Journal of Industrial and Engineering Chemistry 25 (2015) 229–238

Contents lists available at ScienceDirect

Journal of Industrial and Engineering Chemistry

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

Influence of adsorption parameters of basic red dye 46 by the rough and treated Algerian natural phosphates

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ARTICLE INFO

Article history:
Received 23 June 2014
Received in revised form 28 October 2014
Accepted 30 October 2014
Available online 6 November 2014

Keywords:
Phosphate rock
Adsorption
Basic red dye 46
Treatment
Adsorption isotherm
Kinetic parameters

ABSTRACT

The paper reports on the adsorption behavior of basic red dye 46 from aqueous solution onto rough and treated Algerian natural phosphates. Adsorption tests were realized in static mode on natural rock phosphate and treated samples by sifting, chemical or thermal way. The adsorption process was evaluated as a function of various operating parameters such as contact time, pH of the medium, temperature, concentration, agitation speed and adsorbent mass. The adsorption ability depends mainly on the nature of mineralogical species as well as on the smoothness of the grains. It was found that the dye has more affinity for the carbonate-rich than for the phosphate-rich material. The amount of the dye adsorbed increases with the mass of adsorbent. The adsorption process was pH-dependent with a high adsorption capacity at pH 8. The chemical and thermal treatments performed on different phosphate samples have affected negatively their adsorption capacity of the dye used. The experimental isotherm data were analyzed using the Langmuir, Freundlich and Temkin models. The equilibrium data fit well the Langmuir isotherm. The calculations of the maximum amounts (q_m) obtained from this model have shown that it is the fine fraction (T) which adsorbs the highest amount (28.5 mg g^{-1}), followed by the coarse fraction (C) (15.62 mg g^{-1}) and raw phosphate (RP) (14.7 mg g^{-1}). The best results were obtained for dye concentration of 15 mg g^{-1}, adsorbent mass of 3 g L^{-1}, agitation speed of 300 trs min^{-1}, and pH 8 at 20 °C. The experimental data were analyzed using three kinetic models: the pseudo first order, pseudo second order and intraparticle diffusion models. The linear regression, standard statistics of root mean squared error (RMSE) was carried out to support the best fit kinetic models. Based on the low RMSE values, the pseudo second order model is the one that best describes the adsorption of basic red dye 46 on phosphates. The results obtained in this study suggest that Algerian natural phosphates may be used as an efficient and low cost sorbent material for organic pollutants, and thus represent a promising alternative for eliminating dyes from industrial wastewaters.

Introduction

For many years, the effluents containing pollutants are increasing in natural streams due to industrialization. The main contaminants found in wastewater include biodegradable, volatile and recalcitrant organic compounds, toxic metals, suspended solids, pathogens, parasites and dyes [1–3]. The water quality is degraded by the presence in the effluents of these toxic organic and inorganic substances. The dyes used in textile industry count among these substances. Indeed, many industries such as textiles, paper and plastics use dyes to adorn their products, consuming substantial quantities of water. Given their good solubility, synthetic dyes are common water pollutants and are frequently found in trace quantities in industrial wastewater. Recent estimates indicate that approximately 12% of dyes produced disappear during commercial transactions and 20% for the operations of the industrial process of coloring [4]. The quantity of dye lost is found most often in the atmosphere or in the marine environment. Some dyes cause serious problems to the environment because of their stability and low biodegradability. Moreover, many of these dyes can be degraded to carcinogenic and toxic products and thus pose a serious hazard to aquatic living organisms [2,5,6]. The elimination of these pollutants

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http://dx.doi.org/10.1016/j.jiec.2014.10.039
1226-086X/

from wastewater is thus an important environmental issue related to the ongoing development of industrial activities [7,8]. Due to increasingly stringent restrictions on the organic content of industrial effluents, it is mandatory to eliminate dyes from wastewater before it is discharged [2,9,10].

A study carried out on the stepping of the DL50 with chemical and tinctorial classifications of the dyes showed that among organic synthetic dyes, the diazo and the cationic dyes are the most toxic [11]. Indeed, some azo dyes, their precursors and a number of their reaction products are carcinogenic [12]. These dyes are recalcitrant to microbial degradation, because they contain substitution groups such as azo, nitro or sulpho groups [13]. The carcinogenic effects of azo compounds are induced by their amine derivatives. Indeed, the azo bond is the most labile portion of these molecules and can easily break under enzymatic action to turn into carcinogenic amino compounds. The toxicity of azo is increased by the presence of substituent on the aromatic nucleus in particular the nitro ($-NO_2$) and halogen (especially Cl) groups. Therefore, the treatment of the effluent containing these dyes is important for the protection of natural waters.

Several physical or chemical processes are used to treat water charged with dyes. These include flocculation, precipitation, ion exchange, membrane filtration, electrochemical destruction, irradiation and ozonation [1,5]. However, these processes are often expensive and lead to the generation of sludge or to the formation of byproducts [5]. For this purpose, adsorption is one of the most effective methods to remove dyes from wastewater [2,3,5]. Activated carbon is the most widely used adsorbent for removal of dyes, but it is too expensive and difficult to regenerate [1,2,5].

Over the last years, there has been a continuous search for effective and inexpensive adsorbent materials to activated carbon. The removal of colored organic molecules by adsorption onto low cost materials such as natural materials, organic adsorbents, and waste materials from industry and agriculture has been reported by several authors. Some of these sorbents include clay minerals (bentonite, kaolinite), zeolites, silica, agricultural wastes (bagasse pith, maize cob, rice husk, coconut shell), industrial waste products, biosorbents (chitosan, peat, biomass) and others (starch, cyclodextrins, cotton) [2,3].

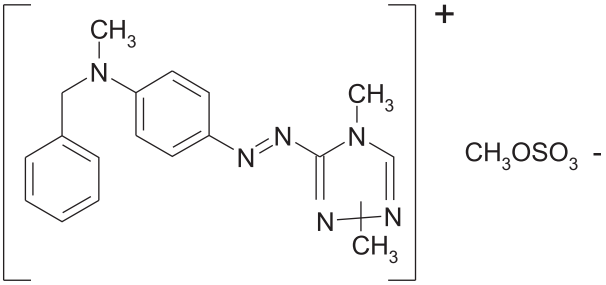
Phosphate rock (PR) is an abundant ore and represents the basic raw material for the phosphatic fertilizer industry with an annual consumption approaching 150 million tons [14]. In the last years, many studies have demonstrated the use of phosphate ore, both natural and activated, as alternative low cost adsorbent. Most of these studies focused on adsorption of heavy metal ions from aqueous solutions [15–21]. To the best of our knowledge, there has been only a few studies on the removal of organic pollutants [22–24]. Since Algeria has significant reserves of phosphates mainly in the Djebel Onk, located 100 km from Tebessa, there is a great potential for its utilization for waste treatment.

The present work focused on the study of the effect of thermal and chemical treatments of phosphates from Djebel Onk on the retention capacity of a basic dye, Basic red, BR46. The experimental data was analyzed using isotherm models namely, Langmuir, Freundlich and Temkin. The effect of pH, adsorbent amount and initial dye concentration was investigated. Kinetic investigation was performed to determine the efficiency of BR46 adsorption onto Djebel Onk phosphates using pseudo-first order, pseudo-second order, and intraparticle diffusion models.

Materials and methods

Materials

The basic dye used as adsorbate in the present study is the cationic Basic Red 46 (BR46) was purchased from Sigma-Aldrich. The BR46 molecular structure is displayed in Scheme 1.



Scheme 1. Chemical structure of Basic red 46 (BR46).

Methods

Preparation of phosphate adsorbents

The crude phosphate rock (PR) comes from the career of Djebel Onk with a particle size ranging from 1000 to 1200 mm. The PR underwent mechanical treatment to release the mineralogical components and to defining the interval of suitable granulometry. It consists of crushing and sieving with a series of sieves of 50, 250 and 500 μm. Four size fractions are obtained: thin < 50 μm (T), medium thin 50–250 μm (MT), medium coarse 250–500 μm (MC) and coarse > 500 μm (C). Their mass yields calculated after sieving are, respectively 4.25, 44.20, 40.13 and 11.42 (%). The raw sample (PR) of 0 to 4 mm in size was subjected to chemical treatments (PC) in 1 M nitric and 1 M sulphuric acid (1 g/500 mL) at 80 °C during 1 h under magnetic stirring.

The sample PR was subjected to thermal activation (PT) under nitrogen (150 mL h^{-1}) at different temperatures (400, 600 or 900 °C) at 5 °C min^{-1} for 2 h. Thus a series of 7 samples (T, MT, MC, C, PR, PT and PC), characterized beforehand is intended for the tests of adsorption of the basic red dye.

Adsorption experiments

The adsorption tests were performed for the system adsorbate (basic red dye 46)-adsorbent (sample series of phosphates) to define the optimal operating conditions of the main parameters related to the adsorption process. The adsorption tests were carried out in a batch reactor with suspensions of various adsorbent solid/liquid adsorbate ratios under magnetic agitation. The reactor was immersed in a water bath to stabilize the temperature. Aliquots (6 mL) were taken out of the solution for different time intervals, centrifuged at a speed of 6000 trs min^{-1} during 4 min and then analyzed using UV–vis spectrophotometry.

The residual concentrations of the dye are calculated by using the equation obtained starting from the calibration line representing the optical density according to the concentration. The quantity of the dye q_t (mg) adsorbed per unit of mass (g) of the adsorbent at the moment t is calculated according to the following relation:

$$q_t = \frac{(C_i - C_t)}{m} \times V \times 10^{-3} \qquad (1)$$

where q_t (mg g^{-1}) is the quantity of the dye adsorbed per unit of mass of adsorbent, C_i (mg L^{-1}) is the initial concentration of dye, C_t (mg L^{-1}) is the residual concentration of dye at the time t, V (mL) is the total volume of the solution, and m (g) is the mass of the adsorbent.

Effect of pH solution on dye adsorption. To study the effect of pH solution on dye adsorption, 0.5 g of adsorbent was agitated for 12 h with 500 mL of dye solution (dye concentration = 20 mg L^{-1}) at 20 °C. The experiment was conducted at different pH values from