Microporous and Mesoporous Materials 217 (2015) 63–70

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

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

A new carbon–diatomite earth composite adsorbent for removal of heavy metals from aqueous solutions and a novel application idea

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ARTICLE INFO

Article history:
Received 12 March 2015
Received in revised form
30 May 2015
Accepted 3 June 2015
Available online 12 June 2015

Keywords:
Composite
Adsorption
Heavy metal
Activated carbon
Diatomite earth

ABSTRACT

A new type of carbon coated diatomite earth (DE) composite adsorbent was prepared using cellulose as carbon source. Carbonization and functionalization were studied by various reactants and finally concentrated sulfuric acid was applied in one-step. The procedure resulted in highly functionalized, porous carbonaceous matter. Cellulose was substituted by low-cost material containing cellulose resulting in unremarkable difference in the properties of the composite. The composite was studied among others, by scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) and elemental and correlation map was created by the obtained data. The composite was successfully used to remove heavy metal ions {Pb(II) and Ni(II)} from aqueous solution. The application was performed in both of the closed and flow systems. In closed system, the adsorption process followed the Langmuir isotherm. The adsorption depended on the pH and the highest adsorption capacities were 80 and 380 mg g^{-1} for Ni(II) and Pb(II) respectively. As a novel application, fractionation solid phase extraction (SPE) technique was applied for investigation of absorption characteristics of the composite in flow system. SEM-EPMA results demonstrated that lead was bonded to C–O bonds on the surface of composite.

1. Introduction

Activated carbon (AC) is one of the oldest adsorbent with a wide application area [1,2]. One of the most important utilization fields of AC is the water-cleaning technology [2,3]. Heavy metal pollution of surface waters is a worldwide problem and one of the simplest and cheapest solutions for removal of inorganic pollutants is the adsorption with carbonaceous matter [4–6]. Application of AC is generally used after various modifications to produce appropriate adsorbent to fit the emerged problem [7–10].

Our previous developments aimed to evolve high capacity low cost adsorbents prepared from waste materials [11]. Charcoals produced by chemical carbonization (by 95% sulfuric acid) and by further activation (by 65% nitric acid) were successfully applied for the removal of lead(II), nickel(II), chromium(VI), arsenic(III) [11–13]. The precise variation of components resulted in highly functionalized charcoal bonding the heavy metals with chemical forces (coordinative and ionic bonds). The adsorption of heavy metals was reversible depending on the pH whereas the decrease of pH permitted the leaching of metal ions. The maximal adsorption capacities (MAC) of charcoals obtained by carbonization with 95% sulfuric acid were 320 and 50 mg g^{-1} for lead and nickel respectively.

Cost saving techniques and application of low cost materials [e.g.3,14,15] have high importance in industrial water cleaning technology. The most commonly used low cost materials are diatomite earth and cellulose-containing waste matters, which are produced in millions of tons worldwide. There are several examples in the literature for various modifications of these well-known adsorbents to increase their adsorption capacities [16–21]. Most of the cases these surface modifications need special reactants and laboratory conditions. The literary reports and our previous studies in the field of carbon chemistry directed our attention to the preparation of surface modified composites.

Articles giving inspiration for us, reported about several examples of carbon-silica composites' production [22–26]. In these

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http://dx.doi.org/10.1016/j.micromeso.2015.06.004
1387-1811/

preparations various silica templates were used which were coated with carbon layer. The utilization areas of these composites are mostly catalysts and adsorbents. Although the applied procedures of composites' preparation allow the precise design of the pore size as well as the number of surface functional groups but they consist of multiple steps and they are time consuming and costly processes.

The objective of our work was to find a simple and cheap preparation of composite material with application of natural raw substances. The generalized procedure should permit to substitute the initial components and to use the locally available precursors. Further on our aim was the application of our earlier carbonization process maintaining the advantageous properties of our charcoal without disadvantages. The highest disadvantage of the charcoal prepared previously in our laboratory was the relatively slow reaction rate of adsorption. This did not allow the favorable application in flow system because the system needed more than half an hour to reach the equilibrium. The adsorption process can be accelerated if a large number of functional groups are present in the adsorbent with high availability. For this reason, our idea was to cover a material having high porosity and serving as carrier with thin carbonaceous layer. To be the carrier, diatomaceous earth was chosen which has typically high porosity containing up to 80–90% voids with free –Si–OH groups on the surface [16,27]. It is known that silicic acid can react with ortho phenols and vicinal diols in condensation reaction [28] and these latter chemical groups are produced during carbonization process. Using 95% H_2SO_4 for carbonization, the conditions are suitable for the condensation reaction so in this way the carbon layer may be fixed not only with weak forces but also with covalent bonds.

2. Experimental part

2.1. Preparation and characterization of composite

For the preparation of composite, the raw materials (cellulose and DE) were mixed in various ratios. The applied masses were 0, 1, 3, 5, 7, 8 g DE and 20, 19, 17, 15, 13, 12 g cellulose. The homogenous mixture was carbonized with 40 mL 95% sulfuric acid. In course of some experiments after addition of sulfuric acid for carbonization, 5 mL 65% nitric acid or 5 mL 30% H_2O_2 was added to the carbonized mixture for further activation. The black slurry was kept in oven at 120 °C for 24 h. The charcoal was washed with distilled water several times until the conductivity of the supernatant decreased below 10 μS cm^{-1} then it was dried at 110 °C, pulverized and sieved on 100 μm sieve. The powders were stored in closed glass vessel until utilization. In certain experiments, the cellulose was substituted with peanut shell's powder.

For characterization of the prepared composites, several methods were used. The BET adsorption was determined after degassing (at 443 K, for 96 h at 10^{-5} mmHg). Nitrogen physisorption measurements were performed at 77 K using a static volumetric apparatus (Quantachrome Autosorb 1C analyzer). The total carbon (TC) content of composites was measured with instrument of Multi N/C 2100 S, Analytik Jena, Germany. The charcoals and composites furthermore their residue on ignition were also determined by a desktop X-ray fluorescence (XRF) spectrometer (MiniPal2, Panalytical, The Netherlands). The rhodium anode micro X-ray tube was operated at U = 20 kV and I = 0.005 mA. The X-ray spectra were collected for 1000 s (live time) by thermoelectrically cooled Si-PIN detector. The residues on ignition were prepared in oven at 1000 °C using 0.2 g samples.

The acidic surface functional groups were measured using modified Boehm titration [29] (applying Automatic Titrator 388 Titrando, Metrohm AG, Switzerland). The evaluation was done by Tiamo software (Version 1.3, Metrohm AG, Switzerland). All titrations were repeated three times. The pH point of zero charge (pHPZC) was determined with potentiometric method according to the literature [30] at three different electrolyte concentrations.

Further characterization of composite was performed by FT-IR method. Internal reflection IR spectra were recorded by Perkin–Elmer 1605 FT-IR spectrometer in a horizontal ATR cell. The spectrometer was equipped with a lithium tantalate detector. The sample was laid flatly and evenly on a 45° trapezoidal ZnSe crystal (ATR plate) and an increasing pressure was applied directly on the sample powder. Spectra were acquired at 2 cm^{-1} resolution and 64 scans were averaged to reduce noise.

In order to the further investigation of composites, scanning electron microscopy (SEM) and electron probe microanalysis (EPMA) measurements were carried out by a FEI Quanta 3D scanning electron microscope equipped with an X-ray silicon drift detector. Samples were deposited on double-sided adhesive conductive carbon tape developed for SEM measurements (SPI Supplies, West Chester, USA) mounted on aluminum sample holder. Since, the samples had relatively high conductivity due to their high carbon content therefore coating was not applied. X-ray spectra were collected from several points of the sample ($U = 30$ kV, $I = 1$ nA) for 100 s (live time). Elemental maps were generated using 15 kV accelerating voltage and with the same electron current as in case of the spectra. The maps consisted of 128*100 pixels; each point was measured for 200 ms. Correlation maps were generated by summing the single color (red, green or blue) elemental maps [31]. In case of elemental maps, the evaluation of data was carried out using the net intensity of K line of the elements, except lead, where L lines were used.

Diatomaceous earth (Kieselguhr, bulk density 200 g L^{-1}, particle size 0.1 mm (98%); Merk) and cellulose powder (Fluka) were chromatographic grade, all other chemicals (sulfuric acid, nitric acid, HCl, NaOH, $NiSO_4$, $Pb(NO_3)_2$ etc.) used in the experiments (except peanut shell) were of analytical grade.

2.2. Study of heavy metal adsorption and desorption in closed system

During the preliminary experiments, the maximal adsorption capacities were determined. 0.05 g composites were saturated with 25 mL solutions containing 400 mg L^{-1} Ni(II) or 1500 mg L^{-1} Pb(II). The pH was set to 6 and to 5 in case of Ni(II) and Pb(II) respectively. After 3 h shaking (Orbital Shaker OS-20, Biotech, Praha), the mixtures were filtered using Visiprep DLVacuum Manifold (Supelco, Bellefonte, PA, USA) and the metal ion concentrations of supernatants were determined with atomic absorption spectrometry (AAS). The quantity of adsorbed ions was calculated based on the atomic absorption spectrophotometric (AAS1N equipped with 10 cm slit burner, Zeiss, Germany) determination of residual Ni and Pb concentrations of the solutions. A stoichiometric air-acetylene flame was used for the determination of Pb concentration and the absorbance was measured at the wavelength of 283.3 nm. The absorbance of Ni was measured at 232.0 nm in a slightly oxidative air-acetylene flame.

To study the pH dependency and to determine the adsorption isotherms, the composite of the highest adsorption capacity (labeled Cell-DE-15-5) was applied. Different aliquots of nickel sulfate and lead nitrate solutions were added to 0.05 g composites suspended in distilled water. The pH of the solutions was set to 3, 4, 5 while in case of Ni to 4, 5, 6 and the volume was completed to 25 cm^3. The mixtures were shaken for 3 h with interruptions in every hour and the pH was set repeatedly until becoming constant. Finally, mixtures were filtered and measured by AAS.

Studying the desorption process 0.5 g composite Cell-DE-15-5 was used in 250 mL volume and the composite was saturated