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# Activated carbons produced by pyrolysis of waste potato peels: Cobalt ions removal by adsorption

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HIGHLIGHTS

- Removal of cobalt ions by activated carbons.
- Activation with H_3PO_4 at 400, 600, 800 °C.
- SEM, BET, FTIR, DTG, Boehm titrations as characterization techniques.
- Effect of pH, contact time, temperature on adsorption.

GRAPHICAL ABSTRACT
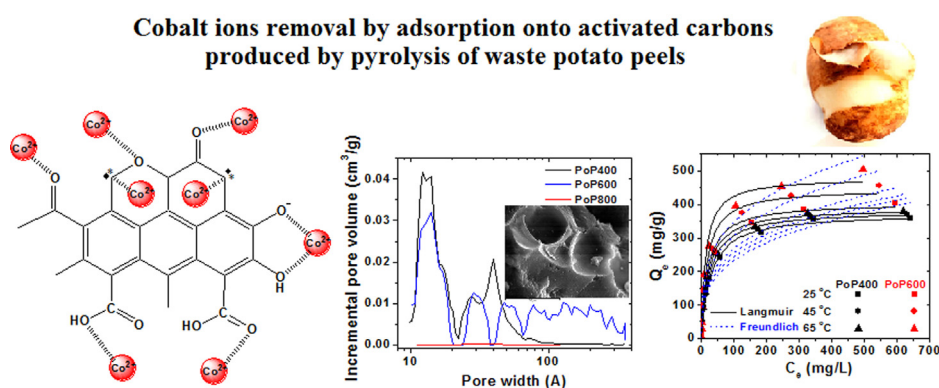
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ABSTRACT

This study investigates the use of activated carbons after pyrolysis of waste potato peels for the removal of cobalt ions from synthetic wastewaters (composed of various Co(II) concentrations in distilled water which adjusted previously at different pH values) without any co-existing ions. The activation agent was phosphoric acid, while three different carbons were prepared based on the different activation temperatures (400, 600, 800 °C). Characterization techniques used for the study of surface chemistry of carbons prepared (Boehm and potentiometric titrations, BET analysis, SEM/EDAX, DTG), while the possible adsorption mechanism between carbons and Co^{2+} was further investigated using FTIR spectroscopy. Equilibrium and kinetic experiments were carried out at the optimum pH (6). Free energy, enthalpy, and entropy were also evaluated.

1. Introduction

The most widely used carbonaceous materials for the industrial production of activated carbons are coal, wood and coconut shell. These types of precursors are quite expensive and often imported, in many places; hence making it necessary, particularly for developing countries, to find a cheap and available feedstock for the preparation of activated carbon for use in industry, drinking water purification and wastewater treatment. Biosorption, a biological method of environmental control was proposed as an alternative to conventional waste-treatment facilities [1]. Several suitable agricultural by-products (lignocellulosics) – i.e., including olive-waste cakes [2], cattle-manue compost [3], bamboo materials [4], apple pulp [5], potato peel [6] – have been investigated in the last years as

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activated carbon precursors and are still receiving renewed attention.

Activated carbons possess large surface area, as mentioned above and different surface functional groups, which include carboxyl, carbonyl, phenol, quinone, lactone and other groups bound to the edges of the graphite-like layers. Therefore, they are regarded as good adsorbents for the removal of heavy metal ions and other inorganic substances, as well as many organic compounds from liquid and gas phases [7]. Both surface chemistry and texture of carbons are affected by the nitrogen source and the type of oxygen functionalities preexisting on the surface [8,9]. Acid–base interactions were found to essentially govern the ammonia removal by modified activated carbons [10].

A mercury removal method using polymer-coated activated carbon was studied for possible use in water treatment [11]; in order to increase the affinity of activated carbon for mercury, a sulfur-rich compound, polysulfide-rubber polymer, synthesized by condensation polymerization, was coated onto the activated carbon. The role of surface functionality on silica and carbonaceous materials for adsorption of cadmium ion was also examined using various mesoporous silica and activated carbon [12]. Introduction of nitrogen functional groups, such as amine, pyridinic and pyrolic onto the surface of adsorbents and replacing them with oxygen groups is known as one of the modification methods for producing strong adsorbents toward heavy metals, like Cu(II) ion; a new procedure for nitrogenation of commercial activated carbon was proposed [13]. An activated charcoal, produced from an agricultural waste product (Lapsi seed), was tested for heavy metal ions removal; according to the experimental results the kinetics of the sorption process was found to be pseudo-second order [14].

Cobalt is a strategic metal (usually obtained from different ores), used widely in the manufacture of catalysts, alloys, steels etc. Various separation processes were applied for cobalt ions, including radioactive ones [15]. Especially, adsorption as one of the most promising techniques [16–26] is applied for Co(II) removal [27–29]. Activated carbon adsorption has been certainly applied; the adsorbent was either commercial [30], synthesized from a sugarcane industry waste [31] or apricot stone [32], among other sources.

The aim of this study is to prepare activated carbons from potato peels and test them as adsorbents for Co(II) ions. Of course there are works regarding the use of potato peels for adsorption applications [33–36], but none with cobalt ions as under-removal pollutant. Moreover, the effect of activation temperature was evaluated with characterization techniques (Boehm and potentiometric titrations, BET, SEM/EDAX, FTIR, DTG) and the best adsorbent samples were further used to adsorption experiments (pH-effect, isotherms, kinetics, thermodynamics).

2. Materials and methods

2.1. Chemical reagents

H_3PO_4 (for potato peels activation) and $Co(NO_3)_2 \cdot H_2O$ were purchazed from Sigma–Aldrich (St. Louis, MO, USA); they were of analytical grade (puriss. pa. $\geq$ 98.5%).

2.2. Preparation of activated carbons

Waste potato peels were washed with distilled water in order to remove dust and other inorganic impurities. Then, they were filtered and oven-dried for 24 h at 393 K for achieving the reduction of moisture content. The dried biomass was ground and sieved to particles (+0.45–0.15 mm). The latter was denoted as "Po".

The chemical activation of dry biomass was achieved with phosphoric acid (H_3PO_4). 10 g of dry potato peels precursor were impregnated with 125 mL of H_3PO_4 (75% w/w) at room temperature and kept under stirring for 24 h. The impregnated biomass was dried in sand bath at high temperature in order to remove residual water and then oven-dried for 24 h at 100 °C. A weighed amount of the dried impregnated samples was placed in a furnace and heated up to (i) 400, (ii) 600, and (iii) 800 °C activation temperatures. The treatments were carried out with nitrogen flow (99.999% pure) of 30 STP cm^3/min; the latter was kept at the same rate during heating and cooling, and at a constant heating rate of 10 K/min. The treatment at the activation temperature lasted 2 h and after cooling the solid residues were washed in a Soxhlet apparatus for 24 h until neutral pH and then with ethanol. The resulted activated carbons were dried at 100 °C for 24 h. In order to make easily understood the abbreviations used for the activated carbons samples, they were designated as PoP400, PoP600 and PoP800 (the term "Po" corresponds to potato peels), "P" to phosphoric acid used for activation, and the numbers "400", "600", and "800" to 400, 600, 800 °C activation temperatures, respectively.

2.3. Characterization—instrumentation

Scanning electron microscopy (SEM) images were performed with electron microscope (model Zeiss Supra 55 VP, Jena, Germany) equipped with an energy dispersive X-ray (EDX) Oxford ISIS 300 micro-analytical system. The accelerating voltage was 15.00 kV, while the scanning was performed in situ on a sample powder. EDAX analysis was done at magnification 10 K and led to the maps of elements and elemental analysis for the investigation of Co(II) distribution on carbon surface.

Thermal stability of the samples was measured (6 mg of sample was used for each measurement) by thermogravimetric analysis (TGA) using Pyris 1 TGA thermal analyzer (PerkinElmer, Dresden, Germany) with the following settings: (i) 10 K/min as heating rate, and (ii) 100 mL/min as flow rate of nitrogen atmosphere.

The FTIR spectra of the samples were taken with a Nicolet 560 (Thermo Fisher Scientific Inc., MA, USA) FTIR spectrometer. The spectra were recorded in transmission mode using potassium bromate wafers containing 0.5 wt% of carbon. Pellets made of pure potassium bromate were used as the reference sample for background measurements. The spectra were recorded from 4000 to 400 cm^{-1} at a resolution of 4 cm^{-1} and are baseline corrected.

Nitrogen isotherms were measured using AS1Win (Quantachrome Instruments, FL, USA) at liquid N_2 temperature (77 K). The samples were degassed at 150 °C in a vacuum system at 10^{-4} Torr before the analysis. The specific surface area (S_{BET}) was calculated from the isotherm data using the Brunauer, Emmet and Teller (BET) model. The micropore volumes (V_{mic}) were obtained with the accumulative pore volume using density functional theory (DFT) method. The total pore volumes (V_{tot}) were obtained from the volumes of nitrogen adsorbed at a relative pressure of 0.99 cm^3/g. The mesopore volumes (V_{mes}) were calculated by subtracting V_{mic} from V_{tot}. The pore size distribution curves were also obtained using DFT method.

For the measurement of the surface pH of carbon samples, 0.4 g of dry carbon sample were added to 20 mL of water, and the suspension was stirred overnight to reach equilibrium. Then the pH of the solution was measured. This method provided information about the acidity or basicity of the material's surface.

The determination of surface functional groups was based on the Boehm titration method [37]. Aqueous solutions of $NaHCO_3$ (0.05 mol/L), Na_2CO_3 (0.05 mol/L), $NaOH$ (0.10 mol/L), and HCl (0.10 mol/L) were prepared. 25 mL of these solutions were added to vials containing 0.5 g of adsorbents, let to be shaken (140 rpm) until equilibrium (24 h), and then filtered. Five blank solution (without adsorbent) were also prepared. In this way, the number of the basic sites was calculated from the amount of HCl which reacted with