Surface chemistry and adsorption mechanism of cadmium ion on activated carbon derived from Garcinia mangostana shell

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INTRODUCTION

Due to the drastic increase in electronics based and electroplating manufacturing industries, more and more heavy metal compounds are mined, used and released into the aquatic water bodies. At present, numerous treatment methods such as flocculation, coagulation, ion exchange, chemical precipitation, filtration, and adsorption are practiced for heavy metals removal [1,2]. Adsorption using activated carbon (AC) is one of the most popular treatment techniques due to its easy handling and sustainability. However, the increasing cost of commercial AC is hindering the development of this technology [3]. Hence, in recent years many researchers have focused on finding suitable and economical adsorbents especially from plant biomass and biomaterial waste [1,4-6]. Agricultural wastes that are widely available and economical are the most suitable precursor for production of such AC in large quantity.

Garnicia mangostana, commonly known as mangosteen, is a fruit known for its remedial properties that is used as alternative medicine [5]. Recently, there has been an increased interest in this fruit in the food and beverage industries, causing the massive generation of mangosteen shells commercially. To address this issue, few researchers have reported the use of mangosteen shell as precursor for AC using K_2CO_3 as activating agent with promising results [5,7]. High fixed carbon and low ash content of this shell makes it a suitable raw material for AC as found by Chen et al. [5]. However, the research on activating mangosteen shells using phosphoric acid is scant.

In the adsorption process, a detailed understanding of metal binding mechanisms with active sites facilitates the determination of the rate-limiting step. Such information is important for the rational

design and optimization of the adsorbents and adsorption conditions. However, study pertaining to the role of surface chemistry and the adsorption mechanism is limited. Thus the focus of the present work is to analyze the surface characteristics of mangosteen shell, before and after treatment, and their role in solid-liquid adsorptions, using Cd_{2+} as a model compound.

MATERIAL AND METHODS

Preparation of Sample

Mangosteen shell (MS), an agricultural waste, is used as the precursor for the production of AC in this study. Initially, the MS was cleaned and air-dried to remove dirt and other impurities. For the production of char sample, the MS was crushed into small pieces ($\approx$1 cm) and was directly burned without acid impregnation at 773K for 1 h in a muffle furnace. The chemically activated carbon (CAC) was activated using the methods reported in our previous work [8]. The activation was done using single stage phosphoric acid (H_3PO_4) activation in self-generated atmosphere. Briefly, the MS were ground and sieved to obtain powder in the size of $\leq$1 mm (18 mesh size) before being impregnated with 85% H_3PO_4 (1 : 1 weight ratio). The slurry was then burned at 673 K under self-generated atmosphere in a muffle furnace. The product was washed in 1% $NaHCO_3$ to achieve neutral pH. All samples were ground and sieved into $\leq$1mm before subsequent testing and analysis. The average particle size of MS, char and CAC used was 1.21mm, 0.65mm and 0.51mm, respectively, as evaluated by Zetasizer Nano particle size analyzer (Malvern Instrument Ltd., UK) (Fig. S1(a)-(c)). The yield of the char and CAC was 21% and 47%, correspondingly.

Preparation of Synthetic Cd_{2+} Solution

A stock solution of cadmium ion (Cd_{2+}) (1,000mg/L) was prepared by dissolving appropriate quantity of cadmium nitrate salt, $Cd.N_2.O_6.4H_2O$ (Sigma-Aldrich) in deionized water. The stock solution was then suitably diluted to required concentrations in the following Investigations

Characterization of Samples

The CHN analysis of all samples was verified by using an elemental analyzer (Perkin Elmer 2400) and functional groups were identified by Fourier transform infrared spectrometer (FT-IR) (Thermo Scientific Nicolet iS10 FTIR) in the range of 500-4,000 cm_{-1}. The surface morphology was observed using field emission scanning electron microscope (FESEM) (Hitachi SU8000 SP), and X-Ray diffraction (XRD) patterns were recorded by the Siemens D5000 powder X-Ray diffractometer for crystallinity check.

Surface charges were examined by point of zero charge (pH_{pzc}) at 298 K. The pH_{pzc} was determined as described by Foo and Hameed [7]. The pH of 0.01 M NaCl (100mL) was varied in the range of pH 2 to 12. Sample, amounting to 0.3 g, was added into the solution and shaken for 48 h. The final pH of the NaCl solution was measured and the point of zero charge was identified at the point where initial pH is equivalent to the final pH.

The N_2 adsorption-desorption isotherms for all three samples were measured using Quantachrome's AUTOSORB-6B surface area and pore size analyzer at 77 K. Prior to analysis, the samples were outgassed at 423K for 5 h to remove the existing moisture. The isotherms data obtained were used to classify the textural parameters of the samples, including surface area, pore volume and pore size using appropriate models.

X-ray photoelectron (XPS) analysis was done with KRATOS Axis Ultra DLD for char and CAC samples to validate the results of elemental and functional group analysis.

Batch Adsorption Experiments

Adsorption experiments were performed in batch mode for CAC. The batch experiments were carried out at fixed dosage (0.05 g/ 100mL). The mixture was shaken in an incubator shaker (Daihan LabTech) at 200 rpm. Other environmental conditions of the experiments were not adjusted unless stated. The isotherm and kinetic studies were performed by varying the initial concentration of Cd_{2+} from 10 to 50mg/L for different time interval up to 6 h at pH 5.6. The effect of pH on adsorption capabilities was observed by altering the pH in the range of 2 to 12 using 20mg/L of Cd_{2+} as initial

concentration at 303K. The pH was adjusted using 0.1 M H_2SO_4
or NaOH solution and measured using Mettler Toledo FE20. For
thermodynamic study, the temperature was adjusted in the range
303, 310 and 320 K. The thermodynamic parameters were calculated
using the van't Hoff equation. The residue concentration of
Cd_{2+} was measured by ICP-OES (Perkin Elmer, Optima 3000).

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