Journal of the Taiwan Institute of Chemical Engineers 45 (2014) 1792–1802

Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

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

Equilibrium and kinetics studies for the adsorption of Basic Red 46 on nickel oxide nanoparticles-modified diatomite in aqueous solutions

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ARTICLE INFO

Article history:
Received 7 October 2013
Received in revised form 27 January 2014
Accepted 25 February 2014
Available online 26 March 2014

Keywords:
Adsorption
Diatomite
Nickel oxide nanoparticles
Isotherm
Kinetics
Basic Red 46

ABSTRACT

The nickel oxide nanoparticles-modified diatomite (NONMD) as a low-cost adsorbent was investigated for the removal of C.I. Basic Red 46 (BR46) from aqueous solution. Various physico-chemical parameters were studied such as solution pH, adsorbent dosage, adsorbent size, initial dye concentration, temperature, contact time and salt (NaCl, $NaHCO_3$ and Na_2SO_4). The mean size and the surface morphology of the adsorbent were characterized by SEM, BET, FTIR, XRD, EDX and elemental analysis. The maximum percentage of BR46 dye removal from aqueous solution was 99.48% (124.35 mg/g) when 0.005 g of NONMD was applied at pH 8, temperature 25 ± 1 °C, agitation speed of 200 rpm, initial dye concentration of 25 mg/L, and a mixing time of 60 min. Furthermore, under the same conditions, the maximum adsorption of dye on raw diatomite was 84.49% (105.61 mg/g). The experimental data showed that the adsorption of dye on raw diatomite follows the Langmuir model, but its adsorption on modified diatomite followed the BET model. The kinetics results were found to conform well to pseudo-second order kinetics model with good correlation. Thus, this study demonstrated that the NONMD could be used as a low-cost natural adsorbent for removal of BR46 from aqueous solution.

1. Introduction

Synthetic dyes have increasingly been used in the textile and dyeing industries because of their ease and cost-effectiveness in synthesis as well as high stability to light, temperature, detergent and microbial attack which can lead to the discharge of highly polluted effluents [1]. More than 10,000 chemically different dyes are being manufactured, and the world dyestuff and dye intermediates production are estimated to be around 7×10^8 kg per annum [2,3]. Colour as one of the effluent characteristics affects the nature of the water, inhibits sunlight penetration into the stream and reduces the photosynthetic activity [4,5]. Moreover, some dyes are carcinogenic and mutagenic which are generally stable to biological degradation [4,6]. Hence, their removal from aqueous solution, before discharging them into the environment is extremely important [7]. Therefore, the development of efficient, low-cost and environmentally friendly technologies to reduce dye content in wastewater is extremely necessary.

New economical, locally available and highly effective biosorbents are still under development. Furthermore, many treatment systems have been proposed for the removal of synthetic dyes from aqueous solutions. Coagulation [8], flocculation [9], photocatalytic degradation [10–12], membrane filtration [13], microbiological decomposition [14], electrochemical oxidation [15], fungus biosorbent [16] and adsorption [17–25] are the most commonly used methods for removing dyes from waste and effluent systems. The microbiological, photocatalytic and electrochemical decomposition procedures are not efficient because many dyes cannot be easily decomposed [15]. Adsorption is considered to be particularly competitive, economically efficient and cost-effective process for the removal of dyes, heavy metals and other organic and inorganic hazardous impurities from aqueous solutions. Although activated carbon is the most efficient and popular adsorbent and has been used with great success, the high cost of activated carbon sometimes restricts its application with regard to dye removal [26–33]. Recently, many researchers have attempted to use alternative low-cost sorbents to replace

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http://dx.doi.org/10.1016/j.jtice.2014.02.020
1876-1070/

Symbols used

C_0	[mg/L] initial concentration of BR46
C_e	[mg/L] residual concentration at equilibrium
C_s	[mg/L] saturation concentration of BR46
$K_{1,ad}$	[1/min] rate constant of Pseudo-first-order
$K_{2,ad}$	[1/min] rate constant of Pseudo-second-order
k_F	[−] Freundlich constant
k_L	[−] Langmuir constant
k_b	[−] BET constant
m	[g] mass of adsorbent used
n	[−] parameter indicating the intensity of adsorption
q_e	[mg/g] residual amount adsorbed at equilibrium
$q_{e,exp}$	[mg/g] experimental residual amount adsorbed at equilibrium
q_p	[mg/g] predicted sorption capacity
q_o	[mg/g] observed sorption capacity
Qo	[mg/g] maximum sorption capacity
r^2	or R^2[−] correlative coefficient for all models
T	[K] absolute temperature
t	[min] contact time
V	[L] volume of BR46 solution

with activated carbons. Some of these alternative biosorbents are banana pith [34], vine [35], eucalyptus bark [36], neem leaf powder [37], Luffa cylindrica fiber [38], sunflower seed hull [39], soy meal hull [40], hazelnut shell [41] and neem sawdust [17]. Nevertheless, the adsorption capacities of most of the above adsorbents were still limited.

BR46 was selected as a model synthetic azo dye due to its extensive use in the textile industry. Azo dyes are a class of dyes characterized by the presence of the azo group. Due to high usage of these dyes, large volumes of coloured effluents are discharged into the environmental and water resources. The release of azo dyes into the environment is of concern due to their toxicity, mutagenicity and carcinogenicity [42]. Hence, removal of azo dyes from wastewater is a major environmental issue.

Diatomite ($SiO_2 \cdot nH_2O$) is made up principally from the skeletons of aquatic plants called diatom that usually is a pale-coloured, soft, lightweight siliceous sedimentary rock [43]. Diatomite contains a wide variety of shape and sized diatoms, typically 10–200 μm, in a structure including up to 80–90% pore spaces [42,43]. Diatomite's extremely porous structure, low density and high surface area make it suitable as an adsorbent for the removal of organic and inorganic chemicals. Diatomite is found in abundance in Iran. Several studies have been carried out on the use of diatomite as an adsorbent for removing some contaminants such as heavy metals [44], basic dye (Methylene blue) [17], basic and reactive dyes (Methylene blue, reactive black, reactive yellow) [45] and some textile dyes (Sif Blau BRF, Everzol Brill Red 3BS, Int Yellow 5GF) [45]. Furthermore, the unique properties of diatomite caused its applications as filtration media in a number of industries [46]. Diatomite is approximately 500 times cheaper than commercial activated carbon [46] and has the potential of being successfully used as a cost-effective alternative to activated carbon.

In the present investigation, the utilization possibility of nickel oxide nanoparticles-modified diatomite (NONMD) as an adsorbent for the removal of BR46 dye from an aqueous medium has been studied. Nickel metal can be a good choice for degrading the dyes and other pollutants from aqueous solutions [47]. Table 1 shows the comparison between maximum monolayer sorption capacities (mg/g) of different adsorbents for the adsorption of BR46. As it is evident, the maximum adsorption capacity of used adsorbents (in this study) is more than others. The equilibrium and kinetics study are investigated and the effects of various process parameters such as pH, contact time, initial dye concentration, calcinations and sorbent dosage on the adsorption process were examined. Equilibrium data are attempted by various adsorption isotherms including Langmuir, Freundlich and Brunauer–Emmett–Teller (BET) isotherms in order to select an appropriate isotherm model. Moreover, a kinetics study of the adsorption process is also considered to describe the rate of sorption.

Table 1
The comparison between different kinds of adsorbent for the adsorption of BR46.

Adsorbent	Maximum adsorption capacity (mg/g)	References
Raw Diatomite	83.67	In this work
NONMD	98.16	In this work
Pine tree leaves	71.94	[48]
Princess tree leaf	43.10	[49]
Moroccan clay	54	[50]
Boron industry waste	74.73	[51]
Gypsum	39.17	[52]

2. Experimental procedure

2.1. Preparation of adsorbent

Diatomite sample was obtained from Tabriz, Iran. The sample was washed several times with distilled water and HCl (1 M) to remove fines and other adhered impurities and to achieve neutralization. Moreover, in the acidic conditions nickel nanoparticles can put better on the surface of diatomite. The sample was finally filtered, dried at 60 °C for 24 h, and stored in closed containers for further use. The nanoparticles of NiO were synthesized by using following reaction:

$$NiSO_4 + 2NaOH \rightarrow Ni(OH)_2 + Na_2SO_4 \quad (1)$$

The nanoparticles of NiO were synthesized by adding $NiSO_4$ and NaOH (1 M) to the solution. It means that 2.0 g of previously dried diatomite (raw diatomite) were added to 25 ml of Nickel hydroxide (1 M) and the sample was stirred in the agitation speed of 200 rpm for 1 h. The new material (mixture of Ni and diatomite) was sequentially separated by filtration that the product of this reaction was $Ni(OH)_2$. The final product that was mixture of raw diatomite and $Ni(OH)_2$ had to been put in the furnace, by that $Ni(OH)_2$ changed to NiO and mixed by raw diatomite. The calcination process was carried out by placing NONMD sample in the furnace at 250 °C for 4.5 h. The sample was then allowed to cool in a desiccator. The modified sample was used to examine the effect of silanol groups and the role of pore size distribution on the adsorption process. It is clear from the FT-IR spectra and EDX analysis, the raise of metal oxide content at the modified diatomite can be the main reason for increasing the adsorption capacity. In industries, there are many heavy metals contaminated materials. Recovery of materials and clean up these contaminations is very difficult and expensive [48–52]. Our investigation is a key to change a poisonous industrial waste to a valuable by product.

2.2. Reagents and solutions

BR46 dye was obtained from Ciba Ltd. and was used without further purification. The chemical structure of this dye is shown in