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Evaluation of physicochemical methods in enhancing the adsorption performance of natural zeolite as low-cost adsorbent of methylene blue dye from wastewater

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A B S T R A C T

The main aim of this study was to evaluate different facile and cost-effective physicochemical methods in enhancing the adsorption capacity of natural zeolite and subsequently demonstrate the removal of methylene blue (MB). Four different physicochemical methods, namely: acid treatment (AT), base treatment (BT), combined acid-thermal (ATT) and base-thermal treatments (BTT) were investigated. This was followed by understanding the impact of the physicochemical methods on the surface characteristics and properties of modified zeolite through advanced characterisations using field emission-scanning electron microscopy, Fourier-transformed infrared spectroscopy and Brunauer–Emmett–Teller specific surface area and porosity measurements. Batch adsorption studies were carried out using the modified zeolite adsorbents, in order to evaluate the highest removal efficiency of MB under varying adsorption conditions of: pH, initial MB concentration and modified zeolite loading. Results showed that both the physicochemical methods of AT (using 0.4 M HCl) and BT (using 4.0 M NaOH) are able to enhance the adsorption capacity of natural zeolite from 41% to 98.8% and 52.2%, respectively. Surprisingly, the combined physicochemical methods of ATT and BTT showed a reduction in adsorption performance when benchmarked to AT and BT alone. The adsorption data were analysed and modelled using Langmuir, Freundlich, Redlich-Peterson and Koble-Corrigan isotherm models, also the adsorption kinetics were evaluated using pseudo-first and pseudo-second order models. It was found that the adsorption data and kinetics were best represented using the Koble-Corrigan and pseudo-second order models. The improvements yielded through both the AT and BT modified zeolites were found to be promising and have the potential to be used as low-cost adsorbents for wastewater treatment.

1. Introduction

Wastewater is a by-product that consists of a mixture of solid and liquid after the usage of water from households, industries and commercial establishments. Typically wastewater is no longer serving a useful purpose compared to high-quality mains water usage, and may contain significant amount of pollutants and microbes (Chong et al., 2010, 2011a) unless it is properly treated (Malik et al., 2015). If wastewater remains untreated and is discharged directly into the environment, water pollutants can enter the natural water systems and cause negative impacts towards the environment and public health (Chong et al., 2011b). Various industries such as textiles, cosmetics, plastics and paper industries are known to heavily use synthetic dyes in their production to impart colour to their finished products. A significant amount of dyes are commonly present in the effluents of these industries and need to be treated before being discharged into the environment (Reddy et al., 2012). In the absence of proper treatment methods, synthetic dyes which have aromatic structures may pose a threat to aquatic life due to their non-biodegradable nature,

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and some are even carcinogenic (Gupta and Suha, 2009). There can also be significant secondary effects of dyes, such as hindering sunlight from penetrating into the water bodies and thus, depriving aquatic life of vital light-sensitive chemical reactions (Robinson et al., 2001; Zhou et al., 2014). Thus, the proper treatment and removal of synthetic dyes from wastewater is essential before the remaining effluent is discharged into the environmental water streams.

At present, there are various wastewater treatment methods available for the proper treatment and removal of synthetic dyes from wastewater sources, such as anaerobic digestion, membrane separation, adsorption (Vimonses et al., 2010; Toor et al., 2015), sedimentation, filtration and photocatalysis (Hameed et al., 2007; Chong et al., 2015). Anaerobic digestion (AD) occurs in the absence of oxygen, whereby large amounts of organic matter are broken down into fundamentally carbon dioxide. AD demands low energy input while having a minimal sludge formation and nutrients demand for its microbial processes. Although AD is an attractive method due to the low energy requirement, the presence of inhibitory substances (i.e., phenolic compounds) are toxic and hinder the activities of vital constituents of the AD process, such as methanogenic bacteria (Jiménez et al., 2003). On the other hand, the membrane bioreactor (MBR) is another widely used wastewater treatment method for the removal of synthetic dyes from wastewater sources. This is due to the high reliability of MBR operation, which is independent of solid and hydraulic loads, low space requirements, as well as producing high-quality treated effluents (Laera et al., 2011). However, it is known that MBR is subject to high operational cost due to the cross-flow along the membrane and required pressure gradient for optimum removal efficiency (Busch et al., 2007). Thus far, adsorption using activated carbon (AC) is the most common and effective wastewater treatment method (Akgül and Karabakan, 2011). This is due to the large specific surface area to volume ratio of AC. However, the effective adsorption using AC comes at the expense of material, treatment and regeneration costs (Gupta and Suha, 2009).

Previously, various alternative adsorbents such as rice husk ash (Liu et al., 2012), sawdust (Shukla et al., 2002), industrial waste (Ali et al., 2012; Crini, 2006), and natural clays (Yan et al., 2009; Cantuaria et al., 2016) have been investigated for their potential applications in the removal of synthetic dyes from wastewater sources. Among all, natural clays have proven to have a high potential to be used as adsorbents in wastewater treatment due to the fact that they are naturally abundant and environmental friendly. Zeolite is a type of naturally abundant clay adsorbent that has a high potential to be used as a low-cost and alternative to AC adsorbent in wastewater treatment. Typically, zeolite has a relatively lower specific surface area (SSA) but pore structure of molecular dimensions, high thermal stability that permits regenerative uses and the ability to host strong Bronsted and Lewis acid sites compared to AC adsorbent (Tarach et al., 2014). However, the adsorption performance of natural zeolite in the removal of synthetic dyes from wastewater sources is limited by its micropore structure as the dye molecules are usually bulky and measure over 1 nm in size (Yan et al., 2009). Previously, Christensen et al. (2007) reported that the adsorption of dyes on natural zeolite is highly restricted by its diffusional limitations. In order to enhance the adsorption performance of natural zeolite, previous studies have attempted various modification approaches such as using acid pre-treatment, surfactant modification and thermal activation on natural zeolite (Li et al., 2011; Le Van Mao et al., 1997). All these studies have shown considerably positive results in terms of enhancing the adsorption performance of natural zeolite.

The main aim of this study was to evaluate different facile and cost-effective physicochemical methods in enhancing the adsorption capacity of natural zeolite and subsequently demonstrating these utilising removals of methylene blue (MB). Four different physicochemical methods, namely: acid treatment (AT), base treatment (BT), combined acid-thermal (ATT) and base-thermal treatments (BTT) were investigated. This was followed by investigating the impact of the physicochemical methods on the surface characteristics and properties of modified zeolite through advanced characterisations using field emission-scanning electron microscopy (FE-SEM), Fourier-transformed infrared spectroscopy (FTIR) and Brunauer–Emmett–Teller (BET) specific surface area and porosity measurements. A batch adsorption study was carried out using the modified zeolite adsorbents, in order to evaluate for the highest removal efficiency of MB under varying adsorption conditions of: pH, initial MB concentration and modified zeolite loading. The adsorption data were analysed and modelled using Langmuir, Freundlich, Redlich-Peterson and Koble-Corrigan isotherm models, in addition adsorption kinetics were evaluated using pseudo-first and pseudo-second order models. Through this study, it is anticipated that a facile and cost-effective physicochemical method can be determined to enhance the adsorption performance of natural zeolite in promoting it as a low-cost and alternative adsorbent for wastewater treatment.

2. Materials and methods

2.1. Materials

Natural zeolite (particle size < 45 μm, catalogue no.: 1318-02-1, Sigma–Aldrich) was subjected to four different physicochemical modification methods, as proposed in this study. MB (catalogue no.: 440167-09087, HmbG Chemicals) was prepared to the experimental concentrations by dissolving the solid dye powder in aliquot volume of deionised water. Hydrochloric acid (HCl) 37% (catalogue no.: H8040-1-2500, Friendemann Schmidt) and sodium hydroxide (NaOH) pellets (catalogue no: S5158-1-1000, Friendemann Schmidt) were prepared accordingly in deionised water, as the pH corrective chemicals.

MB is a cationic dye and is also classified as a heterocyclic aromatic chemical compound (Jamil et al., 2011). Supplementary Fig. 1 shows the molecular structure of MB, with the molecular formula of $C_{16}H_{18}N_3SCl$. Despite the variety of applications of MB in the biology and chemistry fields, it has been reported that the presence of MB could cause harm to human health and the environment (Valdés et al., 2012; Wang et al., 2005). Thus, the removal of MB from wastewater sources before environmental discharge is of paramount importance to ensure a healthy ecosystem. In this study, MB was chosen as the surrogate indicator for treatment efficiency due to its positively charged surface, which could readily be drawn towards the anionic layers of zeolite. This made MB suitable for the evaluation of adsorption performance in modified zeolites (Gürses et al., 2006).

2.2. Physicochemical methods for modification of natural zeolite

Different aqueous HCl solutions with concentrations of 0.05 M, 0.1 M, 0.3 M, 0.4 M and 0.5 M were prepared. In order to carry out the AT method, natural zeolite was mixed with the acid solution in the ratio of 1:10 (g zeolite:mL acid). A magnetic stirrer was used to mix the sample mixture solution for 20 min at 300 rpm. The AT was terminated by adding a large amount of deionised water. The sample mixture solution was then filtered using a vacuum filtration pump set. The filtrate samples were washed repeatedly with deionised water until neutral pH was obtained. Finally, the filter cake was left to dry at 60 °C for 12 h before being stored in a desiccator.

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