ISSN (Print): 0974-6846
ISSN (Online): 0974-5645
Indian Journal of Science and Technology, *Vol 11(26), DOI: 10.17485/ijst/2018/v11i26/129403, July 2018*

Application of Lemon Peels Biomass Chemically Modified with Al_2O_3 Nanoparticles for Cadmium Uptake

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Abstract

Background: Agricultural wastes have attached great attention for developing novel materials with physico-chemical properties favorable for several applications as heavy metal ions uptake from aqueous solution. **Objectives:** In this work, Lemon Peels (LP) residual biomass was successfully modified into a novel biosorbent using alumina (Al_2O_3) nanoparticles and applied to remove cadmium ions. **Methods/Analysis:** Characterizations of LP-Al_2O_3biosorbent by FT-IR and SEM were performed to identify morphology and main functional groups. Batch adsorption experiments were carried out under different pH values (2, 4, 6) and particle sizes (0.355, 0.5, 1 mm). The removal yields were calculated using LP and LP-Al_2O_3 in order to compare these results and determine the effect of alumina nanoparticles on adsorption process. **Finding:** The FT-IR analysis revealed the presence of covalent binding of aluminum with carboxyl and carbonyl groups of this biomass. The porous surface of LP-Al_2O_3biosorbent observed in SEM micrograph suggested a high surface available to metal ions binding. The removal yields were increased from 90.35 to 93.3% after loading alumina nanoparticles into lemon peels biomass due to the larger surface given by nano-scale particle size. **Novelty/Improvement:** These results suggested that lemon peels-based biosorbents can be efficiently used for cadmium ions uptake from aqueous solution.

Keywords: Adsorption, Cadmium Ions, Lemon Peels, Nanoparticles

1. Introduction

Nowadays, industrial anthropogenic activities worldwide have caused contamination of water sources with several heavy metal ions[1]. The environmental and sanitary problems and increasingly restrictive legislation claim the need of treating effluents containing heavy metals, which is becoming an important issue[2]. These pollutants possess low levels of biodegradability, can be absorbed by living organism, stay stable in the environment and tend to accumulate in human bodies[3]. Among heavy metal ions, cadmium is considered a potential metallic toxicant that causes several diseases[4]. Cadmium is widely used in the industry for coating steel, glass and plastics and battery production[5].

Several methods have been studied to remove heavy metal ions from industrial wastewater including chemical precipitation, reverse osmosis, ion exchange, adsorption, membrane technologies and electrochemical treatment[6]. Adsorption is one of the most preferred because of its easy operation, cost-effectiveness and high efficiency[7]. The efficiency of heavy metal ions removal using adsorption technique is influenced by the physico-chemical properties of the adsorbent. Different cost effective adsorbents

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have been developed from agricultural waste material, industrial by products waste and microorganism species[8]. In order to improve adsorption capacity of these biomaterials, novel approaches have been proposed to modify them with magnetic nanomaterials as alumina and titanium dioxide[9].

Many authors have reported the modification of agricultural wastes with alumina nanoparticles. In[10] prepared a novel biosorbent from African oil palm bagasse and alumina nanoparticles in order to use it for adsorbing cadmium, nickel and chromium. Other biomasses have been studied as corn cob and orange peels as pointed out[11-12]. This work attempts to assess adsorption efficiency of lemon peels biomass and its modification with alumina nanoparticles for cadmium uptake from aqueous solution.

2. Materials and Methods

2.1 Preparation of Biomaterials

Lemon peels were used to prepare a novel material for heavy metal ions uptake. In brief, the waste lemon peels were collected from a local fruit market and washed with distillated water[13]. These were dried in an oven at 80°C for 24 h and grounded in order to obtain different particle sizes (0.355, 0.5 and 1 mm).

2.2 Synthesis of Nanoparticles

The synthesis of alumina nanoparticles have been reported using several methods limited by complex procedure, high cost of starting material or large grain size[14]. However, sol-gel methodology seems to be a suitable alternative to increase porous size of nanomaterials as pointed out by[11]. The synthesis procedure was performed according to[15]. In brief, citric acid ($C_6H_8O_7$) solution was added to 0.5 M ($Al(NO_3)_3 \cdot 9H_2O$) solution and stirred at 60°C. The presence of yellow color in this mixture was taken as reference to increase the temperature in 20°C. After forming a gel, the resulting material was heated at 750°C to obtain a powder.

2.3 Biomass Modification with Alumina Nanoparticles

The lemon peels biomass was treated with alumina nanoparticles and Di-Methyl Sulf-Oxide (DMSO) in order to obtain a biosorbent with improved properties to be used in cadmium uptake. The dried biomass was mixed with DMSO solution and stirred for 24 h. Then, alumina nanoparticles and ethyl-o-silicate (TEOS) were added to the resulting suspension. The impurities were removed by ethanol and the biosorbent was dried as reported by[16].

2.4 Characterization Techniques

Fourier Transform Infrared Spectroscopy (FT-IR) technique was carried out to identify main functional groups in the resulting biosorbent after chemical modification of lemon peels biomass with alumina nanoparticles. In addition, the morphology of chemically modified biomass (LP-Al_2O_3) was analyzed by Scanning Electron Microscopy (SEM).

2.5 Batch Adsorption Experiments

The adsorption capacity of this novel biosorbent was evaluated by batch adsorption experiments, which were performed using a stirrer plate. In brief, LP-Al_2O_3biosorbent was mixed with cadmium solution at room temperature for 2 h. Cadmium sulfate ($CdSO_4$) was used to prepare the stock solution of Cd (II) ions. It has been reported that cadmium uptake is enhanced under pH around 6 due to the deprotonation of functional groups in biosorbent surface[10]. However, the effect of pH on adsorption process was evaluated by varying this operating condition (2, 4 and 6). The remaining concentration of heavy metal ions was required to calculate removal yields as indicated by Eq. 1, where the subscripts in concentration refer to the initial and equilibrium in adsorption process.

$$R = \frac{\left(C_0 - C_e\right)}{C_0} \cdot 100\% \quad (1)$$

The particle size of lemon peels biomass was also varied in order to identify suitable conditions for carrying out further experiments.

3. Results and Discussion

3.1 Characterization Techniques

The lemon peels biomass has been widely characterized by several techniques including ultimate and FT-IR analyses. In[6] reported the elemental composition of this biomaterial as follow: C (%wt.) 38.48, H (%wt.) 4.98 and N (%wt.) 1.21. The content of lignin, hemicellulose, pectin and cellulose in lemon peels biomass was determined by[17] in 7.22, 6.07, 5.41 and 18.49 %wt., respectively. The pectin and polygaracturonic acid components in vegetable cell wall are characterized to have carboxyl, hydroxyl and amide groups[18]. Figure 1 shows the FT-IR spectrum of chemically modified lemon peels biomass (LP-Al_2O_3). The absorption band around 2917.81 cm^{-1}, is attributed to the stretching vibrations of carboxyl groups and aluminium (Al-COOH). The lemon peels biomass is characterized to have carbonyl (C=O) stretching vibrations around 1698.34–2000.13 cm^{-1}, which indicates the presence of pectin, hemicellulose and lignin carboxyl groups[17]. The LP-Al_2O_3biosorbent exhibited a band at 1648.87 cm^{-1} assigned to the stretching of the bond Al-C=O. Other peaks were found at 1018.25 $cm^{-1}$and 648 cm^{-1} attributed to the bonds Al-O-Al and O-Al-O, respectively[19]. Figure 2 shows the SEM micrograph of this biosorbent exhibiting an irregular and porous surface that is typical of lignocellulosic materials from fruit peels as lemon, orange or banana as reported by[20]. This morphology is desirable to improve adsorption process due to the availability of active sites on porous surface as pointed out by[21].

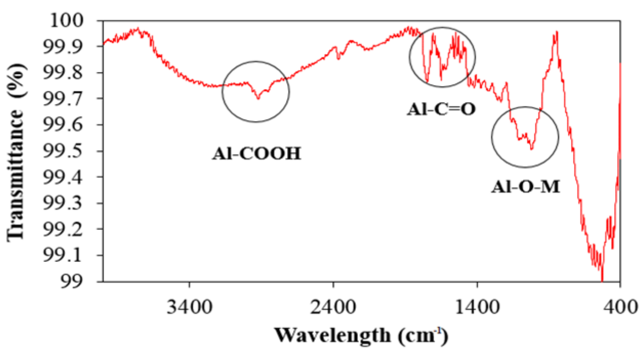

Figure 1. FT-IR spectrum of LP-Al_2O_3 biosorbent

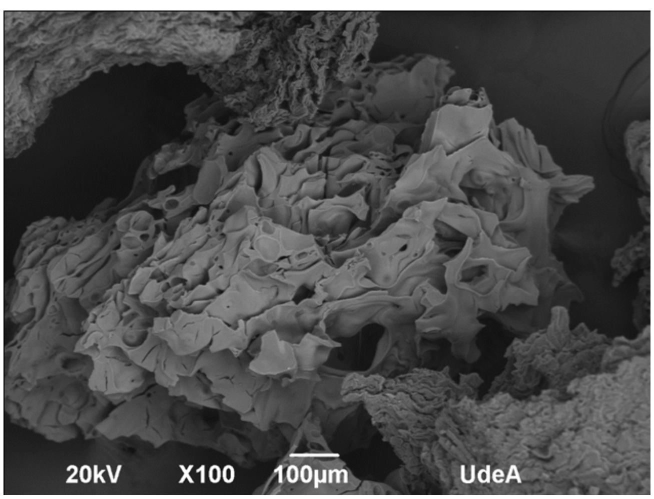

Figure 2. SEM micrographs of L-Al_2O_3 biosorbent

3.2 Adsorption Study

As is well known, the solution pH is an important parameter to control the sorption process by influencing the surface charge of biosorbents[14]. Hence, the effect of varying pH values on removal yields was studied in this work and the results are listed in Table 1. The highest removal yield (90.35%) was achieved at pH = 4 and particle size = 0.5 mm. It is observed that removal yields were proved pH-dependent, which can be attributed to the reduction of Cd(II) ions uptake under low pH. In[22] reported that cadmium ions are not suitable to be removed under acid pH due to: 1. the presence of hydrated Cd^{2+} species, 2. increase in positive charge density in LP material, and 3. competition for available sites between Cd^{2+} and H^+ ions.

Table 1. Effect of pH and particle size on Cd (II) removal yields using lemon peels biomass

pH	Particle size (mm)	Removal yield (%)
2	0.355	36.5
	0.5	33.92
	1	36.97
4	0.355	87.52
	0.5	90.35
	1	84.47
6	0.355	80.97
	0.5	87.36
	1	86.60

On the other hand, particle size is proportional to surface area available to interact with heavy metal ions and it substantially affects the mechanism of metal ions uptake[23-24] pointed out that high surface area of small size-particles increases adsorption capacity. However, this parameter did not affect significantly adsorption process as confirmed by Pareto chart (Figure 3). Similar results were reported by[25], who evaluated the effect of particle size for lead and nickel uptake using Cassava (*Manihot esculenta*) and yam (*Dioscoreaalata*) biomasses modified with TiO_2 nanoparticles. Different fruit peels have been tested for removing cadmium ions and are summarized in Table 2. The results of adsorption experiments suggest that lemon peels biomass can be efficiently used for Cd (II) uptake.

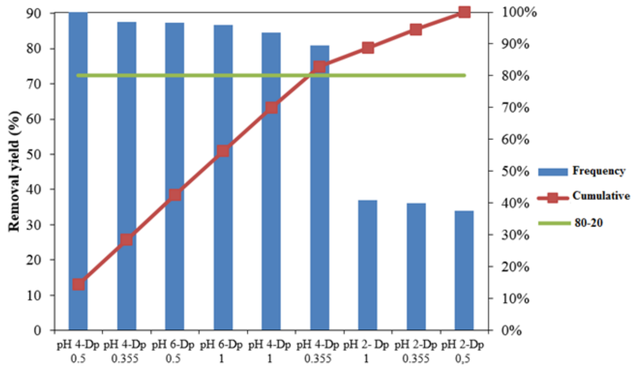

Figure 3. Pareto chart for cadmium uptake using lemon peels biomass

Table 2. A summary of different biomaterials used for cadmium uptake

Biosorbent	Removal yields (%)	Conditions	Reference
Cocoa shells	93	pH = 6	26
African oil palm bagasse	92.02	pH = 6	10
Sugarcanebagasse	90	pH = 6 – 6.5	27
Orange peels-Fe_2O_3	96	pH = 7	12
Banana peels	95	pH = 6	28
Lemon peels	90.35	pH = 4	This work

To assess the improvement in adsorption process after loading alumina nanoparticles into lemon peels biomass, removal yield using both materials were compared as shown in Figure 4. The LP-Al_2O_3biosorbent exhibited higher removal yield (93.30%) than biomass without chemical modifications. This high removal yield may be explained by the nano-scale particle size of the biosorbent giving access to a larger surface area[12].

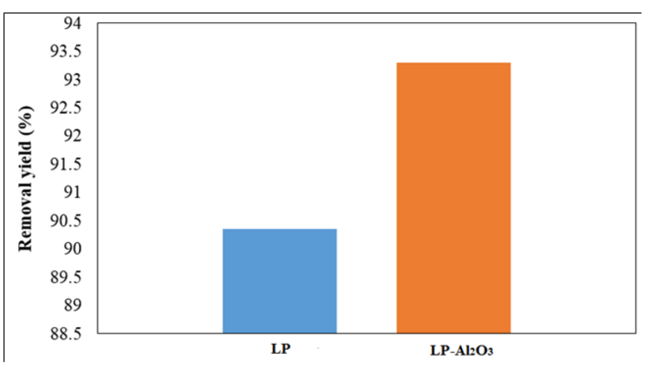

Figure 4. Removal yields for cadmium uptake using LP and LP-Al_2O_3

4. Conclusions

This work focused on assessing the removal yields of a novel biosorbent prepared from lemon peels biomass for cadmium metal ion uptake. Characterization studies revealed interactions between aluminum and main functional groups of this biomass including carbonyl (-C=O) and carboxyl (-COOH), which suggested a successful synthesis. Regarding SEM analysis, the porous surface of LP-Al_2O_3biosorbent is favorable for metal binding due to the high surface available to Cd (II) ions uptake. The solution pH affected adsorption process due to it modifies surface charge density of biosorbentand pH value around 4-6 was recommended for performing further experiments. The particle size did not contribute to increase removal yields. The chemical modification of lemon peels biomass increased removal yields from 90.35 to 93.3% due to the larger surface given by nano-scale particle size. This high adsorption efficiency revealed that lemon peels-based biosorbents can be efficiently used for heavy metal ions uptake.

5. Acknowledgments

Authors thank to Universidad de Cartagenafor providing the materials and equipment required to successfully conclude this research.

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