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Formation of cerussite and hydrocerussite during adsorption of lead from aqueous solution on oxidized carbons by cold oxygen plasma

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ABSTRACT

A new procedure of elimination of Pb^{2+} from aqueous solution using carbon adsorbents, in which high amounts of cerussite and hydrocerussite are deposited on the carbon surfaces, is reported. The procedure includes the preparation of carbons from selected lignocellulosic wastes (pecan nut shells and peach stones) by single carbonization and further oxidation with cold oxygen plasma. The materials prior and after the oxidation treatment were characterized using elemental analysis, FT-IR spectroscopy, SEM/EDX analysis, adsorption of N_2 at $-196\,^{\circ}C$ and X-ray photoelectron spectroscopy. The adsorption of Pb^{2+} was carried out in batch systems under constant agitation. The formation of cerussite and hydrocerussite on the spent carbon surfaces was confirmed by XRD, SEM/EDX and FT-IR. A Pb^{2+} removal mechanism is proposed in which a co-precipitation of lead nitrate and calcium carbonate would render the formation of the lead carbonates. In such mechanism, the occurrence of $CaCO_3$ on the surface of the adsorbents plays a crucial role. The presence of calcium carbonate on the precursors is understood on the basis of the thermal evolution of calcium oxalate originally present in the biomass. The oxygen plasma treatment helps to expose the calcium carbonate nanocrystals thus improving dramatically the removal capacity of Pb^{2+}. Accordingly, retention capacities as high as 63 mg of Pb^{2+} per gram of adsorbent have been attained.

1. Introduction

The contamination of water with heavy metals is caused by industrial activities such as metallurgy, agricultural, mining, automobile, and others [1–3]. Metals such as cadmium, copper, lead, mercury, nickel and arsenic may cause harmful effects on the health of living beings. Specifically, high concentrations of lead harm the ecosystem as lead accumulates in organisms (it may remain for a long period with a half-life of at least 20 years) potentially causing serious damage to the kidneys and organism's hematology [4].

Some lead compounds are currently used extensively in many applications like lead battery pastes, matches, ceramic glazes and lead glasses [5]. Particularly, $PbCO_3$, a white odorless powder stable under ordinary temperatures and pressure, is one of the main additives in lead paint and it is used as an additive in a variety of cements. Also, lead carbonate is a component of both artistic and construction putty [6]. Natural lead carbonate (cerussite) belongs to minerals being formed in the oxidation zones of sulfide deposits [7]. A hydrated form of cerussite, hydrocerussite ($Pb_3(CO_3)_2(OH)_2$), occurs in soils from weathering or oxidation processes of metallic Pb, at recycling sites for lead-acid batteries, at Pb-smelting sites, and in household plumbing from lead corrosion by drinking water [8]. In this context, some studies have been done to recover or recycle lead as lead carbonate from wastewaters [4,9,10]. Actually, one work has reported the recovery of lead carbonate by means of a fluidized-bed homogeneous crystallization (FBHC) system using silica sand as seeds [4]. Other investigations focused on the applicability of the crystallization process in a fluidized-bed reactor on the removal and recovery of lead from synthetic wastewater using a carbonate precipitation agent and lead carbonate seed crystals [10]. In addition, the recovery of lead from cerussite has been studied using methanesulfonic acid (MSA) solutions [9].

The purpose of the present work is to establish a new procedure of elimination of lead from water and wastewater by adsorption, which includes the formation of lead compounds (cerussite and hydrocerussite) on the spent adsorbents. The procedure implied the adsorption of Pb^{2+} in aqueous solution on carbons oxidized by cold oxygen plasma The use of cold plasmas to increase the num-

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Table 1
Modification of carbon materials by oxidation with plasma.

Activated Carbon (AC)	Plasma System	Oxidation conditions					Application (adsorbed amount)	Reference
		Process gas	*Power*	*Exposure time, min*	*Gas flow*	*Gas pressure*		
AC from Coconut/Kwang-Woon C&S, Korea	Dielectric barrier discharge	He/O_2	–	30	5 slm/0–200 sccm	1 atm	Adsorption of Fe^{2+} (0.8 mg g^{-1})	[31]
Coal/Shanghai Xinhui Activated Carbon Co., Ltd. China	Dielectric barrier discharge (25 KHz)	O_2	–	10, 20, 40	100 ml min^{-1}	–	Adsorption of mercury (39.4 μg g^{-1})	[32]
Activated carbon	Dielectric barrier discharge (10 KHz)	Air N_2	–	7, 15, 30 30	–	1 atm	Adsorption of mercury	[33]
Coal/Tianjin Chemical Reagent Factory, China	Dielectric barrier discharge	N_2 O_2	–	30	2 L min^{-1}	–	Adsorption of pentachlorophenol (145 mg g^{-1})	[34]
AC from coconut shell/Zhaoyang Senyuan activated carbon Company, China	Radio frecuency (13.56 MHz)	O_2	100 W	30, 60 and 120	10 ml min^{-1}	–	Adsorption of dibenzothiophene	[35]
Rayon fiber/Jinan Environmental Protection Technology Co., Ltd. Yi Jie Shi	Gilding arc discharge (220 V/10 KV, 50 Hz)	Air	350 W	0, 5, 10, 20 and 30	0.8 – 1 m^3 h^{-1}	–	Adsorption of acid orange II (466.74 mg g^{-1})	[36]
AC from Tianjin Fuchen Chemical Reagent Factory, Tianjin, China	Gilding arc discharge (10 KV, 50 Hz)	Air	–	0, 10, 20, 30 and 40	0.8 – 1 L min^{-1}	–	Adsorption of iron and lead ions (Fe^{2+}0.91 mg g^{-1}) (Pb^{2+}: 2.03 mg g^{-1})	[21]
AC from Bamboo/Zhongzhu Carbon Industry Co., Ltd.	Dielectric barrier discharge	O_2	–	8 and 16	50 ml min^{-1}	1 atm	Adsorption of aniline	[37]
Commercial columned coal-based granular activated carbon/Gongyi Zhulin Filtrate Material Factory, China	Dielectric barrier discharge (50 Hz)	Air	–	180	0.01 m^3 min^{-1}	Atmospheric	Regenerate activated carbon saturated	[38]

ber of oxygen groups, the hydrophilicity and improve wettability and reactivity of activated carbons (Table 1), carbon nanotubes and other materials (Table S1) is well reported [11–14]. Under adequate conditions, the modification of materials with cold plasmas is limited to their outermost layers. In addition, plasma treatment is an environmentally friendly technology since no chemicals are required and the processing time is very short [15]. During the treatment with this technique, chemically active oxygen species such as radicals, ions and electrons are produced [16]. Specifically for carbons, the oxygen groups created on the surface are carboxylic, phenolic and carbonyl groups [16,17].

2. Materials and methods

2.1. Preparation of carbons and their oxidation with cold oxygen plasma

Lignocellulosic wastes, namely pecan nut shells (*Carya illinoinensis*) and peach stones (*Prunus persica*), were used as carbon precursors. These wastes were collected from food industries located in Nuevo Leon and Aguascalientes, Mexico. The biomass was milled and sieved to obtain a particle size of ∼1 mm and the obtained particles were washed with deionized water at 25 °C until constant pH. Finally, the wastes were dried at 70 °C during 24 h and the dry particles were stored in plastic containers for later use. The preparation of carbon was carried out by carbonization in a tubular furnace (Carbolite Eurotherm, model CTF 12165/550), using a quartz reactor packed with 30 g of precursor in the atmosphere of the products released as a result of the carbonization. The temperature program included a heating ramp of 5 °C min^{-1} until the maximum temperature of carbonization was achieved (800 °C) and with a residence time of 4 h. The carbons obtained from pecan nut shell (PNS) and peach stone (PS) at 800 °C were denoted as C-PNS and C-PS, respectively.

The oxidation of the carbons was performed in an Emitech K1050X plasma reactor where the oxygen was excited using radiofrequency (RF) energy (13.56 MHz). The plasma was maintained at 1 mbar by flowing oxygen into the reaction chamber. A defined amount of carbon (0.5 g) was placed in a petri dish and it was exposed to oxygen plasma for 9 min using a RF power of 75 W, which was found optimal in previous studies [18]. For a given conditions, three successive treatments with plasma were performed in each sample in order to attain a homogeneous carbon surface oxidation. The oxidized carbons obtained were denoted as C-PNS-O and C-PS-O for pecan nut shell and peach stone carbons, respectively.

2.2. Characterization of carbons

Selected textural parameters of the carbons were determined from nitrogen adsorption isotherms at −196 °C using an automatic