

Preparation of polyacrylnitrile (PAN)/ Manganese oxide based activated carbon nanofibers (ACNFs) for adsorption of Cadmium (II) from aqueous solution

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Abstract. In this work, activated carbon nanofibers (ACNFs) from precursor polyacrylnitrile (PAN) and manganese oxide (MnO₂) were prepared via electrospinning process. The electrospun PAN/MnO₂-based ACNFs were characterised in term of its morphological structure and specific surface area using SEM and BET analysis respectively. The comparative adsorption study of cadmium (II) ions from aqueous solution between the neat ACNFs, composite ACNFs and commercial granular activated carbon was also conducted. SEM analysis illustrated that composite ACNFs have more compact fibers with presence of MnO₂ beads with smaller fiber diameter of 437.2 nm as compared to the neat ACNFs which is 575.5 nm. BET analysis elucidated specific surface area of ACNFs/MnO₂ to be 67 m²/g. Under adsorption study, it was found out that Cd (II) removal by ACNFs/MnO₂ was the highest (97%) followed by neat ACNFs (96%) and GAC (74%).

1. Introduction

Water contamination by cadmium has led to numerous studies being conducted for its removal. In general, cadmium (Cd) is categorized as heavy metal that is normally found as ores in other elements and exists in the state of 2+ in aqueous solution. It is primarily used for metal plating and coating operation, including transportation equipment machinery and baking enamels as well as in nickel-cadmium and solar batteries. The metallurgic industries and mining mentioned earlier serve as anthropogenic factor for its presence in water. Exposure of cadmium has been profound to be associated with renal damage, osteoporosis, negative bone effects and cancer. Due to that, the maximum contaminant level set by World Health Organization and Environmental Protection Agency (EPA) is 0.005 mg/L [1].

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Due to hazardous impacts of cadmium exposure, many methods are being employed for its removal such as precipitation, coagulation-flocculation, flotation, ion exchange, membrane filtration and adsorption [2]. Among the aforementioned techniques, adsorption has been found to be the most feasible method to eliminate metallic ions imputed by wide range of adsorbents are available, simpler technique and economic. Conventionally, activated carbons (ACs) in powder or granular forms are used as the common materials in adsorption method. Recently, application of activated carbon nanofibers (ACNFs) as adsorbents has attracted greater attention due to their excellent adsorption capacities attributed by their smaller fibre diameter, more concentrated pore size distribution. There are several methods can be used to fabricate nanofibers such as melt fibrillation, island-in-sea, and gas jet technique [3]. Nevertheless, it seems that electro-spinning provides more advantages in term of high production rate and relatively low in cost as compared to the other techniques mentioned previously.

To prepare electrospun ACNFs, polymer polyacrylonitrile serves as a good carbon precursor as it has high carbon yield. Recently, many researches have focused on incorporating various metal oxides such as magnesium oxide, aluminium oxide and manganese oxide into PAN-based polymer solution. It is believed that impregnation of metal oxides as additives could increase the specific surface area of ACNFs as well as the pore volume of electrospun ACNFs. Therefore, this study aimed to prepare PAN/MnO₂-based ACNFs by the process of electrospinning. The electrospun ACNFs were evaluated in term its morphological changes and its performance towards adsorbing cadmium (II) ions from aqueous solution.

2. Experimental procedures

2.1 Materials

Polyacrylonitrile (PAN) with molecular weight of 150 000 kDa was purchased from Sigma Aldrich (USA). Similarly, N,N-Dimethylformamide (DMF) and manganese (IV) oxide (MnO₂) powder with 99% purity were also purchased from Sigma Aldrich (USA). Stock solution of cadmium (II) ions was prepared using cadmium nitrate (Sigma Aldrich, USA) while pH of metal solution was adjusted by using 0.01mol of NaOH and HCl solutions.

2.2 Preparation of PAN-MnO nanofiber mats by electrospinning

In brief, dope solution of PAN-MnO₂ was prepared by mixing 2 wt% of MnO₂ (based on total weight solid) in DMF for 5 hours followed by addition of 10 wt% PAN. The dope solution was stirred on mechanical stirring plate to allow it to become homogenous. The solution suspension was subsequently fabricated by electrospinning process, under fixed electric field of 15kV/20cm and suspension rate of 1.5mL/hour. The collected nanofibrous mats were allowed to dry for at least a day prior carbonisation and activation process.

2.3 Carbonisation and chemical activation of nanofibers

The carbonisation and activation of electrospun nanofibers were carried out by following procedures described by Yusof *et.al* [4]. The nanofiber mats were initially stabilised in air at 280°C for 2 hours, with heating rate of 2°C/min followed by carbonisation was carried out in nitrogen gas at 600°C for 1 hour with heating rate of 5°C/min. The CNFs were activated by chemical activation method by soaking into KOH for 3 hours with ratio 3:1 KOH to CNFs prior heated under carbon dioxide gas at 800°C for 3 hours. The activated CNFs were later rinsed by distilled water until pH 7±0.5 and kept dry in oven at 100°C for 12 hours.

2.4 Characterisation

The morphology of the activated nanofibers were analysed by Scanning Electron Microscopy (SEM) while the specific surface area was examined by using Brunauer-Emmett-Teller and functional groups analysis was carried out by Fourier Transform Infrared (FTIR).

2.5 Comparative adsorption study of Cd

Comparative adsorption study of Cd (II) ions was analysed by investigating the adsorption performance of ACNFs/MnO₂, neat ACNFs and commercial GAC. 0.025g of the respective adsorbents was placed into conical flask containing 50 mL Cd(II) solution with initial concentration of 3.1 mg/L and pH of the solution fixed at 5.0±0.5. The samples were agitated on rotary shaker with speed of 180 rpm at 30°C for 48 hour to reach equilibrium. The sample solutions were later filtered and examined by using Atomic Absorption Spectrometer (AAS).

The adsorption capacity and the percentage of removal of Cd (II) ions of the each type of activated carbons were calculated by following equations [5]:

$$q_t = \frac{(C_o - C_t)V}{M} \quad (1)$$

And the removal efficiency was calculated using :

$$R(\%) = \frac{(C_o - C_t)}{C_o} \times 100 \quad (2)$$

where C_o and C_t is the initial and final concentration of the metallic solution (mg.L⁻¹), V is the volume of the solution (L), and M is the weight of the adsorbent used (g).

2.6 Desorption of PAN-MnO₂ activated nanofibers

Desorption of ACNFs used in this study was performed to identify the recovery rate and reusability PAN-MnO₂ based ACNFs. The ACNFs used for batch adsorption study were rinsed with distilled water to eliminate any residual solutions and subsequently dried in oven at room temperature. Desorption of metal ions were carried out by immersing the ACNFs/MnO₂ in 1M HCl and agitated at 30°C with speed of 100 rpm for 1 hour. The concentration of Cd ions in the solution was analysed using atomic absorption spectrometer (AAS) and the desorption ratio (D) was calculated as follows:

$$D(\%) = \frac{\text{mg of metal desorbed}}{\text{mg of metal ion adsorbed into ACNFs}} \times 100 \quad (3)$$

3. Results and discussion

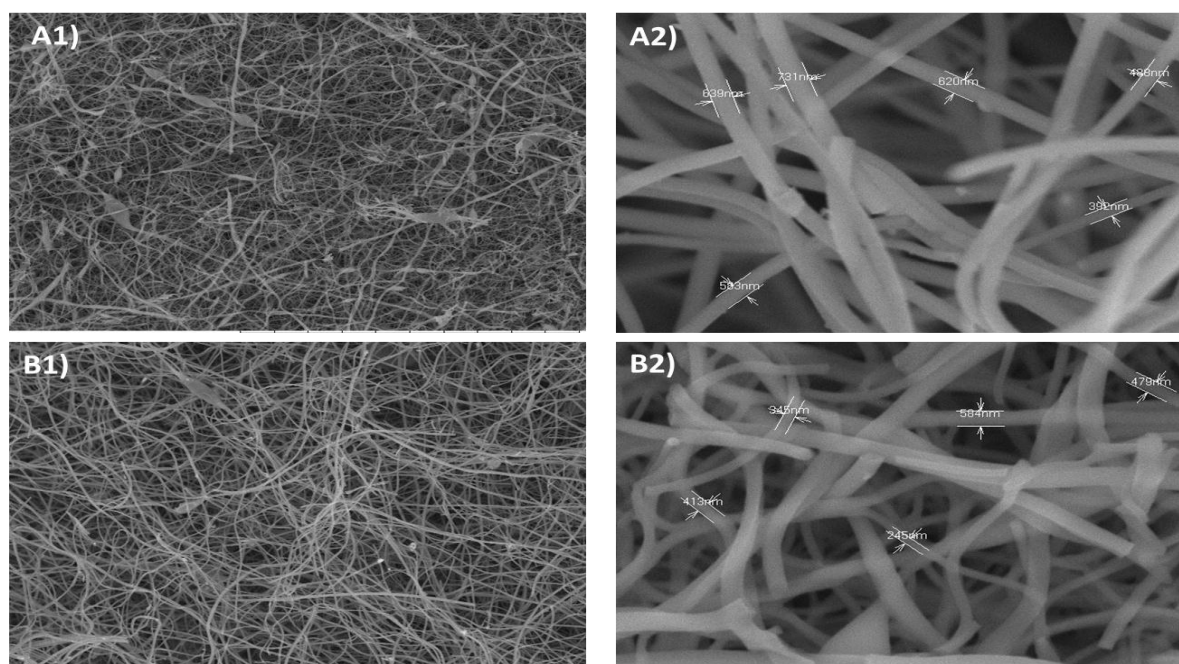


Figure 1. SEM micrograph analysis of A)neat ACNF, B)ACNF/MnO₂ where 1)500x magnification and 2)10000x magnification

Figure 1 exhibits the SEM images of neat ACNFs and ACNFs/MnO₂. From the figure, it can be seen that ACNFs/MnO₂ illustrates more compact nanofibers in comparison to the neat ACNFs which is more aligned and less compact. When compared to the diameter of ACNFs without and with MnO₂, it is revealed that ACNFs embedded with MnO₂ has smaller diameter in range of 473.2 nm while neat ACNF possess fibers with higher average diameter of 575.5nm. In addition, the presence of beads in composite ACNFs may be caused by the MnO₂ particles. The morphology of electrospun ACNFs obtained in this study is concurring to the study conducted by Choi *et.al* [6] in which the ACNF/MnO₂ exhibits as compact nanofibers with dispersion of beads containing MnO₂ particles.

Specific surface area (SSA) analysis of the ACNFs in this study was found to be 16 m²/g for neat ACNFs and 67 m²/g for ACNFs/MnO₂, respectively. Theoretically, the SSA obtained for the electrospun ACNFs was low as compared to other composite ACNFs reported elsewhere. Nevertheless, similar result was obtained by study of Wang *et.al* [7] that also demonstrated lower SSA of carbon nanotubes/manganese oxide. It is believed that the carbonisation and activation process of the composite nanofibers in this study might be incomplete, resulting to low SSA when analysed by BET analysis. For complete activation with low loading of manganese oxide, the specific surface area may increase up to 500 m²/g however any further increment of MnO₂ loading will yield lower SSA as reported by Watanabe *et.al* [8].

Table 1. Comparative study of removal of Cd (II) ions by granular activated carbon (GAC), neat ACNFs and ACNFs/MnO₂. Operating conditions: membrane dose=1g/L, stirring speed = 180 rpm, temperature= room temperature, and contact time = 48 hours.

Cd (II) initial concentration (mg/L)	Adsorbents	Removal efficiency (%)	Adsorption capacity (mg/g)
3.1	GAC	74	5.4
	Neat ACNFs	88	6.2
	ACNFs/MnO ₂	97	6.6

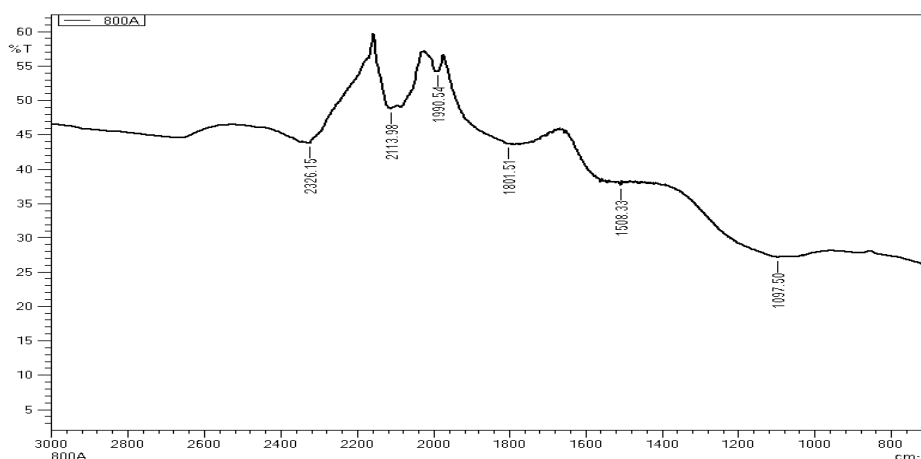


Figure 2. FTIR spectrum of ACNFs/MnO₂

Table 1 tabulates the comparative adsorption study of Cd (II) by granular activated carbon, pure ACNFs and ACNFs/MnO₂. From the table it can be seen that highest removal of Cd (II) was achieved when composite ACNFs/MnO₂ was used as adsorbent in the solution which is 97% followed neat ACNFs (96%) while adsorption by GAC illustrated lower removal efficiency which is 74 %. In theory, the removal capability can be linked to the SSA where more active adsorption sites are available. Nevertheless, in this study the SSA was found to be low. Research by Wang and co-workers [7] stated that despite specific surface area may enhance the adsorption performance, it is however no direct correlation between metal ion adsorption capacity of ACNFs with their specific area, specific pore volume and pore diameter. Thus, the adsorption capacity may also attributable to the amount of surface total acidity present on the surface of ACNFs/MnO₂. Based on this statement, it can be depicted that the adsorption of Cd (II) ions onto ACNFs occur by means of chemisorption where it is mainly controlled by the strong interaction between Cd (II) ions and surface functional groups such as carboxyl and hydroxyl [9,10].

As depicted by figure 2, there are five major peaks observed located at 2326.15 cm⁻¹, 2113.98 cm⁻¹, 1990.54 cm⁻¹, 1801.51 cm⁻¹ and 1097.50 cm⁻¹. The peak 2326.15 cm⁻¹ is assigned as O-H stretch from strongly hydrogen-bonded -COOH. Peaks 2113.98 and 1990.54 cm⁻¹ basically attributed to the strong stretching of C=C groups and peak 1801.51 and 1097.50 indicated as stretching vibrations of C-O groups. These detected functional groups may play role for adsorption of Cd (II). In addition, the mechanism of chemisorption can basically confirmed by testing two common sorption models which

are Langmuir model and Freundlich model based on their respective equations, and evaluation of their regression value (not performed in this study) [5]. It is also demonstrated that the adsorption capacity of composite ACNFs used in this study is 6.1 mg/g that is higher as compared to the commercial GAC (4.6 mg/g). The higher adsorption capacity can be explained by the role of manganese oxide itself that functions as an adsorbent and it has higher affinity towards metallic ions [11].

For desorption study, it was found out that ACNFs used in this study has higher regeneration rate which was more than 95%. This high reusability exhibits its potential as another promising adsorbent for heavy metal adsorption.

4. Conclusion

This present study reports the preparation of ACNFs/manganese oxide by electrospinning process for removal of cadmium (II) ions from aqueous solution. In this study, ACNFs shows promising adsorption capacity upon adsorbing Cd (II) as compared to the commercial GAC. The ACNFs incorporated by MnO₂ has found to be more compact and possessed smaller diameter as compared to the neat ACNFs. In this study, the adsorption process is believed to occur by means of chemisorption that involves the interaction of Cd (II) ions with surface functional groups, regardless of their low specific surface area. The sorption/desorption study indicates the excellent reusability of this new type of activated carbon. Further research on exploring more potential of these ACNFs is recommended.

5. References

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