Journal of Environmental Chemical Engineering 5 (2017) 412–421

Contents lists available at ScienceDirect

Journal of Environmental Chemical Engineering

journal homepage: www.elsevier.com/locate/jece

Preparation, characterization and lead adsorption study of tripolyphosphate-modified waste Lyocell fibers

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ARTICLE INFO

Article history:
Received 15 July 2016
Received in revised form 24 November 2016
Accepted 17 December 2016
Available online 19 December 2016

Keywords:
Heavy metal
Lyocell
Modification
Sodium tripolyphosphate
Adsorption mechanism

ABSTRACT

A facile modification of waste textile cellulose Lyocell fibers with tripolyphosphate and application of the adsorbent thereof to the treatment of Pb(II)-contaminated wastewater was investigated. Characterization and batch adsorption studies were conducted to understand the characteristics of the prepared adsorbent and its metal binding mechanisms. The adsorbent showed 100% adsorptive removal efficiency of Pb(II) at initial concentrations up to 300 mg/L, and the adsorption performance was significant even at low pH ranges. The adsorption isotherm followed the Langmuir model, and the kinetic was described by the pseudo-first and pseudo-second order models. By comparison, the adsorbent showed strong competitiveness to existing ones especially in terms of the adsorption capacity, pH, and kinetics of adsorption, and could be reused. Considering its cheap source and simplicity of preparation, the adsorbent could be applied as a low-cost material for heavy metal scavenging from wastewater streams.

1. Introduction

Toxic heavy metal pollution from mining and manufacturing industries is one among several environmental problems affecting the world today. Metal pollutants cause intense carcinogenic and other adverse health effects when even little amounts are accumulated in the bodies of living species [1–3]. Due to their severe toxicities, strict rules have been set to govern their handling and treatment before discharge from industries into the environment [4–8]. Lead is one of the most toxic heavy metals and is widely linked with many health syndromes [4,9]. It is placed first on a list of hazardous materials prohibited for use in electrical and electronic equipment by the European Directive on Restriction of Hazardous Substances [10,11]. In the 2013 ranking by the Agency for Toxic Substances and Disease Registry, lead was placed second after arsenic on a priority list comprising over 270 hazardous substances [12]. These facts clearly show the high risks associated with lead and the urgent demand for effective treatment of the effluents bearing it, or at least meet the targets set by legislation to avoid its associated health hazards. By these considerations, it is important to develop high-capacity and high-affinity adsorbents for the effective removal of lead to an acceptable limit prior to its discharge from industries.

Among the various techniques developed for heavy metals treatment, adsorption is one of the simplest, economical, efficient, and eco-friendly methods [9,13–16]. Unlike adsorption, most of the conventional methods such as chemical precipitation, electrocoagulation, solvent extraction, and cementation, require large amounts of reagents, high-energy inputs, and/or produce secondary sludge, which limit their environmental benignities [7,17–20]. Other drawbacks include inability to function efficiently when the concentrations of target metals fall below certain minimum values, e. g., 100 mg/L [10,19–21]. These shortcomings render such treatment methods ineffective and uneconomical. Notwithstanding that the adsorption technique is much promising; it is more viable when cost-effective materials are available [22–25]. Therefore, the raw materials used as adsorbents must be obtained at low costs and their processing steps as well as the effluent treatment methods must be simple. Commercial activated carbon materials have large surface areas and high adsorption capacities, making them potentially preferred adsorbents for sequestering heavy metal ions from wastewaters; however, the preparation of activated carbon is relatively complicated and involves carbonization and activation stages, thus limiting its cost-effectiveness and environmental novelty [10,16]. As a result, agro-industrial, plant and microbial wastes have been investigated and proven as potential low-cost adsorbent materials [21,22,25–29].

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http://dx.doi.org/10.1016/j.jece.2016.12.022
2213-3437/

Nomenclature

C_o	Initial adsorbate (metal ions) concentration (mg/L)
V	Volume of adsorbate solution (L)
M	Dry mass of adsorbent (g)
q_m	Maximum adsorbate uptake (mg/g)
K_F	Freundlich constant (L/g)
n	Constant denoting adsorption intensity
b	Langmuir adsorption constant (L/mg)
q	Amount of adsorbate adsorbed at equilibrium (mg/g)
C_e	Concentration of adsorbate at equilibrium (mg/L)
K_{RP}	Redlich–Peterson isotherm constant (L/mg)
a_{RP}	Redlich–Peterson isotherm constant (L/mg)
β_{RP}	Redlich–Peterson model exponent which values range between 0 and 1
q_{e1}, q_{e2}	Amount of adsorbate adsorbed at equilibrium (mg/g)
q_t	Amount of adsorbate adsorbed at any time (min)
k_1	First-order equilibrium rate constant (1/min)
k_2	Second-order equilibrium rate constant (g/mg min)
R^2	Coefficient of correlation

Cellulosic materials especially in their modified forms have been reported to have strong affinities for diverse ionic pollutants [7,9,21,30]. Modified cellulosic materials can generally attain high adsorption capacities, exhibit selective adsorption properties, and also demonstrate high efficiency of regeneration when applied to the treatment of inorganic and organic pollutants [7,21,30]. The modification of cellulosic materials could be achieved by specific chemical methods which provide specific active binding sites for adsorption of target species [7,10,27,28]. It has been identified that although many cellulosic adsorbents exist, it is not common to find adsorbents with phosphate coordinating functionalities grafted onto them [31]. However, phosphate-containing groups are known to have strong chelating abilities with metal ions [32].

Therefore, this study investigated the preparation of cellulosic heavy metal adsorbent via chemical modification with phosphate groups, characterization of the adsorbent, and subsequent application to treatment of model wastewater effluent containing Pb(II). Waste Lyocell fiber was used as a biodegradable low-cost material, and the pentavalent polyanion, sodium tripolyphosphate (STPP) was used as a provider of phosphate binding sites. Lyocell has many industrial applications mainly as textile material and can be obtained cheaply as pre- or post-consumer waste from textile manufacturing process. Therefore, its conversion into adsorbent will provide alternative option for recycling [7,33]. Furthermore, having been used as a component of commercial detergents and preservative for food products as well as in medicine, metallurgy, mining, etc., STPP has no known negative impacts on humans or the environment [32,34]. Owing to its physicochemical properties, it does not spread to the atmosphere or cause irritation to the skin [34,35]. Rather, STPP is able to form stable complexes with metal ions and functions as the nutrients for plants. Therefore, the manufacture and application of STPP-Lyocell adsorbent is expected to be environmentally benign.

2. Materials and methods

2.1. Adsorbent preparation

Spent Lyocell fiber strands (~12 μm thick) were obtained from KOLON Industries Inc., Korea. One gram of the fiber strands (cut into lengths of approximately 10 cm) was immersed in a solution containing a mixture of 40 mL dimethylformamide (DMF, Daejung Chemical & Metals Co. Ltd.) and 10 mL distilled water (DW). This was followed by the addition of 1–3 g of STPP (Junsei Chemical Co.) to start a phosphate modification reaction. The amount of STPP was varied to find the appropriate dose for effective functionalization of the Lyocell fibers. The reaction was allowed to proceed for 24 h in a controlled environment at a temperature of 40 °C. A 1:1 distilled water/ethanol (DW/EtOH) solution was first used to wash off the residual reactants, and then DW was used to thoroughly rinse off any remaining unreacted chemicals. The obtained adsorbent was labeled as STPP-Lyocell and freeze-dried to constant weight, preceding characterization and adsorption studies.

2.2. Adsorbent characterization

The STPP-Lyocell was characterized using standard analytical tools, viz. scanning electron microscopy, SEM, embedded with an energy dispersive X-ray spectroscopy, EDX (JEOL, JSM-6000 series WDS/EDS system, Japan), Fourier transform infrared spectroscopy, FTIR (PerkinElmer spectrophotometer, Spectrum GX, FTIR System), and X-ray diffraction, XRD (multi-purpose high-performance X-ray diffractometer, X'pert Powder, PANalytical, the Netherlands), in order to fully understand the mechanism of modification and underlying principles for effective application of the adsorbent to Pb(II) adsorption. Nitrogen adsorption and desorption isotherms were measured at 77 K on a NOVA2200e surface area and pore size analyzing equipment (Quantach-rome Instruments, USA). Speciation graphs were drawn with the aid of the Medusa chemical software (Candego, Stockholm, Sweden).

2.3. Adsorption experiments

To estimate the optimum pH for effective Pb(II) adsorption, the maximum uptake capacity, and the rate of metal ions removal from the aqueous phase onto the solid phase; pH effect, isotherm, and kinetics studies were respectively carried out. Pb(II) stock solution was prepared by dissolving a weighed amount of $Pb(NO_3)_2$ in distilled water and further diluted for subsequent working solutions. Competitive sorption study was carried out by using aqueous mixtures of Pb(II), Ni(II), Zn(II) Li(I) and Co(II). Approximately 0.03 g sorbent dose per 30 mL of metal solution formed the basis for all the adsorption studies. The experiments were repeated to keep the standard errors below 2%. All the adsorbed samples were analyzed using an inductively coupled plasma spectrometer (Shimadzu, ICP-7510, Japan) after appropriate dilutions. The Pb(II) uptake after each adsorption study was calculated from the mass balance expression in Eq. (1).

$$q = \frac{(C_o - C_e)V}{M} \quad (1)$$

where C_o and C_e are initial and equilibrium Pb(II) concentrations in mg/L, V is volume in L, and M is dry mass of adsorbent in g.

3. Results and discussion

3.1. Effect of STPP amount on adsorption

To assess the effect of STPP on the adsorption capacity, single-point adsorption study was conducted using the adsorbent prepared from different amounts of STPP (Fig. 1). To evaluate any adsorption contribution from the pristine Lyocell, the raw fibers without any treatments were used as control. The results show that there was no significant Pb(II) adsorption when the pristine Lyocell fibers were used. These results indicate that the modification was necessary to introduce active binding sites onto the fibers for Pb(II) adsorption. As can be seen in Fig. 1, the adsorption amount of Pb(II) increased with the amount of STPP