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Zeolite properties improvement by chitosan modification—Sorption studies

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ABSTRACT

In the paper the potential of chitosan modified zeolite (NaP1CS) as a cheap adsorbent for methylene blue (MB) removal from aqueous solutions was determined. Fourier transform infrared spectroscopy analyses, nitrogen adsorption/desorption isotherms and scanning electron microscope were applied to characterize the adsorbent. Batch adsorption studies were carried out to examine effects of various factors such as pH, contact time, initial MB and Cu(II) concentrations, temperature influence on the sorption process. The impact of different ways of zeolites modification with chitosan on sorption capacity and the comparison of adsorption of unmodified zeolite and fly ash are presented. The effect of different metal ions such as Cu(II), Zn(II), Mn(II), Fe(III) and also that of foreign ions on the MB sorption were also studied. The pseudo-first order, pseudo-second order and intraparticle diffusion models were fitted to the kinetic data. The best fit was achieved with both the pseudo-second order and intraparticle diffusion models. The experimental equilibrium data were evaluated by the Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherm models. The calculated thermodynamic parameters indicated a spontaneous and endothermic sorption process. Desorption studies were carried out with different desorbing agents. HCl proved to be the most effective desorption agent for MB and Cu(II).

Introduction

Every year more than 7×10^{-5} tonnes and 100.000 kinds of dyes are produced. In practice, the concentrations lower than 1 mg dm^{-3} of dyes can give undesirable color to water [1]. Methylene blue is a basic dye which belongs to the widely applied main group of dyes. It is used in industry for dying cotton, silk and wood [2]. In water it exists as a cation. Investigations on sorption of methylene blue were carried out by many scientists [3–9]. Generally, most of the dyes used in printing and paper industries cause major environmental problems. They are toxic for both humans and animals, and can cause cancer, besides they are non-biodegradable and stable in the environment. These colorful effluents with different temperatures, pH values, high chemical oxygen demand cause disorder of photosynthesis reducing light permeability. Therefore the removal of synthetic dyes in recent decades has become a global problem [10–14]. Furthermore, during the printing and dyeing processes, copper salts are widely used as additives to optimize various properties of the printing and dyeing products. Copper has attracted much attention because of its harmful effects on humans. Large doses of copper can cause high blood pressure, anemia, widespread capillary damage and permanent damage in the liver and kidney [15,16]. Therefore these two components are present together in the aqueous media. It is important to find a suitable method for simultaneous removal of dyes and heavy metals from wastewaters.

The widely applied method for purification of waters is adsorption on solid sorbents like ion exchange resins [17], active carbon [18], natural and synthetic zeolites and fly ashes [19–21]. A promising area of zeolite synthesis is possibility of reusing solid wastes from power plants. Low cost of raw materials makes them an alternative to traditional sorbents like active carbon [22]. In many papers zeolites showed perfect sorption efficiency for heavy metals [19,23–26], phosphates [27], ammonium [28–30], land-based petroleum spills [31] or BTX [32]. Dyes were also investigated but not so extensively [32]. Negative charges in the porous crystal structure of zeolites make them suitable for adsorbing cationic dyes like methylene blue. However, cheap sorbents such as fly ash or zeolites are very often characterized by insufficient sorption capacities, so new methods of chitosan modification are searched for to increase them to make sorption most efficient.

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Many methods for improving sorption capacity of zeolites are known. The first example is the modification of zeolites by quaternary ammonium salts. As follows from the paper by Muir and Bajda [33] the more effective the modification, the longer the carbon chain of the surfactant is. Modification of the surfactants has also proved effective in the adsorption of dyes [1]. Motlagh Bahadory Esfahani and Faghihian [34] have proposed the modification by ethylenediamine and monoethanolamine for Pb(II) adsorption. There are also known works on sorption of dyes and heavy metal ions on chitosan modified zeolites [35–37]. Khanday et al. used oil palm ash for preparing zeolite A and then modified it by chitosan in order to remove methylene blue and acid blue 29 from wastewaters [38]. However, these processes are not carried out in a multi-component system but only in a one-component system. To this aim different kinds of zeolites can be applied [39,40].

Kyzas and Bikiaris presented an overview of modified chitosan adsorbents application [41]. Generally, chitosan is well investigated in order to improve the sorption capacity of many materials like magnetic Fe_3O_4 nanoparticles [42], active carbon [43] and for preparing new types of compounds. Magnetic chitosan with graphene oxide was prepared in order to remove cationic and anionic dyes. Maximum removal efficiency was found to be 89.9% for the cationic dye methyl violet and 69.5% for the anionic dye Alizarin yellow [44]. Karaer and Kaya studied adsorption of methylene blue and reactive blue4 on the magnetic chitosan/active charcoal composite. The adsorption percentage is dependent on temperature, for reactive blue4 it decreases from 75% to 47%, whereas for methylene blue it rises from 65% to 95% in the increasing temperature range from 25 to 45 °C, respectively [43]. Methylene blue removal was also studied by Cho et al. on the magnetic chitosan composite which was prepared by entrapping crosslinked chitosan and nano-magnetite on the clay surface [45].

In this study zeolite NaP1 which is characterized by two types of channel size and has a potential of sorption in water purification, was modified by CS to obtain an effective sorbent for metal ions sorption in the presence of methylene blue (MB).

Chitosan (CS) as a natural polymer is produced from deacetylation of chitin, extracted from the shells of crustaceans, skin fungal cell walls and insects. It is known as an ideal natural support for enzyme immobilization because of its special characteristics such as hydrophilicity, biocompatibility, biodegradability, non-toxicity as well as adsorption properties. Chitosan can be used as an adsorbent to remove heavy metals and dyes due to the presence of amino and hydroxyl groups, which can serve as the active sites [46]. Amino groups of chitosan can be protonated after strong anionic dyes adsorption by electrostatic attractions in the acidic media. Due to its large size, chitosan possesses negative charges only on the outside surface. Negative interior charges are even accessible to inorganic cationic pollutants [47].

A new type of inorganic–organic hybrid material based on the modified zeolite by chitosan (NaP1CS) was investigated by terms of its efficiency to remove MB and Cu(II) ions from wastewaters. For comparison different types of chitosan (low, medium and high molecular weight) were used and two different methods of modification were applied. The first one using glutaraldehyde and the second one epichlorohydrin and then they compared with raw fly ash. Simultaneous removal of both MB and heavy metal ions such as Cu(II), Fe(III), Mn(II), Zn(II) was also studied.

Experimental

Preparation of adsorbents

Coal fly ash (FA) was obtained from the Power Plant in Kozienice, Poland. The coal fly ash was converted into zeolite (NaP1) in the the sub-pilot scale process. Thus, there were applied the following conditions: 20 kg of fly ash, 12 kg of NaOH, 90 dm^3 of water, the reaction temperature: 353 K and the reaction time: 36 h which were described in papers [48,49]. Chitosan (deacetylation degree of chitosan flakes >75%, flakes) was obtained from Sigma Aldrich.

For the modification of NaP1 by chitosan, a chitosan solution was at first prepared by dissolving 2 g of chitosan in 0.2 dm^3 of 1% glycolic acid. The solution was being stirred using a magnetic stirrer for 24 h at 1000 rpm at room temperature to complete dissolution. Then 16 g of zeolite was added into the solution of chitosan and mixed for next 6 h under the same conditions. After this 1 M NaOH was added dropwise to the mixture to obtain pH 9. Subsequently, the solution was washed with distilled water to obtain neutral pH and then it was filtered. The obtained material (NaP1CS) was dried and ground in the mill.

Moreover, in order to compare the sorption capacity of the resulting modified zeolite NaP1CS, modifications were performed using three different kinds of chitosan: high molecular weight (CS H), medium molecular weight (CS M) and low molecular weight (CS L). Likewise, there were also applied two other methods of modifying zeolite with glutaraldehyde (NaP1CS GLU) and epichlorohydrin (NaP1CS EPI).

Preparation of adsorbates

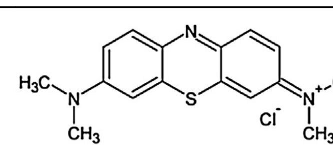
A typical basic, cationic dye, methylene blue (MB) was chosen because of its extensive applications. Its characteristics and structure are presented in Table 1.

A stock solution of 1000 mg dm^{-3} MB was prepared by diluting methylene blue (Chempur, Poland). The adsorption was performed by batch experiments. Before the measurement, a calibration curve was made up using the known concentrations of MB. The determination of dye concentration was made by means of the spectrophotometer Cary 60 (Agilent Technologies) by measuring absorbance at λ_{max} = 665 nm. Fig. 1 shows the evolution of absorbance vs. the concentration of MB.

The Cu(II) metal ions stock solution was prepared using $CuCl_2{\cdot}2H_2O$ (Avantor Performance Materials Poland S.A.) in distilled water. In order to obtain appropriate concentrations, the stock solution was diluted. The Cu(II) concentrations in solution were measured by an atomic adsorption spectrometer Spectr AA 240 FS (Varian, Australia). The appliance is equipped with a deuterium, cathode lamp for Cu. The Cu(II) detection occurs at 324.7 nm.

The stock solutions of Cu(II), Zn(II) Mn(II), Fe(III) and MB were prepared using $CuCl_2{\cdot}2H_2O$, $ZnCl_2$, $MnCl_2{\cdot}4H_2O$, $FeCl_3{\cdot}6H_2O$ and methylene blue (Avantor Performance Materials Poland S.A.). The concentrations of the above mention components were measured by the inductively coupled plasma optical emission spectrometry (ICP-OES).

Table 1 Q8
Characteristics of MB.

Parameter	Value
Chemical structure	
Systematic name	3,7-bis(Dimethylamino)-phenothiazin-5-ium chloride
Molecular formula	$C_{16}H_{18}ClN_3S$
Molecular weight, g/mol	319.85

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