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Copper (II) ions adsorption from aqueous solutions using electrospun chitosan/peo nanofibres: Effects of process variables and process optimization

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ABSTRACT

Water sustainability is becoming a major concern for Canadians. Governments are actually considering various water initiatives to establish recommendations on water governance and policies to ensure the sustainability of water supply for people and industries. The pulp and paper industry is a major user of water. Implementation of such water initiatives will force them to move further towards closed-cycle papermaking. Advanced wastewater treatment methodologies will be mandatory to reduce fresh water consumption with minimum detrimental effects on papermaking operations and paper quality. Adsorption experiments were carried out using electrospun chitosan (CS)/polyethylene oxide (PEO) nanofibres to investigate adsorption of copper (II) ions from aqueous solutions. A central composite design (CCD) was used to investigate the influence of temperature, copper concentration, and adsorbent mass on adsorption efficiency. An optimal adsorption of 94.7% was obtained by using 75 mg of nanofibres in 200 min at pH 5.5 and a temperature of 55.7 °C with initial copper concentration of 100 ppm.

1. Introduction

Canada is privileged with abundant natural resources of which forests, minerals, metals, energy sources, and water. A recent survey conducted among Canadians indicated that they ranked fresh water as the most valuable natural resource ahead of forests, agriculture, oil, and fisheries [1]. However, Canadians are among the largest water users in the world. In 2004, a report by the National Research Institute carried out for Environment Canada revealed that Canadians used about 1650 cubic meters of fresh water per capita each year, which was more than double the average European rate [2]. From this, the average household use was estimated at about 330 litres per person per day (or 120 m^3 per person per year) and accounted for less than 10% of the total use [3]. The rest was mainly used by the manufacturing, mining and thermal-electric generating industries.

With expected intensification of the consequences of climate change and increased demands for the resource, Canadians are now becoming aware of the critical role water is having in their lives, on health of ecosystems, and on the economic sustainability of the natural resource sectors that contribute significantly to Canada's economic wealth and social well-being. Water sustainability is thus becoming a major issue even though Canada is perceived as a water-rich country with abundant water resources. Provincials and Federal governments are actually studying various water initiatives to establish recommendations on water governance and policies to ensure the sustainability of water supply. Water footprinting, business risk assessment frameworks, reporting and disclosure protocols, as well as standards and certification frameworks are examples of tools that are actually considered to identify and manage business risks related to water [4,5]. These efforts will result in recommendations to governments and industries on policies, approaches, and mechanisms through which water can be better managed and to protect the resource.

In 2009, Statistics Canada gathered information on the intake and discharge of water by major industrial users [6]. The survey revealed that the total water intake by manufacturing industries (paper, primary metals, chemical, food, petroleum and coal) was 3806.2 million cubic meters, with the largest quantity withdrawn by the paper industry at 41.9% of the total [6]. The survey also showed that the total water discharged was 3450.6 million cubic meters from which the paper industry accounted for 45.2% of the

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total water discharged and 80.1% of their discharge went to surface freshwater bodies [6]. Although the paper industry is among the largest water users of the manufacturing group, the majority of this water is returned to surface waters following treatment. Water management and recycling strategies have been implemented in pulp and paper mills since the 1980s resulting in a significant reduction of the average specific water consumption from 120 m^3/ton of paper produced to about 45–50 m^3/ton. However, a limitation seems to be reached due to technical and economic factors and further reduction will be challenging [7]. This is mainly attributed to the fact that as more process water is recycled, an accumulation of various contaminants including dissolved matter from wood and other raw materials entering the process is occurring which results in major problems such as deposition and scaling, foaming, corrosion, and degradation of the end product quality.

Economic issues combined with strict environmental regulations and standards are the driving forces for water reduction use at pulp and paper mills. To further reduce fresh water intake, improvement in process water recycling levels are required. One way to increase process water recycling would be to reuse treated water from the biological wastewater treatment system. However, this effluent is not sufficiently clean for reuse in the production of most paper grades. Actually, it can only be reused for production of packaging paper [8]. Although this treatment system reduces the concentrations of organic material [9], biologically treated effluents still contain significant amounts of colour compounds, microorganisms, recalcitrant organics and suspended solids. Biological treatment does not significantly reduce the inorganic content in the effluent and further processes to remove hardness salts and heavy metals must be carried out prior to recycling water back to the mill in order to avoid paper machine runnability problems, corrosion and product quality issues. Therefore, an advanced process technology is required to improve wastewater discharge quality and to reuse wastewater as process water.

Adsorption is one of the most effective processes for removal of heavy metals from wastewater due to its simplicity, moderate operational conditions and economic feasibility. Activated carbon adsorbents are widely used due to their great adsorption capacity resulting from their large surface area. However, they suffer from costly regeneration and high attrition rate. Moreover, they are generally non-selective towards contaminants, making it difficult to selectively recover certain organic chemicals for reuse. The search for low cost adsorbents has intensified in recent years. Natural polymers such as polysaccharides and their derivatives have been investigated by many research groups as alternative adsorbents to replace activated carbons [10]. Among these, chitin, starch, chitosan, and cyclodextrins have been identified as potential candidates. Development of low cost chitosan-based adsorbents is actually achieving much attention especially for the removal of heavy metals from wastewater [11–13]. Chitosan is considered to be a well-known adsorbent since it has a strong chelation potential for heavy metals due to the presence of amine and hydroxyl groups on the surface that are involved in the adsorption process [14,15]. It is also a biodegradable, natural, and non-toxic polymer derived from chitin which is abundant and readily available from shell wastes from crustaceans.

Chitosan-based materials for applications in wastewater treatment can be produced with various structural forms including nanoparticles, gel, beads, membranes, films, sponges, and fibres (nanofibres). In adsorption processes, they are generally made of solid particles such as fine powders, granules or beads which are then packed in adsorption columns (bed) where wastewater is flowing through [16–18]. However, applications in adsorption columns are restricted due to high capital and energy costs as well as unfavorable hydrodynamic properties (high pressure drops). Chitosan can also be used in membrane filtration but the process can be strongly affected by membrane fouling resulting in significant reduction of the permeate flux [19]. The process also develops large pressure drops which are energy consumptive.

Non-woven nanofibre filter media have been widely used for filtration applications [20–23]. They are made of randomly laid nanofibres forming a three dimensional porous mats which provide a physical, sized-based separation mechanism for the filtration of air and water borne contaminants [24]. Nanofibres in the size range of 3 nm to greater than 5 μm can be produced by electrospinning. Their very small diameter brings polymeric nanofibres with a set of unusual properties, such as high specific surface area, flexibility in surface functionalities and superior mechanical properties [25,26]. With such unique nanofibre properties, it is possible to make nanofibrous media with low basis weight, high permeability and small pore size that should overcome previously described problems associated to packed bed adsorption column and membrane filtration. Electrospun chitosan/PEO nanofibres have been used to adsorb heavy metals such as copper, lead, cadmium and nickel ions from aqueous solution [27,28]. However, process optimization techniques were not used in these studies. Therefore, the objectives of this study were to develop chitosan nanofibres with specific properties suitable for adsorption of copper (II) ions, and to test and optimize their adsorption capacity towards copper ions in aqueous solutions.

2. Experimental

2.1. Materials

A low molecular weight chitosan (75–85% deacetylated) was used as the main raw material in this study. A highly concentrated acetic acid (CH_3COOH) (80–90%) diluted to 50%, was used as a solvent for the chitosan polymer. Polyethylene oxide (average Mw~900 000) was used as an electrospinning co-agent by blending it with chitosan solution. Copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$) was used as a contaminant model for the adsorption study. Chitosan, acetic acid, polyethylene oxide (PEO), and copper sulfate pentahydrate were purchased from Sigma–Aldrich (USA) and used as received. Sodium carbonate (Na_2CO_3, 99+% A.C.S) was used for nanofibres neutralization. Ethylene diaminetetraacetic acid (EDTA) was used for titration of copper ion in solutions. Na_2CO_3 and EDTA were both purchased from OMEGA chemical company (USA).

2.2. Methodology

2.2.1. Electrospinning of nanofibres

Chitosan (4%wt) in 50% acetic acid and polyethylene oxide (4%wt) in distilled water were prepared separately for 18–24 h at ambient temperature. Then, 4%wt chitosan was electrospun in presence of polyethylene oxide (4%wt), with a weight ratio blend of 50:50 at ambient temperature, using an horizontal electrospinning setup containing a variable high DC voltage power supply (Gamma High Voltage Research, USA), a programmable micro-syringe pump (KD Scientific, model 100) equipped with a plastic syringe with a metallic needle, and a cylindrical collector as shown in Fig. 1. A high voltage from the power supply was then applied between the needle and the collector. The electrospinning conditions used for experiments where:

- Voltage: 25 kV.
- Solution flow rate: 0.4 mL h^{-1}.
- Nozzle-collector distance: 10 cm.
- Needle diameter: 0.6 mm I.D.
- Collector type: cylindrical.