

Adsorption of radiocesium from aqueous solution using chemically modified pine cone powder*

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Abstract: In this study, toluene–ethanol mixtures were investigated as chemical modifying agents for pine cone powder (PCP) and the optimum modification ratio determined by measuring the improvement in surface properties of the PCP such as Brunauer–Emmett–Teller (BET) surface area, bulk density, and surface negative charge. The modified adsorbents were then applied for the removal of cesium ions from aqueous solution. The result revealed that the chemically modified PCP had better surface properties than the raw BET surface area, and X-ray diffraction (XRD) spectra revealed that the surface area improved and cellulose crystallinity reduced. Cesium adsorption by the chemically modified PCP was much higher than for the raw PCP. Desorption studies were also performed to evaluate the mechanism of adsorption.

Keywords: absorption; adsorption; analytical chemistry; aqueous solutions; carbohydrates; cellulose crystallinity; chemical modification; radio-caesium; toluene–ethanol mixture.

INTRODUCTION

Several sources of radionuclides in soils and water have been identified to include natural processes, global fall-out from nuclear weapon testing, discharges from nuclear installations, disposal of nuclear waste, or leakage from storage tanks [1,2]. The occasional nuclear accidents [3] from these sources present serious concerns for the environment. One radionuclide of concern is cesium; cesium-137 (¹³⁷Cs) is a fission product of concern due to its long physical half-life of 30.2 years and its high bioavailability. ¹³⁷Cs is water-soluble and can rapidly enter the biological cycles and accumulate in terrestrial ecosystems, behaving in a very similar way to potassium and sodium [4].

Several adsorbent types have also been employed in cesium removal from aqueous solution as reported in literature, the most popular being the use of natural minerals such as clays and zeolites. These natural adsorbents found in soils are known to have high fixation capacity for cesium [5–7]. But these materials have the drawback of highly reduced selectivity for cesium in the presence of sodium and ammonium ions in solution [8]. Natural biomaterials have been shown to have high affinity and selectivity for cesium ions in aqueous solution [9,10]. The application of untreated biomaterials (agricultural wastes) as adsorbents is accompanied by several disadvantages including low adsorption capacity, high chemical oxygen demand (COD) and biological oxygen demand (BOD), as well as total

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organic carbon (TOC) due to release of soluble organic compounds contained in the plant material [11,12]. The increase of the COD, BOD, and TOC can cause depletion of oxygen content in water and can threaten aquatic life. Modification of agricultural wastes before their application as biosorbent is, therefore, necessary to extract soluble organic compounds and enhance chelating efficiency [11].

Several investigations have been reported in the literature on the use of chemicals agents for modifying plant materials for their application as adsorbents, and some of these include base solutions (sodium hydroxide, NaOH), mineral and organic acid solutions (hydrochloric acid), organic compound (ethylenediamine, formaldehyde, epichlorohydrin, methanol), and dye and oxidizing agent for removing soluble organic compounds and increasing efficiency of metal adsorption [13].

Marchetti et al. [14] extracted wood meal (*Picea abies*) with a mixture of toluene–ethanol subsequent to its application as adsorbent for cadmium ions removal from aqueous solution. This chemical extraction was reported to remove plant extractives such as plant pigments, colored organic compounds, lignin, resin acids, and water-soluble tannins [15].

Pine cone biomass has chemical composition: α -cellulose 18.8 %, hemicellulose 46.5 %, lignin 37.4 %, and alcohol/benzene 15.4 % [16,17]. In the present study, pine cone biomass was chemically treated using a 2:1 mixture of toluene–ethanol with the aim to eliminate plant extractives and improve its affinity and selectivity for cesium ions adsorption from aqueous solution. The effect of the chemical treatment of pine cone biomass was determined by monitoring changes in surface properties such as bulk density, surface negative charge, crystallographic structure, and surface area. The applicability of modified pine cone for removal of cesium ions from aqueous solution and its desorption mechanism was examined.

MATERIALS AND METHODS

Materials

Pine tree cones were collected from a plantation in Sasolburg, Free State Province, South Africa. The cones were washed to remove impurities such as sand and leaves. The washed cones were then dried at 90 °C for 48 h in an oven. The scales on the cones were removed and crushed using a pulverizer. The pine cone powder (PCP) was then sieved, and particles between 90 and 45 μm were collected and used for analysis.

Method

The following techniques were used in measuring the surface properties of the PCP:

- bulk density to measure the size of void spaces or volume in the material;
- surface negative charge to determine the ionization of acidic functional groups on the material surface;
- the Brunauer–Emmett–Teller (BET) equation to measure the surface area and pore size distribution using computer-controlled nitrogen gas adsorption analyzer;
- X-ray diffraction (XRD) to identify the chemical composition and crystallographic structure of the raw and modified PCP; and
- atomic absorption spectrometer to measure concentration of cesium adsorbed and desorbed.

RESULTS AND DISCUSSION

Bulk density

The bulk density of a powder is proportional to the amount of void spaces or volume in the material. The higher the bulk density, the lower the amount of void volume present in the powder [18]. The results

of the bulk density of the raw and treated pine cone are shown in Table 1. The reduction in bulk density (from 0.6457 to 0.4296) can be attributed to extraction of plant organic components such as sugars. Wartelle and Marshall [18] attributed the decrease in bulk density of almond hulls from 0.63 to 0.25 to be larger due to the removal of soluble sugars, which comprise 27 % of the unextracted almond hull.

Table 1 Surface properties for pine cone and toluene–ethanol-treated PCP.

Sample	Property				
	Bulk density (g/cm ³)				
Raw	0.6457				
Toluene: ethanol-treated	0.4296				
Surface area			Pore volume		
	BET (m ² /g)	Langmuir (m ² /g)	V _{total} (cm ³ /g)	V _{micro} (cm ³ /g)	V _{micro} /V _{total}
Raw	4.39	4.60	0.004	0.011	2.707
Toluene: ethanol-treated	26.30	28.90	0.173	0.245	1.416
	Surface negative charge (mmol/g)				
Raw	3.82 ± 0.02				
Toluene: ethanol-modified	3.76 ± 0.03				

V_{total} = total pore volume; V_{micro} = micropore volume.

Surface area

The implication of the extraction of plant components is reflected in the opening up of pores within the plant matrix. The BET surface area of PCP before and after treatment is shown in Table 1. It is observed that both the BET and Langmuir surface areas for the raw PCP are 4.39 and 4.60 m²/g, respectively, and the total pore volume and micro pore volume are 0.040 and 0.011 cm³/g, respectively. On modification with toluene–ethanol mixture, the BET and Langmuir surface area values increased to 26.30 and 28.90 m²/g, respectively, while the total pore volume and micro pore volume increased to 0.173 and 0.245 cm³/g, respectively. Increase in surface area with toluene–ethanol modification has been attributed to extraction of plant components such as sugars, cementing materials, and lignin, which usually block pores on biosorbent materials [18,19] leading to further exposure of the biosorbent surface. These results indicate that extraction of plant components improved both internal and external surfaces to a large extent [20].

Surface negative charge

The surface negative charge of a biological material is attributed to ionization of acidic functional groups on the material surface [21]. These sites are usually responsible for interaction with positively charged species in solution [22]. The surface negative charge of the raw PCP was found to be 3.82 ± 0.02 mmol/g. On modification with toluene–ethanol mixture, the surface negative charge of the modified PCP was found to be 3.76 ± 0.03 mmol/g. The reduction in surface charge may, therefore, be due to extracted negatively charged plant components such as resin acids from the pine cone. Marshall et al. [19] showed that the surface negative charge value of soybean hulls was reduced from 1.33 to 1.01 mmol g⁻¹ when soybean hulls were washed with 0.1 mol dm⁻³ NaOH solution.

X-ray diffraction

The XRD technique measures the chemical composition and crystallographic structure of the material. The XRD technique was carried out on raw and toluene–ethanol modified pine cone. Toluene–ethanol modification of pine cone may lead to changes in its chemical structure, therefore understanding these changes in structural properties will provide valuable information regarding the adsorption reaction [12]. The results in Fig. 1 show the XRD spectrum of the raw PCP. For the raw PCP, the characteristic main peaks of cellulose (I) at the 2θ of 15.3° , 21.3° , and 34.0° can be observed. The spectrum indicates that the pine cone is composed basically of crystalline cellulose.

The results in Fig. 2 show the XRD pattern of raw and the 2:1 toluene–ethanol extracted PCP. When PCP was treated with 2:1 toluene–ethanol solvent mixture, the characteristic main peaks of cel-

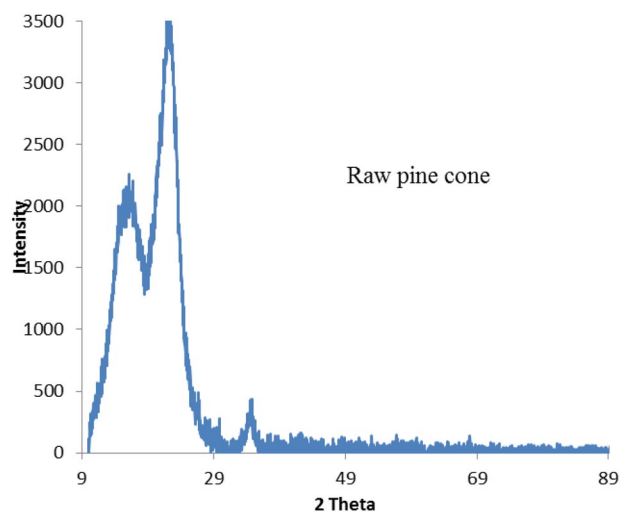


Fig. 1 XRD spectra of raw pine cone.

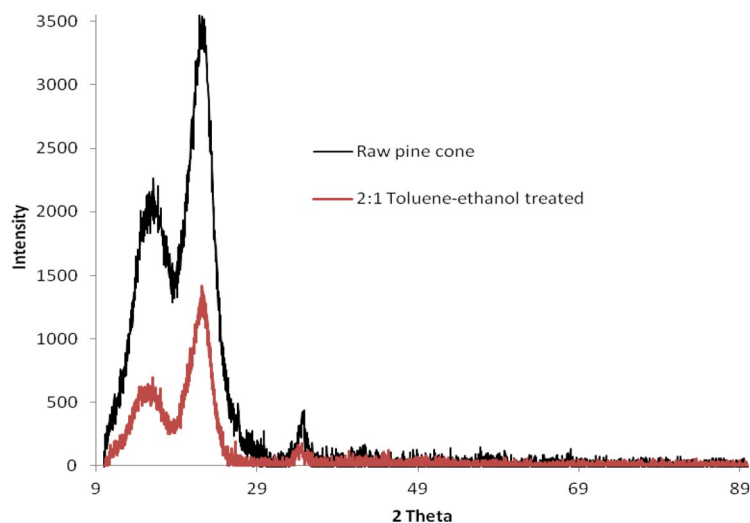


Fig. 2 XRD spectra of raw pine and 2:1 toluene–ethanol-treated pine cone.

lulose (I) were observed to decrease drastically. The primary peaks can still be seen slightly at 2θ at 15.5° , 22.2° , and 34.1° . The secondary peaks on the other hand were almost nonexistent in the extracted PCP except at 2θ at 22.2° and 44.7° , indicating the solvent extraction may have removed the amorphous fraction of the PCP.

Cesium adsorption experiment

The experiments were carried out to test the efficiency of the sorbents for cesium removal from aqueous solution. The cesium adsorption capacities (q_e , mg/g) for raw pine cone was found to be 1.46 mg/g, on modification with toluene–ethanol mixture, the cesium adsorption capacity was found to be 1.83 mg/g. From these results, it can be said that toluene–ethanol modification improved the cesium adsorption capacity of PCP.

Cesium desorption experiments

Desorption studies are vital in determining the mechanism of the sorption process and its applicability in industrial practice. Desorption characteristics of a sorbent could be evaluated by extracting adsorbed metal ions by different solvents. If the metal ion adsorbed can be desorbed by water, it is believed that the attachment of the metal ion onto the adsorbent is by weak bonds (physical bonds). If a solution of strong base such as potassium hydroxide (KOH) or NaOH can desorb the metal ion, it is believed that the attachment of metal is by ion-exchange. If a solution of acetic acid (CH_3COOH) can desorb the metal, it is believed that the biosorption of metal is by chemisorption.

Batch desorption experiments were carried out, and desorption efficiencies compared in Fig. 3. The percentages of cesium ions desorbed from raw and toluene–ethanol-treated PCP are compared for all five desorbing agents used [NaOH, KOH, $\text{Ca}(\text{OH})_2$, CH_3COOH , and H_2O]. From Fig. 3, it is observed that KOH and NaOH solutions desorbed the highest percentage of cesium in both samples. This mechanism accounted for the largest fraction of cesium desorbed with both PCP samples. Desorption of cesium with KOH and NaOH had the highest percentage in raw PCP (87.2 %), (56.8 %) than the toluene–ethanol-treated PCP (63.6 %), (36.1 %), respectively.

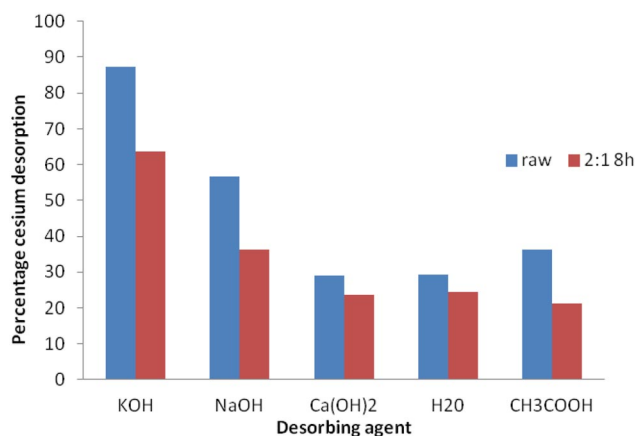


Fig. 3 Desorption efficiencies of cesium from pine cone and toluene–ethanol-extracted PCP by various desorbing agents.

The percentage of cesium desorbed by acetic acid on the other hand, which accounts for irreversibly bounded cesium, is the mechanism responsible for the third highest fraction of cesium desorbed from the pine samples. Desorption using acetic acid solution was found to remove a small amount of cesium ions in the toluene–ethanol-extracted PCP (21.2 %). These may be due to certain components in lignin and tannin fraction, such as (phenolic compounds) of the raw PCP, which may account for the greater chemisorption percentage in the raw PCP (36.1 %). These components are leached out during the toluene–ethanol extraction process, thereby reducing their quantities in the treated samples. The trend was similar for the percentage cesium desorbed by water, which accounted for the weakly bound cesium. Lower percentage desorption of cesium was recorded for the toluene–ethanol-extracted PCP (24.3 %) and the raw sample (29.3 %). Finally, the sample extracted with $0.1 \text{ mol/dm}^3 \text{ Ca(OH)}_2$ was the least fraction of cesium desorbed from raw PCP sample (29.1 %) and toluene–ethanol-extracted pine cone (23.8 %). Although bound cesium ions desorbed by Ca(OH)_2 may also indicate ion-exchange mechanism, its lower percentage desorption may be due to its poor ionization in water.

CONCLUSION

Changes in surface properties were observed after surface modification by solvent extraction. Bulk density and surface negative charge values were found to decrease after solvent extraction, indicating that plant pigments and extractives were removed during modification leading to the opening of pore spaces and extraction of organic components carrying organic functional groups. The increase in both BET and Langmuir surface areas confirmed the surface modification. XRD spectrograph of the raw and modified PCP showed that the modification of pine cone with toluene–ethanol mixture decreased the crystalline fraction of cellulose substantially. Cesium adsorption using both raw and modified PCP revealed that the modified sample removed more cesium ions from solution than the raw PCP. Therefore, toluene–ethanol modification was found to enhance the cesium adsorption. Desorption studies revealed that cation exchange accounts for a large percentage of the cesium binding mechanism.

SUPPLEMENTARY INFORMATION

Supplementary information is available online (<http://dx.doi.org/10.1351/PAC-CON-12-11-02>).

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