Chemical Engineering Journal 193–194 (2012) 328–338

Contents lists available at SciVerse ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Adsorption of Hg^{2+} onto *Borassus Flabellifer*: A redox mechanism

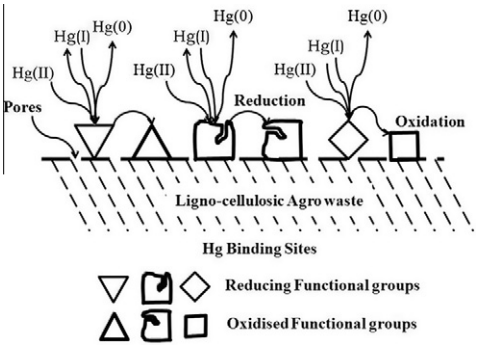
Shilpi Kushwaha [a], B. Sreedhar [b], Padmaja P. Sudhakar [a,*]

[a] Department of Chemistry, The M. S. University of Baroda, Vadodara 390 002, India
[b] Department of Inorganic & Physical Chemistry, Indian Institute of Chemical Technology, Hyderabad, India

HIGHLIGHTS

- Results highlight controlled adsorption of mercury on Palm shell powder (PSP).
- Dramatic influence of phenolic, carboxyl and aldehydic groups in sorption.
- Interestingly reduction of Hg^{2+} to Hg^0 by virgin agrowaste PSP.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 January 2012
Received in revised form 17 April 2012
Accepted 17 April 2012
Available online 26 April 2012

Keywords:
Redox mechanism
Mercurous
Mercuric
Elemental mercury
X-ray photoelectron spectroscopy
X-ray diffraction
Kinetics
Isotherms

ABSTRACT

In this study palm shell powder (*Borassus Flabellifer*) has been used for mercury removal. The surface properties of *palm shell powder* were examined by potentiometric titrations, X-ray photoelectron spectroscopy (XPS), X-ray Diffraction and Fourier transform infrared (FTIR) spectroscopy and the possible functional groups available for mercury binding were found to be carboxyl, ether, alcoholic and amino functional groups. Interestingly it has been observed that mercury was present on PSP as Hg^0, Hg^+ and Hg^{2+}. Kinetic, isotherm and column modeling studies reveal that complexation, ion exchange, and electrostatic interactions play a role in mercury adsorption on palm shell powder, but the relative predominance of each of these mechanisms varies with the pH of the medium. The isotherm thermodynamic parameters indicate the adsorption of mercury to be a spontaneous, exothermic process.

1. Introduction

Toxic heavy metals coming from many industrial effluents have adverse effects on our environment. Mercury has widespread applications in diverse fields like chloralkali industries, wood pulping industry, thermometer, barometers, batteries, dentistry, paints and military applications. Mercury is known to be highly toxic for aquatic life and human beings even at trace levels. Adsorption is a cost effective technology for the decontamination of heavy metals. Several inexpensive adsorbents have been tested for the removal of Hg^{2+} like copper shavings [1], aspergillus versicolor [2], *carica papaya* [3], microorganisms [4], furfural adsorbents [5], waste tire rubber [6] and organic waste materials such as rice husk [7], coconut husks [8]. Chemically modified or impregnated adsorbents are much more expensive than their virgin precursors. Metal ion binding to lignocellulosic materials is known to occur through various functional groups like carboxyl, amines or phenolic groups. Research has to be thus focussed on the use of low cost adsorbents like virgin agro wastes with good adsorption capacity.

* Corresponding author. Tel./fax: +91 265 2795552.
E-mail address: p_padmaja2001@yahoo.com (P.P. Sudhakar).

1385-8947/$ - see front matter © 2012 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cej.2012.04.050

As a local agrowaste we have used palm shell (*Borassus Flabellifer*) which is available throughout coastal Asia. In continuation of our work on use of palm shell powder as an adsorbent [9,10], in this study, emphasis is on the use of palm shell powder as cost effective adsorbent for the removal of mercury. The aim is to understand the mechanisms of mercury adsorption onto palm shell powder. Batch adsorption experiments were conducted under various solution pH values. Potentiometric titrations, Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) spectra and kinetic, isotherm as well as column modeling was used to identify the adsorption mechanisms. The applicability of various isotherms and kinetic models were determined by their r^2 value and error analysis.

The results suggest that complexation, ion exchange, and electrostatic interactions may all plays role in mercury adsorption on palm shell powder. Furthermore the XPS spectra revealed the presence of Hg^0 and Hg^{2+} on the surface of PSP after mercury adsorption suggesting that reduction of Hg^{2+} to Hg^0 took place on PSP surface which is a novel finding in this study as there are no literature reports on reduction of Hg^{2+} using pristine lignocellulosic materials.

2. Materials and methods

2.1. Preparation of adsorbent material

The shell of palm fruit (*B. Flabellifer)* was collected from coastal Andhra Pradesh, India. The collected palm shells were cut into small pieces, washed extensively with running tap water for 30–40 min. followed by double distilled water and then dried in an air oven at 70 °C. The dried biomass was ground in a laboratory blender and sorted using standard test sieve of 40 mesh and termed as palm shell powder (PSP).

Potentiometric titrations were carried out using 0.1 g adsorbent mass suspended in 50 mL of 0.1 M KNO_3 solution, and the suspension was equilibrated for 24 h. The suspensions were acidified to pH 3.0 using 0.1 M HNO_3 and then titrated to pH 11 using 0.1 M NaOH. All experiments were conducted in triplicate in a glass vessel with a lid as part of a Spectralab AT-38C Automatic potentiometric titrator. The temperature was recorded with a temperature sensor; the error of the temperature probe was 0.1 °C. The pH electrode was three-point calibrated with buffers (pH 4, 7 and 10) before each experiment, and the slope did not deviate more than 1% from the Nernst value. The titrator unit was programmed with a step volume dose mode for the titration, which adds 0.001 ml of titration solution according to the pH changes.

2.2. Batch uptake

A stock solution of Hg^{2+} was prepared by dissolving 1.36 g of mercuric chloride E-Merck (Darmstadt, Germany) in slightly acidified double distilled water and making up to 1 L to give 1000 mg/L of Hg^{2+} solution. Working standards were prepared by diluting different volumes of the stock solution to obtain the desired concentration.

Batch adsorption experiments were conducted at 30 °C by agitating 0.1 g of PSP with 25 mL of mercury ion solution of desired concentration maintained at pH 6.0 (except for pH experiments) in 100 mL stoppered conical flasks in a thermostated rotary mechanical shaker at 180 rpm for 4 h (except for the contact time experiments) at 30 °C. Experiments were done to determine the pH range at which the maximum mercury uptake would take place on PSP by varying the initial pH of the solution in the range 1–10 using 0.1 N NaOH and/or HCl. The effect of the initial concentration (1–1000 mg/L) was also studied in order to determine the effect of the parameter on the adsorption of metal from the solution. The optimum equilibrium time was determined as the contact time required for the concentration of metal in the solution to reach equilibrium and was obtained by varying the contact time in the range 30–240 min.

At the end of the predetermined time intervals, the suspensions were filtered and the mercury content in the filtrate was analyzed by using AAnalyst 200 Perkin–Elmer atomic absorption spectrophotometer. The uptake of Hg^{2+} by the adsorbent under study (q_e) was calculated from the difference between the initial and final concentration as follows:

$$q_e = (C_i - C_e)/m; \quad (1)$$

Where, C_i – initial concentration of metal ion mg/L; C_e – Equilibrium concentration of metal ion mg/L; m – Mass of adsorbent g/L; q_e – Amount of metal ion adsorbed per gram of PSP. Each experimental result was obtained by averaging the data from three parallel experiments.

Adsorption isotherm experiments were also performed by agitating 0.1 g of PSP with a series of 25 mL solutions at pH 6.0, containing different initial concentrations of (1–1000 mg/L) at 30 °C. After the established contact time (4 h) was attained, the suspension was filtered, and supernatant was analyzed for the metal concentration. The adherence of the equilibrium isotherm and data obtained to different adsorption isotherms models as given in Table S1 was tested. Similarly the mercury adsorption data obtained after agitating solution containing 10 mg/L of mercury for various contact times with PSP at pH 2, 5 and 8 were calculated to determine the order of reaction rate and the adherence to different kinetic models as given in Table S1 was tested. Thermodynamic parameters of the adsorption process (ΔG^0, ΔH^0 and ΔS^0) could be determined from the experimental data obtained at various temperatures. Values of correlation coefficients and standard deviation were used to compare the models. SD was calculated using the equation.

$$\mathrm{SD} = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(x_i - \bar{x})^2} \quad (2)$$

$$\mathrm{SSE} = \sqrt{\frac{1}{N(N-1)}\sum_{i=1}^{N}(x_i - \bar{x})^2}$$

2.3. Desorption studies

A 0.1 g of mercury loaded PSP was treated with 10 mL of different desorbing solutions like 0.1 M EDTA, 0.1 M NH_3 and 0.1 M HCl for a period of 30 min in a thermostated rotary mechanical shaker. After 30 min the amount of mercury desorbed from PSP was determined by AAS. After complete desorption PSP was thoroughly washed with distill water 2–3 times, dried at 70 °C in an air oven. Further adsorption–desorption experiments were repeated by following the same process for two more cycles.

2.4. Column studies

Column experiments were conducted in a glass column packed with PSP having an internal diameter of 1 cm and a bed height of 5 cm. Hg^{2+} solution of known concentration (1000 mg/L) at pH 6 was passed through the column of adsorbent at a flow rate of 1 mL/min. Samples from the column effluent were collected at regular intervals and analyzed by atomic absorption spectrometry. The break-through time has been chosen when the ratio of final to initial concentration of the effluent is 1 mg/L. Adherence of the