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Optimizing adsorption of blue pigment from wastewater by nano-porous modified Na-bentonite using spectrophotometry based on response surface method

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ABSTRACT

This work highlighted the effective activation of bentonite paste to produce nano-porous powder for removal of cationic dye from wastewater. The effects of activation parameters such as soda and moisture contents, ageing time and temperature were analyzed using response surface methodology (RSM). The significance of independent variables and their interactions were tested by blending the obtained powders with wastewater and then the adsorption was evaluated, spectrophotometrically. The experiments were carried out by preparation of pastes according to response surface methodology and central composite design, which is the standard method, was used to evaluate the effects and interactions of four factors on the treatment efficiency. RSM was demonstrated as an appropriate approach for optimization of alkali activation. The optimal conditions obtained from the desirable responses were 5.0 wt% soda and 45.0 wt% moisture, respectively in which the powder activation was carried out at 150 °C. In order to well understand the role of nano-structured material on dye removal, the adsorbents were characterized through X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy and Brunauer–Emmett–Teller surface area measurement. Finally, the analysis clearly demonstrates that the dye removal onto prepared adsorbent is well fitted with Langmuir isotherm compared to the other isotherm models. The low cost of material and facile process support the further development for commercial application purpose.

1. Introduction

Colorant contaminants which are recognized easily in water have to be removed from wastewaters before discharging it into environment. Most of the industries such as textile, paper, plastic and food employ dyes to color the final products [1]. Approximately, 100 tonnes per year of dyes is discharged into water streams by textile industries [2]. The contamination of surface and ground water by dyes, even at low concentration, could impart the significant problems from both toxicological and esthetical points for human and leaving things. Most of dyes are stable to photo-degradation, bio-degradation and oxidation. Although, several physical or chemical processes are developed to recover wastewaters contaminated by dyes [3–5] however, these processes cannot effectively be used in industrial scale. Adsorption has been found to be highly efficient for removal of color in terms of cost, simplicity of process and insensitivity to toxic substances [1,6].

In all over the world, Na-bentonites are widely employed in foundries [7], drilling fluids [8], civil engineering [9] and wastewater recovery applications [1]. In the latter treatment process, the adsorption efficiency is of major importance. Natural bentonite is the most widely used as adsorbent because of excellent adsorption efficiency for removal of organic compounds [10]. Furthermore, low cost and easily available materials are of great importance for the removal of different dyes from aqueous solutions at different operating conditions. Physical, chemical and adsorption properties of clay-based adsorbents depend on the crystal structure of constituent minerals [11]. Adsorption properties of bentonites are a function of the montmorillonite content and nature and number of interlayer cations [12]. Recently, numerous approaches have been studied for the development of cheaper and effective bentonites. It is well known that the synthetic dyes cannot be efficiently removed by natural bentonite and the color removal of wastewaters by adsorption on inexpensive and efficient solids was considered as a simple and economical technique [13]. In this respect, the low-grade bentonites can be greatly improved by activation [14]. This method has been common practice in the bentonite industry for many years. In order to remove impurities and various exchangeable cations

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from smectite and produce a homogeneous and well-defined materials for use as adsorbent, different treatments have been developed, most frequently with inorganic agents like alkali [15,16] and acidic solutions [17,18]. Important physical changes in alkali-activated smectite are the increase of the specific surface area, average pore volume, depending on alkali strength, time and temperature of reaction environment [19]. A large increase of pore volume and a broadening of pore size distribution in the nano-scale indicate that higher alkali concentrations cause structural changes and partial decomposition of montmorillonite [20,21]. Activation proceeds with partial dissolution of smectite and is characterized by an initial replacement of the interlayer cations by Na^+, followed by dissolution of octahedral sheets and subsequent release of the structural cations [22]. Octahedral cations such as Fe^{2+}, Fe^{3+}, and Mg^{2+} can be depleted by treating the clay minerals with alkali agent [8,21].

Despite numerous studies about purification of wastewaters by bentonite [1,22,23], no definite relationship exists between the performance of clay and alkali activation factors in comparing to the properties of original clay. It should be note that the selected clay has to be specifically activated and tested for its performance. In this study, statistically designed experiments were performed to investigate the performance of an Iranian alkali-activated bentonite in adsorption of cationic dye. Many bentonites mined in Shahrood region of Iran are appropriate for application in wastewater treatment. The low sodium content with predominantly calcium and magnesium exchangeable cations need alkali activation to employ in recovery process. The removal efficiency was chosen as process response and the role of four relevant factors, such as paste moisture, soda concentration, ageing time and activation temperature were evaluated on removal efficiency. The work is in progress to evaluate the possibility of alkali-activated bentonite paste for wastewater pollution management. The aim of the present study was to determine the optimum conditions for the removal of a cationic dye, methylene blue, from simulated wastewater. The article also represents the textural characteristics of soda-activated bentonite.

2. Materials and Methods

2.1. Materials

Natural bentonite has been collected from Shahrood region in Iran. The collected bentonite grinded to powder (<75 μm) with a laboratory jar mill and stored in a polyethylene bag for subsequent use in activation. Sodium carbonate (1.06392.1000, Merck, Germany) and methylene blue (6045, Merck, Germany) were used as received. The water distilled in inert atmosphere was used for soda solution and paste preparations.

2.2. Alkali Treatments of Bentonite

One part of obtained bentonite was kept for characterization and the rest was submitted to alkali-activation. The treatment of paste was carried out by varying soda dose, moisture content, ageing time and temperature. The influence of soda dose (1.0–5.0 wt% per dry mass of powder), moisture content (30–45 wt% per dry mass of bentonite) ageing time (0–72 h) and temperature (100–150 °C) were evaluated during the present study.

Central composite design (CCD) is widely used in statistical evaluation to obtain empirical models between the process response and operational factors. The experiments were designed to estimate the main effects, as well as the interactions, where each variable was investigated at three levels, low, medium and high values. In the planning and analysis of the experiments, coded values are usually applied instead of the absolute values of the variables by Minitab software (Version 16, USA). The studies based on CCD were performed by evaluating the response of adsorption efficiency (R) as a function of operational variables: soda dose (X_1) moisture content (X_2) and ageing time (X_3) and temperature (X_4). The mentioned method was applied to (i) investigate the effect of parameters, (ii) create model between the variables and (iii) optimize the synthesis condition. In order to study the combined effect of these factors, experiments were performed at different conditions as reported in Table 1.

For alkali treatments, the activation agents were prepared by water and soda contents reported in Table 1 then, the 500 g of bentonite powder was mixed with alkali solutions at room temperature and mixed for 1 h. The pastes were left for different ageing times in plastic bag to obtain the materials with homogenous humidity. After this step, the pastes were heated at different temperatures in an electrical laboratory oven for 24 h. The solids were washed with distilled water until to achieve the suspension free sodium cations and dried at 50 °C.

The chemical formula of used methylene blue (MB) is $C_{16}H_{18}ClN_3S$, corresponding molecular weight of 319.85 $g \cdot mol^{-1}$. This dye is hydrolyzed as $C_{16}H_{18}N_3S^+$, in the aqueous solution which is a large polar organic cation. Hence, the adsorption properties of prepared powders can be determined by the amount of removed dye. The methylene blue removal efficiency indicates adsorption capacity of a treated bentonite for molecules having similar dimensions compared to MB. This method is a rapid technique for evaluation of activation process. The removal efficiency of standard MB decolorized solution by per gram of powder can be used for determination optimum activation conditions. The higher efficiency indicates the higher adsorption capacity of activated powder. The methylene blue solution was prepared by blend of dye with deionized water, 20–100 $mg \cdot l^{-1}$, and then the powders, 25 mg, were added to prepared solution, 100 ml. The suspensions were magnetically stirred in different residence times to achieve the adsorption-desorption equilibrium. During adsorption, the powders were kept in suspension state by a magnetic stirrer. The samples for UV analyses were extracted through pipette and centrifuged at 3500 rpm, immediately. The absorbance pattern of suspensions and initial solution were recorded by a UV–vis spectrophotometer (Jenway, 6705, UK) in the visible light wavelength, 200–800 nm. The final MB concentration in the

Table 1
Experimental design for evaluation of alkali activation of natural bentonite.

Composition code	Na_2CO_3 (wt%)	Moisture (wt%)	Ageing time (h)	Temperature (°C)
C1	1.0	30.0	0	100
C2	5.0	30.0	0	100
C3	1.0	45.0	0	100
C4	5.0	45.0	0	100
C5	1.0	30.0	0	150
C6	5.0	30.0	0	150
C7	1.0	45.0	0	150
C8	5.0	45.0	0	150
C9	1.0	30.0	72	100
C10	5.0	30.0	72	100
C11	1.0	45.0	72	100
C12	5.0	45.0	72	100
C13	1.0	30.0	72	150
C14	5.0	30.0	72	150
C15	1.0	45.0	72	150
C16	5.0	45.0	72	150
C17	1.0	37.5	36	125
C18	5.0	37.5	36	125
C19	3.0	30.0	36	125
C20	3.0	45.0	36	125
C21	3.0	37.5	36	100
C22	3.0	37.5	36	150
C23	3.0	37.5	0	125
C24	3.0	37.5	72	125
C25	3.0	37.5	36	125
C26	3.0	37.5	36	125
C27	3.0	37.5	36	125
C28	3.0	37.5	36	125
C29	3.0	37.5	36	125
C30	3.0	37.5	36	125
C31	3.0	37.5	36	125