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Research paper

Plasma-surface modification on bentonite clay to improve the performance of adsorption of methylene blue

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ABSTRACT

The present study consists of the cold plasma treatment was applied for the surface modification of bentonite to improve the removal of methylene blue (MB) from aqueous solution. To achieve the aim, the conditions for adsorption, including cold plasma application time, plasma gas effect, and pH were investigated with respect to the adsorption capacity of MB. The changes of the surface property before and after cold plasma treatment were discussed. Cold plasma treated bentonite is characterized by Scanning Electron Microscopy (SEM), Fourier Transform Infrared (FTIR), BET surface area, and X-ray diffraction (XRD). Equilibrium adsorption data were analyzed by Freundlich and Langmuir equations. Langmuir isotherm exhibited the best fit with the experimental data. Adsorption kinetics were fitted with pseudo-first-order, and pseudo-second order. Cold plasma treated bentonite was exhibited largest adsorption capacity (303 mg/g) at 30 °C.

1. Introduction

There are nowadays more than 100,000 commercially available dyes with an estimated annual production of over 70,000 tons. Dyes are widely used in textile, paper, rubber, plastic, leather, cosmetic, and pharmaceutical and food industries. The discharge of wastewaters containing dyes into rivers and lakes even at very low concentrations is a source of esthetic pollution that increases toxicity and chemical oxygen demand of the effluent, and also reduces light penetration, which has a derogatory effect on photosynthetic phenomena (Nigam et al., 2000; Saka et al., 2012a,b,c). For all these reasons, colored effluents are a serious environmental problem and it is essential to develop proper treatment processes.

Several treatment methods have been developed for dye removal including coagulation, chemical oxidation, membrane separation, electrochemical process, and adsorption technique. Among these processes, adsorption is an effective method for color removal. There are very different studies on the use of low-cost materials for removing dyes, such as various agricultural wastes (Saka and Şahin, 2011; Saka et al., 2011, 2012b,c, 2013), chitosan (Pitakpoolsil and Hunsom, 2014), fly ash (Mohan et al., 2002), kaolinite (Yavuz et al., 2003; Volzone and Ortiga, 2011; Yavuz and Saka, 2013), perlite (Doğan et al., 2004), sepiolite (Özdemir et al., 2006; Doğan et al., 2007), montmorillonite (Gemeay et al., 2002), zeolite (Meshko et al., 2001; Hernandez-Montoya et al., 2013), bentonite (Hong et al., 2009; Li et al., 2010; Hashemian et al., 2014; Musso et al., 2014; Rahni et al., 2014), other soils (Çöle et al., 2013; Quan et al., 2014; Yin and Shi, 2014), etc. Clay minerals have been increasingly receiving attention because it is promising low-cost adsorbent (Panneer et al., 2008).

Clays are good adsorbents because of the existence of several types of active sites on the surface, which include Bronsted and Lewis acid sites and ion exchange sites. Clay minerals have different adsorption capacities for dyes. Adsorption capacities depend on the properties of the clay minerals and the adsorbate as well as experimental conditions. Clay minerals have many applications in industry due to their high surface area, porosity, thermal stability, specific active sites, and attractive adsorptive properties (Laszlo, 1987; Tanabe and Holderich, 1999; Varma, 2002).

The application of clays, especially bentonite, has attracted more and more attention because of their low-cost, easy availability, high cation exchange capacity and surface area. Because of their low cost, abundance in most continents of the world, high adsorption properties and potential for ion exchange, clay materials are strong candidates as adsorbents.

Bentonite is mainly composed of montmorillonite, which has interlayer cations to compensate the negative net charge on the surface. This negative charge is due to isomorphic substitutions on the montmorillonite structure. These inorganic cations can be replaced with cationic surfactants or polycationic species, and the resulting materials are regarded as organobentonite or pillared bentonite, respectively (Zhu et al., 2009).

However, the studies about adsorption properties and optimal adsorption conditions of modified bentonite are limited. The adsorption capacity of bentonite may be enhanced by thermal or chemical modifications. Various surface modification methods such as, heat and acid

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treatment may be used for improving the adsorption capacity of bentonite.

However, most of these modifications are either prepared in certain conditions, e.g., high temperature and additional of chemicals which increase operation costs and their efficiency is low. Therefore, there is a need to develop low cost, easily available, effective and reusable adsorbents for the removal of dyes from the aqueous environment. Recently, cold plasma techniques have received special attention because of their advantages in comparison with the traditional modification techniques including high efficiency, simple operation, energy source saving and, non-pollution, which play an important role in pollution prevention.

The surface properties of adsorbents are important for adsorption, because the adsorption process is about specific interactions between the target molecules and the adsorbents surface. Plasma includes less water usage and energy consumption, with very small material damage (Tusek et al., 2001; Lehocky et al., 2003; Grythe and Hansen, 2006; Ren et al., 2008; Sparavigna, 2008). Depending on the gas used for plasma generation and on the general treatment conditions it is possible to activate a surface by inserting active species, by surface abrasion or etching, by cross-linking processes or, in many cases, by obtaining combined effects (Ratner, 1995; Guruvenket et al., 2004; Lixon Buquet et al., 2010; Fatyeyeva et al., 2011).

In the plasma treatment process, gases such as, Ar, O_2, N_2, CO_2 are applied to a surface of materials. As a result, the surfaces of the materials are treated with chemical functionalities that bind polymers or other molecules to the surface in order to achieve desired surface properties (Desmet et al., 2009; Wen et al., 2012). During the plasma treatment, chemically active species, such as hydroxyl, carbonyl, and carboxylic acid occur only on the surface of adsorbents, which react at the adsorbent surface with specific chemical functions (Park and Kim, 2001; Shen et al., 2008).

Until now, some studies have been reported in improving the surface properties of adsorbents using cold plasma and microwave radiation (Saka and Şahin, 2011; Saka et al., 2011, 2012b,c, 2013; Yavuz and Saka, 2013). However, no studies have been reported on the modification of bentonite using cold plasma. This paper is, to the best of knowledge, the first study on the modification of bentonite using cold plasma. The purpose of this study was to compare the effect of cold plasma modification on the surface of the bentonite in any way. The changes of the surface physical and chemical properties were characterized and analyzed by SEM, FT-IR, BET surface area and XRD after modification. MB is selected as a model dye.

2. Materials and analytical methods

The clay used in this study as dye adsorbent was collected from the Eskisehir region of Turkey. The bulk chemical analysis (mass %) of the bentonite sample is: SiO_2, 70.8; Al_2O_3, 16.2; Fe_2O_3, 0.70; TiO_2, 0.18; MgO, 1.25; CaO, 1.62; Na_2O, 0.11; K_2O, 2.12; and loss on ignition, 6.63.

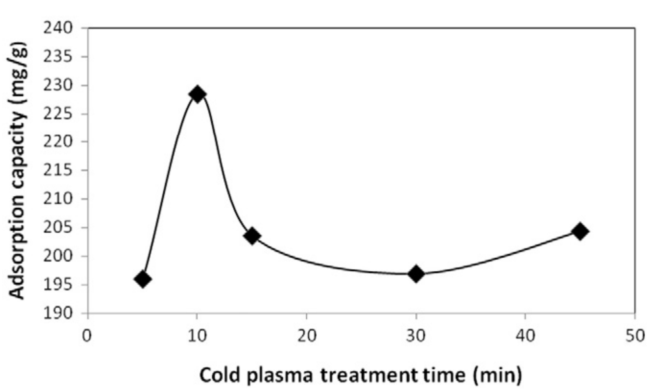

Fig. 1. Effect of cold plasma treatment time on bentonite surface.

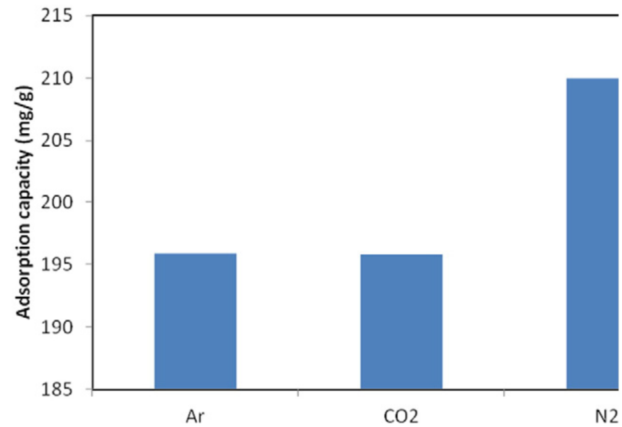

Fig. 2. Effect of cold gas plasma on bentonite surface.

Cation exchange capacity determined by the methylene blue method was 837.5 mmol/kg (Özcan and Özcan, 2004).

MB was chosen because of its known strong adsorptions onto solids. The adsorbate MB (C.I.: 52030, chemical formula: $C_{16}H_{18}N_3OS$, MW: 333.6 g/mol) was supplied by Merck, Germany. Concentrations of dye were determined by measuring the absorbance at 663 nm with a spectrograph Perkin Elmer model, AAnalys 700 spectrophotometer.

2.1. Preparation of cold plasma treated bentonite

Plasma Prep 5-plasma machine (GaLa Gabler Labor Instrumente, Bad Schwalbach, and Germany) was used to treat the sized samples. The gases of N_2, Ar, and CO_2 were employed in the Prep 5-plasma machine treatment. The output power was 80 W. Treatment times were 5, 15, 30, 45 and 60 min, respectively. Cold plasma treatment was applied on 3 g bentonite. The obtained material was stored in airtight plastic container for further use.

2.2. Characterization

XRD patterns of the samples were acquired in a Bruker D8 Advance X-ray diffractometer with Cu Kα sources by using Cu Kα radiation ($\lambda = 1.5418$ Å), over the range of $2\theta = 10$–$80°$. The surface morphologies of the untreated and plasma treated bentonite were analyzed by means of scanning electron microscopy (SEM) (Zeiss EVO 50 Model).

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 clay powder (5 mg) was mixed with KBr (100 mg).

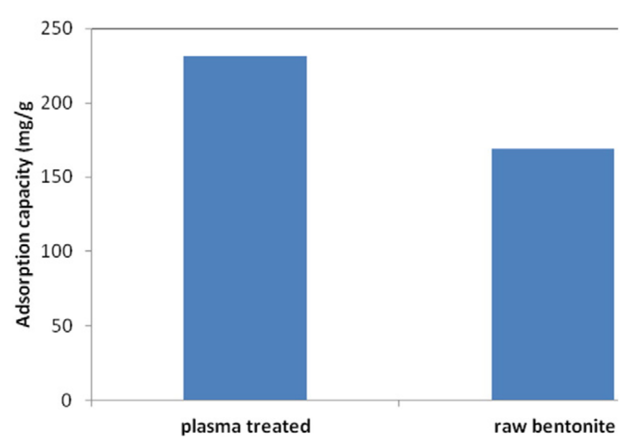

Fig. 3. Yields of MB adsorption capacity for raw and cold plasma treated bentonite.