BINARY MIXTURE COMPOSITE ADSORBENTS FROM CRUSHED COCKLESHELLS AND NATURAL ZEOLITES FOR RIVER WATER TREATMENT

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Specially dedicated to

my husband

Mohd Fadhli Bin Sa’adon

and my parents

Allahyarhamah Siti Masriah binti Ahmad

and

Allahyarham Moideen bin C.Saidaly

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ABSTRACT

Development and maintenance of water treatment systems are extremely costly thus a cost-effective and environmental-friendly adsorbent is considered to be an attractive solution and was evaluated comprehensively in this research. The aim of this study was to assess the potential usage of dual-phase composite adsorbents from the mixtures of cockle shells and natural zeolites. This includes two important factors for dual-phase adsorbent development: 1) finding the optimal amount and exhaustive time of cockle shells and natural zeolites required in the jar test experiments; 2) determining the optimal mixture ratio of cockle shells relative to natural zeolites in the column experiments. River water samples were collected from the Desa Bakti River, Universiti Teknologi Malaysia where the total removal efficiencies of chemical oxygen demand (COD), biochemical oxygen demand (BOD), total phosphorus (TP) and total nitrogen (TN) were monitored. Firstly, jar test experiments were carried out. Based on the experiments, the optimal amount was found to be 3 gL^{-1} for cockle shells and natural zeolites. The exhaustive time for both adsorbents was at day 3. Next, a series of mix ratios within the search area were selected using the Design Expert software. The D-optimal mixture (DMD) method was chosen from the software and an input obtained from the jar test experiment was used in order to generate a list of random mixture ratios. All generated mixture ratios were validated according to the sequence in the Easy Care Pipe System (ECPS). From the analysis provided by the software, the optimal mixture ratio was found to consist of 25% of natural zeolites and 75% of the cockle shells. The targeted values of the total removal were then compared with the experimental data. The percentage removal of BOD, COD, TP and TN were found to be 53.24%, 74.29%, 72.59% and 81.98% respectively. The adsorption mechanism was analytically explained using the adsorption isotherm to complement the results obtained from the jar and column tests. It was found that the cockle shells and natural zeolites in jar test experiments were best-fitted by the Langmuir isotherm. The dual-phase composite adsorbent consisting of cockle shells and natural zeolites in the column test was best fitted with the Yoon-Nelson and Thomas model.

ABSTRAK

Pembangunan dan penyelenggaraan sistem rawatan air adalah sangat mahal oleh itu penjerap kos efektif dan mesra alam sekitar telah dijadikan sebagai satu penyelesaian yang menarik dan dinilai dalam kajian penyelidikan ini. Tujuan kajian ini adalah untuk menilai penggunaan potensi penjerap komposit dua fasa daripada campuran kulit kerang dan zeolit semulajadi. Ia melibatkan dua faktor penting dalam membentuk penjerap dua fasa: 1) mencari jumlah optimum dan masa tepu kulit kerang dan zeolit semula jadi yang diperlukan dalam eksperimen ujian balang; 2) menentukan nisbah campuran optimum kulit kerang berbanding dengan zeolit semula jadi dalam eksperimen turus. Sampel kajian telah dikumpulkan dari sungai Desa Bakti, Universiti Teknologi Malaysia yang mana jumlah kecekapan penyingkiran permintaan oksigen kimia (COD), permintaan oksigen biokimia (BOD), jumlah fosforus (TP) dan jumlah nitrogen (TN) telah dipantau. Dalam fasa pertama, eksperimen ujian balang telah dijalankan. Berdasarkan eksperimen tersebut, jumlah optimum kulit kerang dan zeolit semulajadi adalah 3 gL^{-1}. Untuk kedua-dua penjerap memerlukan tempoh 3 hari untuk mencapai masa tepu. Seterusnya, satu siri nisbah campuran dalam kawasan carian telah dipilih dengan menggunakan perisian *Design Expert*. Kaedah D-optimum campuran (DMD) telah dipilih daripada perisian dan input yang diperolehi daripada eksperimen ujian balang telah digunakan untuk menghasilkan senarai nisbah campuran rawak. Semua nisbah campuran yang dihasilkan telah disahkan mengikut urutan dalam Sistem Paip Penjagaan Mudah (ECPS). Daripada analisis yang disediakan oleh perisian, nisbah campuran optimum adalah 25% zeolit semulajadi dan 75% kulit kerang. Nilai yang disasarkan daripada jumlah penyingkiran itu kemudian dibandingkan dengan data eksperimen. Jumlah pengurangan peratus BOD penyingkiran, COD, TP dan TN adalah 53.24%, 74.29%, 72.59% dan 81.98%. Mekanisme penjerapan telah dijelaskan secara analitikal dengan menggunakan isoterma penjerapan untuk melengkapkan keputusan yang diperolehi daripada ujian balang dan turus. Keputusan menunjukkan bahawa kulit kerang dan zeolit semula jadi dalam eksperimen ujian balang lebih menjurus kepada isoterma Langmuir. Dwi-fasa penjerap komposit yang terdiri daripada kulit kerang dan zeolit semulajadi dalam ujian kolum melengkapi ciri-ciri model Yoon-Nelson dan Thomas.

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CHAPTER 1

INTRODUCTION

1.1 Background of the Study

In Malaysia, due to a spike in population growth, the generation of solid wastes has become a critical issue that needs to be rectified (Sin *et al.*, 2013) to alleviate the impact to the environment (Zia and Devadas, 2007). The utilization of waste materials as alternative adsorbents is an attractive solution to reduce the volume of wastes. According to Giusti (2009), the waste management authority has been working on minimization, re-use, recycle of wastes prior to sending for composting.

Water treatment typically involves physical, chemical and biological processes and requires substantial financial input. Thus development of a cost-effective adsorbent is important. (Bhatnagar and Silanpaa, 2010). Adsorption is considered as a good option for superior water treatment due to its accessibility, ease of operation, maintenance and simplicity in design (Ademiluyi *et al.*, 2009; Bhatnagar and Silanpaa, 2010). In addition, this process has been found to be capable of minimizing different types of pollutants and therefore has very wide applicability in pollution control and water treatment.

Cockleshells are scientifically known as *Anadara granosa* which is a species of bivalve shellfish. It contains high level of calcium carbonate ($CaCO_3$) (Yao *et al.*, 2014). According to Kamba *et al*. (2013), cockleshells comprise 98 to 99% of calcium carbonate in the forms of aragonite whereas mussle shells consist of a mixture of calcite and aragonite (Cubillas *et al.*, 2005). Previous research studies have demonstrated that aragonite (a form of calcium carbonate) exhibits outstanding phosphate sorption functionality and Millero *et al.* (2001) has successfully demonstrated that the adsorption of phosphate contents by aragonite was much higher than calcite. Studies on the utilization of raw wasted cockleshells as adsorbent materials have yet to be carried out comprehensively, hence this study will provide insightful information in developing an alternative adsorbent to reduce the consumption of commercial adsorbents

Development of a novel dual-phase composite adsorbent has been considered as an attractive solution to enhance the removal efficiency with respect to utilizing a single-phase adsorbent material. Hu and Vansant (1995) presented a chemically activated composite adsorbent from using elutrilithe and zinc chloride as a substitute to activated carbon. As a result, the new composite adsorbent demonstrated high affinity to the organic compounds and its adsorption capacity was higher than that of commercially available activated carbons. In 2011, Halim *et al.* (2011) also proved that the composite adsorbent comprising rice-husked carbon wastes, activated carbons and ordinary Portland cements was capable of adsorbing ammonia molecules and COD contents. It was also observed that the proposed composite adsorbent had a higher adsorption capacity than commercially available activated carbons. Hence, in the present study, the second was to focus on minimizing the cost through the implementation of a commercially available adsorbent. The dual-phase composite adsorbent was prepared from raw cockleshells and unmodified natural zeolites (clinoptilolite). A number of factors consisting of adsorption capacity, total removal efficiency of the dual-phase composite adsorbent and optimal mixture ratio of cockleshells relative to natural zeolites were also comprehensively evaluated.

1.2 Problem Statements

Large number of research studies have been working on the development of cost-effective adsorbents; however, majority of the reports focused solely on single-phase materials without exploring the feasibility of dual-phase composite adsorbents. Single-phase materials showed impressive results in adsorbing various types of pollutants in water and conclusively adsorption is the most reliable method to treat water and wastewater. In spite of this, the performance of dual-phase composite adsorbent is still lacking for future references, hence, by developing dual-phase composite adsorbent consisting of a raw marine waste material and a commercially available adsorbent could improve the adsorption capacity.

The feasibility of utilizing cockleshells as adsorbent has not been evaluated comprehensively and the information was not widely accessible. There were many research studies on the implementation of bivalve shells as adsorbent materials but mostly focused on other bivalve shells such as oyster shells and mussel shells. Therefore, the efficiency of cockleshells as adsorbent material is to be unraveled in this study. This is due to the compositions in the cockleshells are comparable to other bivalve shells, especially oyster shells.

1.3 Objectives

The objectives are as follows:

1. To identify the optimal concentration, saturation time and adsorption capacity of crushed cockleshells and natural zeolites via jar test analysis.
2. To determine the characteristics of cockleshells and natural zeolites by FT-IR analysis.
3. To randomly generate mixture ratios of crushed cockleshells relative to natural zeolites required from the Design Expert software and unravel the optimal mixture ratio through the column test experiments.

4. To study the adsorption behavior through the use of adsorption data employing a mathematical model to imitate static and dynamic adsorptions.

1.4 Scope of the Study

The first stage was to carry out the jar test experiments. This was a preliminary screening test to ascertain a potential optimal mixture ratio for the dual-phase composite adsorbent development. Next, the potential optimal mixture ratio of the dual-phase composite adsorbent was further optimized in the column tests. A list of mixture ratios were randomly generated from the Design Expert® 7.0 software. The element of operating and environmental parameters such as factor, component and response were included into the software and generate random mixture ratios where the ratios were used in the fabricated column model. In the column test, each ratio generated from the software was tested and the removal BOD, COD, TP and TN readings were recorded and analyzed using the software. The final stage was to determine if the adsorption of the absorbent was static or dynamic from the jar and column model experiments.

The jar test experiments were conducted spanning across 7 consecutive days. The effects on the adsorbent concentrations and contact times were also evaluated. The water samples were acquired from the Desa Bakti River near Universiti Teknologi Malaysia where each sample was made up to the volume of 1 liter. A series of concentrations of crushed cockleshells and natural zeolites were prepared in 0, 1, 2, 3 and 4 where 0 represents the control sample as reference.

The removal COD percentage and adsorption capacity of each sample were determined. FT-IR analysis of each research sample was obtained to unravel the discrepancy of pre- and post-addition of the absorbent.

Various isotherms were employed to uncover if the adsorption of the research samples was static or dynamic during the data interpretation. The Langmuir and Freundlich isotherm models were used to mimic the maximum adsorption capacity and the behavior of each adsorbent. Meanwhile, the Adam-Bohart, Thomas and Yoon-Nelson isotherms were utilized to comprehend the data from the column model experiments; a breakthrough curve was plotted based on the optimal mixture ratios and the saturation time of the adsorbent determined.

1.5 Significance of the Study

Generally, the application of raw cockleshells is limited notwithstanding the production of cockles in Malaysia surges with years. For example, the applicability of cockleshells can be extended to biomaterials for bone repair (Awang-Hazmi *et al*., 2007) and additive in soil remediation (Hanif *et al.*, 2015). Nonetheless sizeable number of research investigations employing cockleshells, as adsorbent materials were not reported. On the other hand, there is significant number of studies utilizing different types of seashells such as mussel, oysters and scallops. These applications have been widely known in the use of fertilizers, construction materials, cement clinkers and tiles (Barros *et al*., 2007). Therefore, an in-depth evaluation on the removal efficiency of adsorbent was carried out to ascertain the functionality of the cockleshells.

Natural zeolites are widely known for its outstanding adsorption properties and recently natural zeolites have been modified to boost the efficiency in the adsorption process (Mateen *et al*., 2016; Motsi *et al*., 2009; Wang and Peng, 2010). Having said that, time consumption has become an issue when using zeolites for chemical water treatment process. In order to reduce time constraint, a dual-phase adsorbent containing unmodified natural zeolites and other materials was analyzed. Hence, the present study will show the potential usage of composite adsorbent made up of crushed cockleshells and natural zeolites.

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