ARTICLE IN PRESS
Egyptian Journal of Petroleum (2016) xxx, xxx–xxx

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Egyptian Petroleum Research Institute
Egyptian Journal of Petroleum

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FULL LENGTH ARTICLE

Rice husk templated water treatment sludge as low cost dye and metal adsorbent

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Received 12 May 2016; revised 18 September 2016; accepted 12 October 2016

KEYWORDS

Adsorption;
Water treatment sludge;
Rice husk;
Mesoporous adsorbents

Abstract The preparation of adsorbents at low cost as alternatives to the expensive ones in the treatment processes of water and wastewater is the interest of the researchers worldwide. Here, a novel cheap mesoporous adsorbent was prepared via the recycling of wastes namely water treatment sludge and rice husk (RH) as textural modifier. Surface area and pore dimensions were optimized against RH ratio. The mesoporous sludge was employed in adsorption of rosaniline dye, Pb^{2+}, Ni^{2+} and chlorine from aqueous solutions under dynamic experimental conditions. It was found that the initial dye concentration and textural structure of the adsorbent played important roles in adsorption capacity. The reusability test shows the ease desorption of dye with slightly alkaline water (pH = 8) indicating the stability and reusability of the ceramic adsorbent for several times. For metallic cations, the characteristics (ionic radius and ΔH_{hyd}) of ions affect the adsorption affinity. Chlorine adsorption is controlled by the cation exchange capacity(CEC).

1. Introduction

During the last decades, the exponential population and social civilization expansions, changes in the habits of life and resources used coupled with continuing progress of the industrial and technologies have led to a sharp modernization and metropolitan growth [1]. With the growing awareness of the occurrences of industrial activities, many alterations on several ecosystems have been intensified and began to seriously threaten human health and the environment. Among the many cases of pollution of the aqueous medium, the contamination of water by dyes and heavy metals when a wide range of chemical products and dyes are discharged directly or indirectly in the course of the water without adequate treatment to remove and degrade these harmful compounds. More than 100,000 commercially available dyes are known and approximately 1 million tons of these dyes are produced annually worldwide. The main sources of dye contamination are considered to be from textile industry [2].

Wastewater from the textile industry is a complex mixture of many polluting substances ranging from residual dyestuffs to heavy metals associated with the dyeing and printing processes. Wastewater from processes of reactive dye is particu-

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Peer review under responsibility of Egyptian Petroleum Research Institute.

http://dx.doi.org/10.1016/j.ejpe.2016.10.006
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larly problematic because these dyes have low levels of attachment to the fibers. 30% or more of the dyes used are hydrolyzed and then released into waterways. The brightly colored unfixed dyes are highly water soluble, have poor adsorption properties and are not removed by conventional treatment systems. Although these dyes are not in themselves toxic, they may be converted into potentially carcinogenic amines after release into the aquatic environment. Their disposal is always a matter of great concern because they are considered as a whole in fact dangerous source of pollution of the environment and may result in the direct destruction of aquatic life due to the presence of chlorides of metals and aromatics which interferes with the penetration of the light and the oxygen in water bodies leading to a conflict between the upstream discharger and downstream user water.

Various techniques [3–6] have been developed for the removal of dyes and heavy metals from wastewater. Among them, adsorption is an especially effective approach. The adsorbents at low cost for the air/water purification have much attracted the attention of researchers around the world. One of these cheap materials is the water treatment sludge (WTS) produced during the pre-treatment of Nile water before demineralization as a feed-water for boilers at power stations and at the domestic water treatment plants. The composition and properties of WTS depends on the quality of the raw water, and the type of chemical treatment used in the treatment processes. The recycling of sludge from water treatment plants is usually an attempt to reduce its volume, make it harmless and stable, retrieve and facilitate its content useful safe disposal without imposing a burden for the environment [7,8]. The sludge contains mainly a high concentration of salts of aluminum or iron, with a mixture of organic and inorganic materials and the precipitates of hydroxide [7].

Adsorption of large molecules (e.g. drug delivery, biomedical application, dyes, purification of biofluids, water purification technologies) requires the design of new porous materials with extended pore diameter in the mesoporous range (pore dimensions above 2 nm) [9–11]. Mesopores constitute the pathways for large molecules to access the inner porous structure (primary adsorption sites), thus improving the adsorption kinetics.

On the other hand, large quantities of crop residues in term of rice husk (RH) are produced annually worldwide, and are vastly underutilized. Since Egypt's rice plantation is among the highest in the world, 4.0 million tons of wastes are left behind annually. Some residues are used to feed animals or recycled, yet open burning remains the most widespread technique of disposal. Such practice, which is only one of many other open burning activities, deteriorates air quality of Cairo and the Delta governorates contributing to the black cloud phenomenon, acts as the potential risk of developing serious health problems (due to the emission of carbon monoxide and other toxic emissions) and consequently, poses potential economic threats. Therefore, it is necessary to find a suitable method to solve the disposal problem. Using of this cheap material as a natural organic template in modification and improvement of textural structure of water treatment sludge as ceramic adsorbent, contributes to the solution of this problem and achieve the principle "waste-waste self-cleaning".

This work aims at developing of porous material from RH and water treatment sludge as low cost dyes and metals adsorbent.

2. Experimental

2.1. Materials

The raw sludge used in this study was sourced from the water treatment plant at El-Kureimat power station (Giza, Egypt), rice husk (RH) is provided by the rice mills at Cairo, Egypt. All chemicals used (rosaniline dye, $Pb(NO_3)_2$ and $Ni(NO_3)_2 \cdot 6H_2O$) are analytical grades and purchased from Prolabo. Stock solutions of the dye at concentrations of 1.48×10^{-4} mol/L, 8.88×10^{-5} mol/L and 4.44×10^{-5} mol/L were prepared. The solutions of Pb^{2+} and Ni^{2+} were prepared at concentrations of 1.7×10^{-4} mol/L. A sample of water contaminated with residual chlorine of concentration 1.41×10^{-5} mol (1 ppm) was drowned from the pretreatment cycle of demineralizer feed water at Upper Egypt Electricity Production Company (UEEPC).

2.2. Preparation of mesoporous sludge

5, 10 and 15% wt.% rice husk were well-mixed with raw sludge (RS) to ensure homogeneity of the mixture. The mixed pastes were molded in wood mold and left to dry away from the sun for seven days. After that, the samples were dried at 95 °C for 24 h then were fired in a temperature programing muffle furnace (Nabertherm 330 P, Germany) at 900 °C for 3 h with a heating rate of 5 °C/min. The prepared samples were denoted as RS-RH5%, RS-RH10% and RS-RH15%, respectively.

2.3. Testing procedures

Nitrogen adsorption/desorption isotherms were performed to characterize the texture of the calcined samples at 900 °C. Nitrogen adsorption and desorption isotherms at −196 °C of the calcined samples were collected at 77 K using a Quantachrome Autosorb-1C apparatus. Prior to the measurements, the samples were degassed in vacuum at 250 °C for 3 h. Specific surface areas (SSA) of these samples were calculated using the Brunauer-Emmett-Teller (BET) equation (p/p_0 = 0.05–0.15). The total pore volume was determined at relative pressure $p/p_0 = 0.98$. The pore size distribution was estimated according to the quenched solid density functional theory (QSDFT) equilibrium model for slit pores using the Autosorb 1.56 software from Quantachrome. The micropore volume and surface area were also calculated by the above mentioned DFT model.

XRD analysis of the calcined raw sludge was performed by X-ray diffractometer, PANalytical model X, pert PRO, equipped with a Cu Kά radiation (λ = 1.5418 Å) at scanning rate of 0.3° min^{-1}. Structural characteristics of the sorbent samples were studied via FTIR analysis, using ATI Mattson WI, 53717 model Genesis spectrometer, USA. The metal content of rice husk ash(RHA) and the cation exchange capacity (CEC) of the obtained mesoporous sludge were determined at Desert Research Center, El Matariya, Cairo. The metal content was determined using Inductively Coupled Argon Plasma, iCAP 6500 Duo, Thermo Scientific, England standardized with 100 mg/L multi-element certified solution, Merck, Germany. The CEC was determined using sodium acetate method which was found 12.5 mEq/100 g. Chemical analysis of sludge was