Journal of Industrial and Engineering Chemistry 19 (2013) 1617–1623

Contents lists available at SciVerse ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Cold plasma and microwave radiation applications on almond shell surface and its effects on the adsorption of Eriochrome Black T

Ömer Şahin [a], Cafer Saka [b,*], Sinan Kutluay [a]

[a] Faculty of Engineering and Architecture, Siirt University, 56100 Siirt, Turkey
[b] School of Health, Siirt University, 56100 Siirt, Turkey

ARTICLE INFO

Article history:
Received 7 December 2012
Accepted 29 January 2013
Available online 5 February 2013

Keywords:
Modification
Microwave radiation
Cold plasma
Almond shell
Eriochrome Black T

ABSTRACT

Almond shell based adsorbents were thermally modified by cold plasma and microwave radiation for improving adsorption ability of Eriochrome Black T. The maximum adsorption capacities were 6.02, 18.18, and 29.41 mg/g for untreated, cold plasma and microwave radiation treated almond shell, respectively. The removal percentages of EBT compared with untreated almond shell were increased from 39.96% to 81.46% and 84.31% after modification by cold plasma and microwave radiation treatments, respectively. SEM, FT-IR spectroscopy and point of zero charge measurement were applied to analysis the almond shell surface. Data on equilibrium were evaluated by using Langmuir and Freundlich models.

1. Introduction

Waste effluent from industry such as dyestuff, textiles, rubber, plastics, leather, cosmetics and pharmaceutical can be particularly problematic due to the presence of color in the final effluent. The dyestuffs have a complex chemical structure and are stable to light, heat, and oxidation agents [1]. Some of the reports show that today there are more than 10,000 dyes available commercially dyes with a production greater than 7×10^5 metric tones per year [2]. The discharge of colored wastewater with the synthetic origin and complex aromatic molecular structures into natural streams has caused many significant problems such as increasing the toxicity and chemical oxygen demand of the effluent. Kadirvelu et al. reported that dyes could cause severe damage such as dysfunction of kidney, reproductive systems, liver, brain, and central nervous system [3].

The adsorption technology onto activated carbon is one of the most effective technologies for the decolorization of wastewater. However, commercially activated carbons are considered very expensive [4–7]. Therefore, as technology has advanced, many researches have been applied the inexpensive, efficient, and easily available adsorbents for the removal of various dyes from aqueous solutions.

There have been many studies to obtain low cost adsorbents from agricultural wastes, such as rice husk [8], wheat shells [9], garlic peel [10], onionskins [11–13], neem leaf powder [14], spent coffee grounds [15], walnut sawdust [16], coffee husks [17], acorn shell [18], etc.

Surface chemical functional groups can be modified through physical, chemical, and electrochemical treatments. The modification processes are activation processes, heat treatment, and post chemical treatment [19–22].

Cold plasma and microwave radiation are the two most important thermal processes. The plasma treatment is one of the promising techniques to modify the surface chemical property. In the plasma treatment process, gases are applied to surface of materials. The function of surface modification is to change the physical and chemical properties of surfaces to improve the functionality of the original material. Cold plasma is an effective surface treatment technique that be used to enhance the surface properties of materials. As a result of cold plasma treatment, the surfaces of the materials are modified with chemical functions groups that used to bind polymers or other molecules to the surface in order to achieve desired surface properties [23,24].

During the plasma treatment, chemically active species (e.g., hydroxyl, carbonyl, and carboxylic acid) are occurred only on the surface of activated carbon, which react at the sorbent surface with specific chemical functions groups [25,26].

In recent years, microwave radiation energy leading to homogenous and quick thermal reactions has attracted attention [27,28]. Microwave heating has the advantages, such as improved reaction rates and yields, performing reactions at

* Corresponding author at: School of Health, Hospital Street, 56100 Siirt, Turkey. Tel.: +90 484 223 12 24; fax: +90 484 223 66 31.
E-mail address: sakaca1976@gmail.com (C. Saka).

1226-086X/$ – see front matter © 2013 The Korean Society of Industrial and Engineering Chemistry. Published by Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.jiec.2013.01.032

lower temperatures, better structural properties, rapid temperature rise and uniform temperature distribution [29,30]. Microwave energy influences samples through electric- and magnetic-fields; polar and ionic molecules within the sample try to align themselves with the oscillating electric-field [30]. Microwave radiation has been successfully used for the preparation of activated carbon [31–34]. So far, there are relatively few studies in surface modification field of adsorbents with cold plasma and microwave radiation. Saka et al. [12] have reported the removal of methylene blue from aqueous solutions by using microwave heating and pre-boiling treated onionskins. The removal of methylene blue from aqueous solutions by using cold plasma and formaldehyde treated onionskins was studied by Saka and Şahin [13]. In addition, the removal of methylene blue from aqueous solutions by using cold plasma, microwave radiation, and formaldehyde treated acorn shells was presented by Saka et al. [18].

The almond (*Prunus dulcis*) is a species of tree native to the Middle East and South Asia. The almond is one of the most valuable crops in Turkey and in the world. Turkey is the 7th largest almond producer in the world by annual production of more than 2,005,306 tons. Approximately 70,000 tons almond are being generated annually [35]. Almond shells are abundant, inexpensive and readily available lignocellulosic material.

This paper is the first report on the modification application of almond shell adsorbent with cold plasma and microwave treatments for the removal of EBT from wastewaters. The main objective of this work is to study the adsorption potential of a low-cost adsorbent prepared from almond shell modified with cold plasma and microwave radiation. The changes of the surface physical and chemical properties after modification were characterized and analyzed. To investigate the effects of the modification treatments on the adsorption performance of the almond shell, the adsorption isotherm of EBT from aqueous solution on adsorbent were studied. EBT is selected as a model dye, which are commonly large and difficult to be degraded in natural environment. The changes in the surface physical and chemical properties after modification of almond shell are characterized by FTIR and SEM techniques.

2. Materials and analytical methods

All chemicals used in this study purchased from Merck, and used without any further purification. EBT (C.I. number 14645); sodium-4-[(1-hydroxynaphthalen-2yl-hydrazinylidene]-7-nitro-3-oxo Y-naphthalene-1-sulfonate was obtained from Glaxo Ltd. The structure of EBT is given in Fig. 1. The EBT concentrations in the sample were determined using UV spectrophotometer (Perkin Elmer model, AAnalys 700). A rotosynth rotative solid-phase microwave reactor with continuous output power and a frequency of 2.45 GHz was applied for the treatment. Almond shell was treated with a Plasma Prep 5 plasma machine (GaLa Gabler Labor Instrumente, Bad Schwalbach, and Germany). The FT-IR spectrum of the sample was recorded using a Model Perkin Elmer 1100 series Fourier transform infrared spectrometer operating in the range 4000–400 cm^{-1}. The surface morphology of the adsorbents was visualized via SEM (LEO FE-SEM model 982, Carl Zeiss SMT Inc.). The pH measurements were made using a pH meter (Mettler Toledo MP 220).

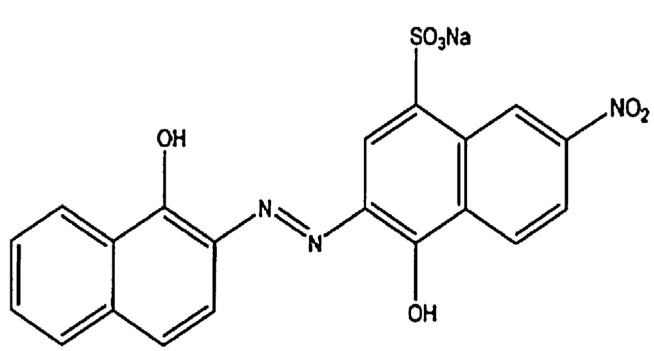

Fig. 1. Chemical structure of EBT.

2.1. Preparation of CPTAS and MTAS

Almond shell was washed with distilled water to eliminate the impurities (dust and water soluble substances) and dried at 110 °C for 24 h, and sieved to obtain particles size between 600 and 355 μm diameter prior to their modification.

Cold plasma treated almond shell (CPTAS) was prepared by subjecting the 3.0 g almond shell to nitrogen plasma treatment for different time intervals (5, 15 and 30 min) at 80 W using a Plasma Prep 5 plasma machine. The obtained CPTAS material was stored in airtight plastic container for further use [13,18].

A microwave oven with continuous output power and a frequency of 2.45 GHz was applied for the microwave radiation treatment. Almond shell of 3.0 g was placed in a tubular quartz reactor. A connector was fixed in the middle of the reactor, which allowed the introduction of nitrogen flow. The head of the reactor was sealed with a plug. The microwave power was set as 1000 W, and different time intervals (5, 10, and 15 min) were applied to prepare microwave treated almond shell (MTAS) and study the modification effects. The MTAS material was stored in airtight plastic container for further use [12,18].

2.2. Zero point of charge determination

The zero point of charge (pHzpc) values of CPTAS, MTAS and untreated almond shell were determined with solid addition method by introducing 0.1 g almond shell into 50 mL of a 0.01 M KNO_3 solution. Then, the pH was adjusted to successive initial values between 2 and 11, by using either NaOH or HCl. After a contact time of 24 h, the final pH was measured, and plotted against the initial pH [11,18].

2.3. Adsorption experiments

The adsorption studies were carried out at 30 °C. 200 mL of the solution containing the desired quantity of the EBT was treated with 0.25 g of modified almond shell in stoppard conical flasks for the different times using a temperature-controlled shaker.

After 180 min, all solutions were filtered and centrifuged to remove solids and then analyzed using a Perkin Elmer Analys 700 UV–VIS spectrophotometer.

The pH effect of the initial solution on the equilibrium uptake of dyes was analyzed over a range of pH 3–10. The pH effect of the solution adjusted by either 0.05 M NaOH or 0.05 M HCl solutions. The batch adsorption studies were conducted as function of contact time (5, 10, 20, 30, 45, 60, 90, 120, 150 and 180 min) and dye concentration (25, 50, 75 and 100 mg/L) for maximum adsorption. Under the experimental conditions, the adsorption capacity for each concentration of dye at equilibrium was determined by using Eq. (1).

$$q_e\,(\mathrm{mg/g}) = \left[\frac{C_i - C_e}{M}\right] \times V \tag{1}$$

C_i and C_e were the initial and final concentration of dyes in the solution respectively. V is the volume of solution (L) and M is the mass of adsorbent in (g) used. The % removal was measured by