( C_0 \)) of metal ions and temperature on the adsorption was presented in Fig.7. It showed that the adsorption capacity of Cu(II) and Pb(II) was increased with the increase of the initial concentration \( C_0 \). Without exception, the removal efficiency of metal ions with IDA type chelating nano-fibers also improved with the temperature was increased. The adsorption
percentage reached 93.08% for Cu(II), 96.69% for Pb(II) adsorption while the initial concentration was 50 mg/L and the temperature was 40°C. The maximal adsorption capacity was 101.28 mg/g and 111.15 mg/g for Cu(II) and Pb(II), respectively. Which was much larger than that of IDACF [17]. These results indicated that the studied IDA type chelating nanofiber was probably useful for the advanced wastewater treatment.

![Figure 7](image.png)

**Figure 7.** The effect of temperature on adsorption isotherm: (a) adsorption percentage for Cu(II); (b) adsorption capacity for Cu(II); (pH=3.0 for Cu(II); 50 mL) (c) adsorption percentage for Pb(II); (d) adsorption capacity for Pb(II) on IDA type composite chelating nano-fibers (pH=5.5 for Pb(II); 50 mL).

To further understand the adsorption mechanism of IDA type chelating nano-fibers, two isotherm models [27,28], namely Langmuir and Freundlich models were employed to analyze the experimental data as following equations.

\[
\frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{C_e}{q_m}
\]

\[
\log q_e = \log K_F + \frac{1}{n} \log C_e
\]

where \(q_e\) (mg/g) is the adsorption capacity at equilibrium time, \(C_e\) (mg/L) is the equilibrium concentration of metal ions in solution, \(q_m\) (mg/g) is the theoretical saturation adsorption capacity, and \(K_L\) (L/mg) is the Langmuir constant. \(K_F\) (mg/g) is the binding energy constant reflecting the affinity of the adsorbents to metal ions and \(n\) is the Freundlich parameters related to the adsorption intensity.

| Metal ion | T (K) | Q_{max} (mg/g) | \(K_L\) (L/mg) | \(R^2\) | K_F (mg/g) | n | \(R^2\) |
|-----------|-------|----------------|----------------|--------|------------|---|--------|
| Cu(II)    | 293   | 107.5          | 0.0388         | 0.999  | 8.812      | 1.901 | 0.961 |
|           | 303   | 117.6          | 0.0521         | 0.998  | 11.28      | 1.919 | 0.965 |
|           | 313   | 128.2          | 0.0722         | 0.997  | 14.62      | 1.921 | 0.974 |
| Pb(II)    | 293   | 128.2          | 0.0563         | 0.996  | 12.81      | 1.906 | 0.988 |
|           | 303   | 135.1          | 0.0792         | 0.996  | 16.22      | 1.926 | 0.986 |
|           | 313   | 138.9          | 0.113          | 0.994  | 20.39      | 1.960 | 0.986 |

As shown in Table 2, the high regression correlation coefficients (\(R^2 > 0.99\)) were presented. It suggested that the adsorption of both Cu(II) and Pb(II) onto IDA type chelating nano-fibers fitted...
particular well with Langmuir model compared with Freundlich model. This indicated that the adsorption occurred only on the surface of IDA type nano-fibers, and there existed the monolayer adsorption phenomenon.

3.5. Thermodynamic Parameters

Thermodynamic parameters (such as Gibbs free energy, enthalpy change and entropy change) play vital roles in the adsorption process. It illustrates the degree of spontaneity and feasibility of process. Thermodynamic parameters might be calculated by the following equations [29].

\[
\ln K = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}
\]

(9)

\[
\Delta G = -RT \ln K
\]

(10)

where \( R \) is the gas constant, \( T \) is the absolute temperature (K), \( \Delta H^0 \) is the enthalpy change (kJ /mol), \( \Delta G^0 \) is the free energy change (kJ /mol), the \( \Delta H^0 \) can be obtained from the slope of \( \ln K \) versus plot \( 1/T \). \( K \) (L/mg) is the adsorption equilibrium constant, which equals to Langmuir constant (\( K_L \)) owing to the adsorption process fitted well with Langmuir model [30].

| Metal ion | \( \Delta G^0 \) (KJ/mol) | \( \Delta H^0 \) (KJ/mol) | \( \Delta S^0 \) (KJ/mol) |
|-----------|--------------------------|--------------------------|--------------------------|
|           | \( 293 \) K              | \( 303 \) K              | \( 313 \) K              |
| Cu(II)    | -25.74                   | -27.35                   | -29.11                   | 23.65                   | 0.168                   |
| Pb(II)    | -26.65                   | -28.42                   | -30.28                   | 26.60                   | 0.181                   |

As shown in Table 3, the values of \( \Delta G^0 \) were negative for both Cu (II) and Pb (II) at the studied conditions, and they were inclined to be more negative with increasing temperature, it indicated that the adsorption process was feasible and the reaction was spontaneous and more favorable at the higher temperatures. The positive value of \( \Delta H^0 \) also implies that the adsorption process is endothermic. Furthermore, both the \( \Delta H^0 \) for Cu (II) and Pb(II) are greater than 20.9 KJ, which reveals that the adsorption is a chem.-sorption process due to chelation mechanism.

3.6. Regeneration Characteristics

The reuse of the adsorbent is the key factor in industrial application. To demonstrate the reusability of the IDA type chelating nano-fibers, it was used for five times in the adsorption-desorption of copper and lead ions onto IDA type nano-fibers, it performed almost the same in the same conditions. The relative adsorption percentage of IDA type nano-fibers versus adsorption/desorption cycle was presented in Fig. 8. It showed that RSP (%) could still reach 90% for Cu (II) and 88% for Pb (II) of initial sorption percentage value after five cycles. This indicated that IDA type chelating nano-fibers could be reused without the significant loss in the adsorption property and they could be a very potential adsorbent utilized extensively in aqueous solution.
Figure 8. The relationship between the changes of adsorption percentage and adsorption/desorption cycles (pH=3.0 for Cu(II) and pH=5.5 for Pb(II); Initial concentration of 50 mg/L; Temperature of 293 K)

4. Conclusion
In the present work, IDA type chelating nano-fibers was prepared by electro-spinning technique, and the potential of IDA type nano-fibers as the adsorbent for the adsorption of copper and lead ions from the aqueous solutions was investigated. The maximal sorption percentage (SP) of the metal ions could reach to 93.08% for Cu (II) and 96.69% for Pb (II), respectively. The kinetic data of metal sorption onto the nanofiber membrane fitted well with the pseudo-first-order kinetic model. The comparison of isotherm models showed that Langmuir model could describe the equilibrium data of copper and lead sorption more appropriately than Freundlich model. The thermodynamic parameters show that both of metal ions sorption by the IDA type composite chelating nanofibers is endothermic and spontaneous nature. Furthermore, the adsorption capacity of IDA type nano-fibers can remain almost unchangeable even after being used as adsorption-desorption for five times. This result suggests that the IDA type composite chelating nano-fibers can be a promising adsorbing material for removing heavy metal ions in the aqueous solution.

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References
[1] L. Bai, H. Hu, W. Fu, J. Wan, X. L. Cheng, L. Zhuge, L. Xiong, Q. Y. Chen, “Synthesis of a novel silica-supported dithiocarbamate adsorbent and its properties for the removal of heavy metal ions,” J. Hazard. Mater, vol. 195, pp.261-275, , August 2011.
[2] M. Alabadi, M. Irani, J. Ismaeili, H. Piri, M. J. Parnian, “Electrospun nanofiber membrane of PEO/Chitosan for the adsorption of nickel, cadmium, lead and copper ions from aqueous solution,” Chem. Eng. J, vol. 220, pp. 237-243, January 2013.
[3] Q. Zhang, K. Xia, Y. Liu, Y. C. Liu, C. Zhang, X. Liu, H. Xu, J. D. Chen, “Genome-wide identification and characterization of cadmium-responsive microRNAs and their target genes in radish (Raphanus sativus L. )roots,” Chem. J. Chinese. Univ, vol. 34, pp. 2667-2673, September 2013.
[4] I. Memon, Q. Ali, A. Zubedi, F. A. Mangi, "DPMM: dynamic pseudonym-based multiple mix-zones generation for mobile traveler." Multimedia Tools & Applications, pp. 1-30, 2016.

[5] L. Y. Tong, J. D. Chen, Y. Y. Yuan, Z. H. Cui, M. F. Ran, Q. Zhang, J. Bu, F. Q. Yang, X. H. Su, H. Xu, "A Novel Lead Ion-Imprinted Chelating Nanofiber: Preparation, Characterization, and Performance Evaluation," J. Appl. Polym. Sci, vol. 132, pp. 41507, September 2014.

[6] F. L. Fu, Q. J. Wang, "Removal of heavy metal ions from wastewaters: a review." Environ. Manage, vol. 92, pp. 407-418, March 2011.

[7] S. Abbbasazadeh, A. R. Keshtkar, M. A. Mousavian, "Preparation of a novel electrosyn polyvinyl alcohol/titanium oxide nanofiber adsorbent modified with mercapto groups for uranium(VI) and thorium(IV) removal from aqueous solution." Chem. Eng. J, vol. 220, pp. 161-171, January 2013.

[8] L. R. Rad, A. Momeni, B. F. Ghazani, M. Irani, M. Mahmoudi, B. Noghred, "Removal of Ni2+ and Cd2+ ions from aqueous solutions using electrosyn PVA/zeolite nanofibrous adsorbent." Chem. Eng. J, vol. 256, pp. 119-127, November 2014.

[9] S. Wu, F. Li, H. Wang, L. Fu, B. Zhang, G. Li, "Effects of poly (vinyl alcohol) (PVA) content on preparation of novel thiol-functionalized mesoporous PVA/SiO2 composite nanofiber membranes and their application for adsorption of heavy metal ions from aqueous solution." Polym, vol. 51, pp. 6203-6211, October 2010.

[10] F. Ruggieri, A. A. D’Archivio, D. Camillo, L. Lozzi, M. A. Mercorio, S. J. Santucci, "Optimization in control: methods and applications." Sep. Sci, vol. 38, pp. 1402-1410, August 2002.

[11] Hai. T. Zhang ; Q. Wang ; Z. Y. Chen ; F. L. Wei ; "Dynamics and Feedback Control of Electrosprinning Processes." IEEE Transaction on Control Systems Technology, vol. 25, no.2, pp. 2017.

[12] T. B.Qian, W. Q., "Effect of lignocellulose-derived inhibitors on growth and hydrogen production by Thermoanaerobacterium thermosaccharolyticum W16." Techno. of Water. Treat, vol. 12, pp. 300-304, November 2009.

[13] L. Yang, Y. Li, L. Wang, Y. Zhang, X. Ma, Z. Ye, "Preparation and adsorption performance of a novel bipolar PS-EDTA resin in aqueous phase." J. Hazard. Mater, vol. 180, pp. 98-105, March 2010.

[14] I. Memon, "Authentication User’s Privacy: An Integrating Location Privacy Protection Algorithm for Secure Moving Objects in Location Based Services." Wireless Personal Communications, vol. 82, no.3, pp. 1-16, 2015.

[15] Y. B. Li, B. J. Gao, R. X. Wang, R. K. Du, "Cardiomyocyte-derived adiponectin is biologically active in protecting against myocardial ischemia-reperfusion injury." J. Funct. Polvm, vol. 23, pp. 236-242, December 2009.

[16] S. Kagaya, H. Miyazaki, Y. Inoue, T. Kato, H. Yanai, W. Kamichatani, T. Wajiwara, M. Saito, K. Tohda, "Chelating fibers prepared with a wet spinning technique using a mixture of a viscosce solution and a polymer ligand for the separation of metal ions in an aqueous solution." J. Hazard. Mater, vol. 203-204, pp. 370-373, December 2011.

[17] J. X. Qian, "A statistical analysis of coal mine accidents caused by coal dust explosions in China." Study on preparation and application of iminodiacetic acid chelate fiber. Thesis, Beijing. Institute of. Technology, vol. 22, pp. 528-532, 2009.

[18] I. Memon, L. Chen, A. Majid, M. Q. Lv, I. Hussain, G. C. Chen, "Travel Recommendation Using Geo-tagged Photos in Social Media for Tourist." Wireless Personal Communications, vol. 80, no.4, pp. 1347-1362, 2014

[19] E. Bastürk, S. Demir, Ö. Danış, M. V. Kahraman, "Covalent immobilization of α-amylase onto thermally crosslinked electrosyn PVA/PAA nanofibrous hybrid membranes." J. Appl. Polym. Sci, vol. 127, pp. 349, May 2012.

[20] L. L.Wu, X. Yuan, S. Sheng, "Immobilization of cellulase in nanofibrous PVA membranes by electrospinning." J. Membr. Sci, vol. 250, pp. 167-173, March 2005.
[21] C. Tang, C. D. Saquing, J. R. Harding, S. A. Khan, “In Situ Cross-Linking of Electrospun Poly(vinyl alcohol) Nanofibers.” Macromolecules, vol. 43, pp. 630-637, December 2009.

[22] Y. H. Yuan, “Study on the adsorption of copper ions by epichlorohydrin-crosslinked chitosan/sodium alginate adsorbent.” Preparation, Structure and Properties of Modified Polymers Based on Chitosan and Sodium Alginate Ph.D. Thesis, South China University of Technology, vol. 40, pp. 148-154, July 2012.

[23] M. A. Ghalia, Y. Dahman, “Radiation crosslinking polymerization of poly (vinyl alcohol) and poly (ethylene glycol) with controlled drug release.” J. Polym. Res, vol. 22, pp. 1-9, November 2015.

[24] X. Li, C. Zhang, R. Zhao, X. Xu, X. T. Jia, C. Wang, L. Li, “Efficient adsorption of gold ions from aqueous systems with thioamide-group chelating nanofiber membranes.” Chem. Eng. J, Vol. 229, pp. 420-428, August 2013.

[25] Y. Zhang, Y. Chen, C. Wang, Y. Wei, “Immobilization of 5-aminopyridine-2-tetrazole on cross-linked polystyrene for the preparation of a new adsorbent to remove heavy metal ions from aqueous solution.” J. Hazard. Mater, vol. 276, pp. 129-137, July 2014.

[26] Y. S. Ho, G. McKay, “Comments on using of “pseudo-second-order rate equation” in Journal of Radioanalytical and Nuclear Chemistry, Volume 283.” Process. Saf. Environ. Prot, vol. 76, pp. 332, August 2010.

[27] S. J. Allen, G. McKay, J. F. Porter, “Adsorption isotherm models for basic dye adsorption by peat in single and binary component systems.” J. Colloid. Interface. Sci, vol. 280, pp. 322, December 2004.

[28] A. R. Keshtkar, M. Irani, M. A. Moosavian, “Removal of uranium (VI) from aqueous solutions by adsorption using a novel electrospun PVA/TEOS/APTES hybrid nanofiber membrane: comparison with casting PVA/TEOS/APTES hybrid membrane.” J. Radioanal. Nucl. Chem, vol. 295, pp. 563-571, January 2013.

[29] M. Irani, A. R. Keshtkar, M. A. Moosavian, “Removal of cadmium from aqueous solution using mesoporous PVA/TEOS/APTES composite nanofiber prepared by sol–gel/electrospinning.” Chem. Eng. J, vol. 200, pp. 192-201, August 2012.

[30] E. S. Kunarti, “Production of metal ion imprinted polymer from mercapto–silica through sol–gel process as selective adsorbent of cadmium.” Desalination, vol. 251, pp. 83-89, February 2010.