

# Preparation of Nanofiber Affinity Membrane by Electrospinning and its Application in Metal Ion Recovery

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## Abstract

**With the rapid development of modern industry and agriculture, metal ion wastewater is being discharged unchecked, resulting in serious pollution of water and soil resources systems. At the same time, the unrestrained exploitation and waste in recent decades have led to the gradual depletion of metal ion mineral resources. Among them, rare earth metal ions, as national strategic resources, have application value in many high-tech fields. Therefore, how to effectively separate and recycle metal ions in wastewater is one of the research hotspots. Adsorption separation technology has the advantages of high efficiency, low cost, simple operation and equipment, and low energy consumption, and is widely used in metal ion wastewater treatment.**

## Keywords

**Metal Ions; Adsorption; Electrospinning.**

## 1. Introduction

In recent years, especially in developing countries, with the rapid development of modern industry, mining and energy, a large amount of heavy metal ion wastewater has been directly or indirectly discharged into the ecological environment, aggravating water and soil pollution and water resource shortage[1]. In particular, the wastewater containing 9 heavy metals such as chromium, cadmium, copper, mercury, nickel and lead generated in the process of machinery manufacturing, chemical industry and electronic industry is one of the industrial wastewater with the most serious water and soil pollution[2]. According to relevant data, the situation of heavy metal pollution in our country is already quite serious, and the direct economic losses caused by heavy metal pollution are already up to 20 billion yuan per year. In addition, unlike organic pollutants, toxic and carcinogenic heavy metal ions do not degrade and decompose over time in nature. They persist in surface and groundwater for long periods of time and can easily accumulate in organisms, causing serious damage to the ecosystem and accumulating in the human body through the food chain. Ultimately, it will pose a serious threat to human health[3]. The World Health Organisation has set clear standards for the content of various heavy metals in water. The levels of heavy metals must be kept at very low levels to ensure human health. Therefore, in order to stabilise the ecological environment and the safety of human drinking water on the one hand, and to effectively recycle precious metal resources on the other hand,

the development of a new efficient and low-cost purification technology for metal ion recovery has become one of the urgent problems to be solved in the 21st century. At present, metal ion recovery methods generally include chemical precipitation, electrolysis, ion exchange, solution extraction and adsorption.

## 2. Chemical Precipitation Method

The chemical precipitation method is to add precipitant to metal ion wastewater to convert dissolved metal ions into water-insoluble precipitate, and then remove the sediment by filtration and separation method. However, the concentration of the wastewater solution treated by the precipitation method is often still not up to the requirements, which requires further treatment and requires the consumption of a large number of chemical precipitators. The treatment process is long, the cost is high and the precipitate produced can easily cause secondary pollution.

## 3. Ion Exchange Method

Ion exchange is a commonly used method in the early stages of rare earth ion separation. The step is to fill the column with ion exchange resin and then adsorb the ion mixture at one end. The eluent is allowed to flow through the column from top to bottom, and the ions that form the complex with the resin will flow down with the eluent. Although this method can achieve multiple ion separation and high throughput, it cannot achieve continuous operation, and the operation cycle is long, the cost is high, the resin is prone to failure, and the cost of regeneration and replacement is very high.

## 4. Membrane Filtration

Membrane separation technology refers to the separation and enrichment of metal ions in wastewater by using a selective semi-permeable membrane under the driving force of external pressure [4]. The key technology of this method is the properties of the membrane, which mainly relies on the selective permeability of the membrane to separate metal ions from water. Although membrane filtration has the advantages of high separation efficiency, simple operation and no secondary pollution, its further application is limited by its complex separation equipment, high energy consumption, poor membrane stability and easy pollution.

## 5. Adsorption Method

Adsorption method as a relatively popular method to remove metal ions in water and soil resources system, which has the advantages of high recovery and separation efficiency, no chemical pollutants, easy to operate and so on. The most important core and factor of the adsorption effect is the type and property of adsorbent. A good adsorbent should have stable chemical properties, good mechanical properties and environmentally friendly properties and so on.

## 6. Electrostatic Spinning Nanofiber Affinity Membrane

Affinity membrane separation technology is a new type of separation technology. Its principle is to introduce different functional ligands into affinity membranes by using the specific interaction between target molecules or ions and ligands, and to separate and detect different molecules or ions, which is the development trend of affinity membranes. The technology of electrostatic spinning of nanofibers can effectively improve the above problems and become a new technology for the preparation of affinity membranes. First of all, electrospinning is a

simple and widely used method that can be applied to produce most polymeric membrane materials. The modification of the raw materials does not affect their fibre properties. In addition, due to the fully porous structure of the electrospun nanofibre membrane, it has a higher porosity so that surface grafting modification can be used to introduce the ligands into the interior of the membrane.

Ki [5] made a first attempt to prepare the electrostatic spinning nanofibre affinity membrane blended with silk fibroin and keratin/silk fibroin, and tested its adsorption performance of heavy metal ions. Due to the large specific surface area and porosity, the adsorption capacity of nanofibre membranes for  $\text{Cu}^{2+}$  ( $2.88 \mu\text{g}/\text{mg}$ ) is 4-10 times that of commercial filters (wool strips and filter paper). Ding et al. recently used a simple method to prepare a series of cellulose nanofibre membranes with carboxylated surfaces. For example, after hydrolysis of cellulose acetate, the surface was chemically grafted with homophenic tetrachloric anhydride and maleic anhydride, which had high adsorption capacity and good regeneration capacity for  $\text{Pb}^{2+}$  and lysozyme, respectively. In addition, some researchers have tried to introduce functional groups on the surface of nanofibres by in-situ polymerisation of monomers. Si [6] synthesized a  $\text{Fe}_3\text{O}_4$ @carbon nanofiber membrane with a specific surface area up to  $1885 \text{ m}^2/\text{g}$ , which showed good organic dye removal ability.  $\text{NiFe@SiO}_2$  mesoporous nanofiber membranes and  $\text{ZrO}_2$ @ $\text{SiO}_2$  mesoporous nanofiber membranes were prepared by electrospinning  $\text{SiO}_2$  nanofibers combined with dipping coating.  $\text{Fe}_3\text{O}_4$ /PAN composite nanofibers and  $\text{SiO}_2$ @ $\gamma$ -Al $_{2\text{O}_3}$  nanofibers were prepared by electrospinning combined with solvothermal technology. GO/ $\text{Fe}_3\text{O}_4$ -embedded PAN nanofiber membranes were synthesised by one-step electrospinning. They all have relatively high surface area and can effectively remove pollutants from wastewater.

## 7. Conclusion and Outlook

With the development and maturity of electrospinning technology, functional electrospinning nanofiber membrane, as a novel adsorption material, is more and more favored by the majority of scientific researchers, so the development of functional electrospinning nanofiber affinity membrane is one of the major development directions in the field of adsorption and separation. Although the technology of electrospinning nanofibers is developing rapidly, there are still many challenges in the preparation of electrospun affinity membranes and the optimization of adsorption properties.

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## References

- [1] Hong G., Xiong L., Shen L., Min W., Wang C., Yu X., Wang X., High Recovery of Lead Ions from Aminated Polyacrylonitrile Nanofibrous Affinity Membranes with Micro/Nano Structure, *J. Hazard. Mater.*, 2015, 295: 161.
- [2] Greiner A., Wendorff J. H., Electrospinning: A Fascinating Method for the Preparation of Ultrathin Fibers, *Angew. Chem., Int. Ed.*, 2007, 46: 5670-703.
- [3] Frenot A., Chronakis I. S., Polymer Nanofibers Assembled by Electrospinning, *Curr. Opin. Colloid Interface Sci.*, 2004, 8: 64-75.
- [4] Bai J., Li Y., Zhang C., Liang X., Yang Q., Preparing AgBr Nanoparticles in Poly(vinyl pyrrolidone) (PVP) Nanofibers, *Colloids Surf., A*, 2008, 329: 165-168.
- [5] Ki C. S., Gang E. H., Um I. C., Park Y. H., Nanofibrous Membrane of Wool Keratose/Silk Fibroin Blend for Heavy Metal Ion Adsorption, *J. Membr. Sci.*, 2007, 302: 20-26.

- [6] Si Y., Ren T., Ding B., Yu J., Sun G., Synthesis of Mesoporous Magnetic Fe<sub>3</sub>O<sub>4</sub>@ Carbon Nanofibers Utilizing in Situ Polymerized Polybenzoxazine for Water Purification, J. Mater. Chem., 2012, 22: 4619-4622.