Magnetite activated carbon/chitosan composite from biomass for removal of diclofenac in aqueous solution

Yee How Yoong¹, Woon Chan Chong¹*, Ying Tao Chung², Hui Chieh Teoh¹

¹ Department of Chemical Engineering, Lee Kong Chian Faculty of Engineering and Science, Universiti Tunku Abdul Rahman, Jalan Sungai Long, Bandar Sungai Long, Cheras, 43000 Kajang, Selangor, Malaysia.

² Department of Chemical Engineering and Petroleum Engineering, Faculty of Engineering, Technology and Built Environment, UCSI University, No.1, Jalan Menara Gading, UCSI Heights, 56000 Cheras, Kuala Lumpur, Malaysia.

*E-mail: chongwoonchan@gmail.com

Abstract. Diclofenac (DCF) is a type of micropollutant from pharmaceutical waste which brings adverse effect to the aquatic environment if the wastewater is not well-treated. The impregnation of biopolymer on activated carbon has recently gained increasing attention to improve the removal efficiency of micropollutant from wastewater. Magnetite rice husk activated carbon/chitosan composite (MACCS) with high adsorption capacity was developed in this study by modifying rice husk activated carbon (RHAC) with iron oxide ($\text{Fe}_3\text{O}_4$) nanoparticles and cross-linked with chitosan. The adsorption performance of the synthesized MACCS was compared with rice husk activated carbon (RHAC) and magnetite chitosan (MCS) for DCF removal from aqueous solution. The physical and chemical properties of the synthesized biosorbents were investigated via scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR). MACCS was identified as the best performing biosorbent and its DCF removal ability was further tested in batch with different parameters. The parameters reported in this study were solution pH and the synthesis ratio of activated carbon and chitosan. The most effective adsorption of DCF with MACCS was achieved at solution pH of 2.5 and activated carbon to chitosan ratio of 1:2. In acidic condition, the perfect coating of chitosan which contained abundance of amine group attached on the RHAC with high porosity had achieved 94% removal of DCF with maximum adsorption capacity of 270 mg/g. Besides, the MACCS could easily be separated from the aqueous solution due to its magnetic property. From the results, the MACCS biosorbent showed its potential to be an excellent alternative adsorbent for the removal of micropollutant from wastewater.

Keywords: Diclofenac, chitosan, magnetic property, adsorption, rice husk

1. Introduction
Pharmaceuticals wastes as emerging pollutants in the water bodies has become the subject of interest to environmental sector in most of the countries. The pharmaceuticals waste presents in the water normally contains antibiotics, lipid regulators, anti-inflammatory agents, neuroactive compounds etc. [1]. These compounds could contaminant the water sources and cause adverse effects to the ecosystem and biodiversity. Amongst these pollutants, diclofenac (DCF) is a commonly used anti-inflammatory
nonsteroidal agent. The excess dosage of the DCF is excreted from human and animal bodies through urine and faeces and finally entering the sewage treatment plant [2].

To date, the existing wastewater treatment plants in most of the developing countries are not predominantly designed for micropollutants elimination. Therefore, micropollutants could have been excluded from the treatment processes due to its nature of persistency or the continuous feeding of the waste [3]. According to Akhtar et al. [4], tertiary treatment method such as adsorption appeared to be an effective solution in eliminating the accumulation of these micropollutants. Biomass as a precursor for the development of low-cost activated carbon is highly preferable by reasons of its unlimited supply and harmless effect to the nature.

Recently, activated carbon/chitosan composites had shown high removal of heavy metal such as Ni(II), Cu(II) and Cd(II) from aqueous solutions. These activated carbons are produced from sugarcane bagasse [5] and spent coffee grounds [6]. In another study, Tzereme et al. [7] grafted chitosan with different materials for diclofenac removal. It was found that trans-aconitic acid grafted chitosan showed the maximum adsorption capacity with 86.68 mg/g at 25 °C. To our knowledge, utilization of rice husk activated carbon incorporated chitosan with magnetic property for the removal of diclofenac has not been investigated. Rice husk has both physic and bio-chemical nature which made it suitable for the preparation of activated carbon [8]. Similarly to other agriculture by-products, rice husk also consists of lignin, cellulose and hemicellulose as main components. Lignin is responsible for the adsorption mechanism for pollutants removal whereas cellulose and hemicellulose will be vanished during the thermal treatment and generates highly porous carbon structure [9]. On the other hand, chitosan which contains amine group incorporated with the activated carbon could increase the number of active sites of the biosorbent [10]. Hence, it could be utilized in the biomodification of activated carbon toward organic compound adsorption in this study. Furthermore, the incorporation of Fe\textsubscript{3}O\textsubscript{4} nanoparticles in the composite could ease the separation process of the biosorbent from the wastewater after the treatment. This study aimed to produce an adsorbent from biomass with high diclofenac removal capacity from aqueous solutions.

2. Experimental

2.1 Preparation of Biosorbent

2.1.1 Preparation of Rice Husk Activated Carbon (RHAC) To produce RHAC, 25 g of rice husk was mixed with 1.0 M nitric acid (HNO\textsubscript{3}) and stirred for 24 h. After washing with de-ionized water, the rice husk was dried at room temperature. The sample was then mixed with 1.0 M sodium hydroxide (NaOH) and stirred for 24 h, followed by filtering and drying. Then, the sample was heated at 400°C in furnace for 4 h to form carbon. The carbon obtained was then mixed with 1.0 M NaOH for 20 min, followed by washing and drying. Later, potassium hydroxide (KOH) was added into the carbon and heated at 650 °C under nitrogen atmosphere. Finally, the RHAC formed was rinsed with distilled water to achieve neutral pH, followed by drying in oven.

2.1.2 Preparation of Magnetite Chitosan (MCS) To prepare MCS, 0.1 g of Fe\textsubscript{3}O\textsubscript{4} nanoparticle was dissolved in 1% of acetic solution. Then, 0.2 g of chitosan was added into the solution. After stirring for 90 min, 25% of glutaraldehyde was dropped wisely into the mixture and stirred at 70°C until the solution precipitated. The sample was then dried at 70 °C for 3 h.

2.1.3 Preparation of Magnetite Activated Carbon/Chitosan Composite (MACCS) The preparation steps of MACCS was similar to the preparation of MCS. The difference was that initially 0.1 g of RHAC and 0.1 g of Fe\textsubscript{3}O\textsubscript{4} nanoparticle were added into the 1% of acetic solution. Similar procedure was repeated by varying the weight of activated carbon and chitosan to obtain different ratio (1:1, 1:2, 1:3, 1:4) of the composites.
2.2 Characterization of Biosorbent

2.2.1 Scanning Electron Microscopy (SEM) The surface morphology of the prepared samples was studied using scanning electron microscopy (Hitachi S-3400N) fitted with energy dispersive X-ray (EDX) for elemental analysis. The sample was coated with gold before the analysis.

2.2.2 Fourier Transforms Infrared Spectrometer Analysis (FTIR) The basic functional groups of all the absorbents were identified by FTIR spectroscopy (Thermo Nicolet IS10 FTIR Spectrometer) in the range of 4000 – 500 cm⁻¹.

2.3 Adsorption Experiments

To prepare DCF aqueous solution, diclofenac sodium (G.R) was dissolved in distillate water to form DCF stock solution (10 ppm) without any pH adjustment. Initially, 0.25 g of biosorbents (RHAC, MCS, and MACCS) were added into the DCF solutions (100 mL) individually and the residual of the DCF was taken after 60 min where the adsorption equilibrium had been achieved. To study the effect of solution pH on the adsorption performance, the solution pH was adjusted using 0.1 M hydrochloric acid (HCl) or 0.1 M NaOH to achieve pH 2.5, 7 and 11.

The adsorption study was performed in room temperature. UV-vis was applied to determine the initial and equilibrium DCF concentration. The removal percentage of DCF was calculated using equation (1):

\[
\% \text{Removal} = \frac{C_i - C_e}{C_i} \times 100\%
\]

where, \(C_i\) is the initial concentration (mg/L) and \(C_e\) is the equilibrium concentration (mg/L) of DCF

The adsorption capacity of DCF on the biosorbents was calculated using equation (2):

\[
q = \frac{V(C_i - C_e)}{M}
\]

where, \(q\) is adsorption capacity (mg/g), \(M\) is the mass of the bioadsorbent (g) and \(V\) is the volume of DCF (L).

3. Results and Discussion

3.1 Characterization of Biosorbents

According to the FTIR analysis as shown in Figure 1, significant variations are observed between the RHAC and the modified adsorbents. However, the variations between the MCS and MACCS were less significant due to the presence of high amount of chitosan. The presence of peaks in the region of 1500-1650 cm⁻¹ band also implied the existence of carbonyl (C=O) groups [11] that could be attributed to the lignin and hemicelluloses aromatic groups or the stretching of unsaturated aliphatic (C=C) structures for RHAC and both composites [12]. Besides, N-H group was observed around 1635 cm⁻¹ for both MCS and MACCS, which exhibited the presence of primary amine [10]. In addition, a strong band around 3300 cm⁻¹ was detected due to overlapping of the O-H and NH₂ stretching vibration of functional groups engaged in hydrogen bond [13]. These hydroxyl and amino groups were responsible to form hydrogen interactions with functional groups of pharmaceuticals pollutants. According to Desbrières and Guibal [14], amino group played an important role in the binding interaction with the DCF.
Figure 1. FTIR Spectra of biosorbents.

SEM was utilized to examine the surface morphology of the biosorbents. A highly developed porous structure of RHAC with regular mesopores was observed in figure 2a. The development of porous activated carbon was due to the decomposition of the volatiles when the rice husk was being activated at high temperatures during pyrolysis [8].

The surface morphology of MCS and MACCS are presented in figure 2b and 2c, respectively. Fe₃O₄ nanoparticles were randomly deposited on both biosorbents. Meanwhile, the activated carbon was observed to has been covered by the cross-linked chitosan gel as shown in figure 2c. It has proven that the chitosan and Fe₃O₄ nanoparticles were impregnated perfectly onto the activated carbon during the composite process. As a result, chitosan would form a rigid matrix layer onto the activated carbon and increased its adsorption site per surface.

Figure 2. SEM image of a) RHAC, b) MCS and c) MACCS.

3.2 Effect of Composite Ratio of MACCS

Figure 3 presents the removal efficiency of DCF with different content of chitosan in the MACCS composite after 60 min of treatment. From the results, the activated carbon to chitosan ratio of 1:2 showed the highest absorption capacity (91%) among the biosorbents. The adsorption performance was reduced when the chitosan content increased afterwards and it could only achieve 59% of removal at ratio of 1:4. This was possibly due to the excessive amount of chitosan which had blocked the pores of the activated carbon, and thus decreased the composite's porosity and reduced the DCF adsorption efficiency.
3.3 Adsorption Performance of Different Biosorbents

Figure 4 illustrates that the removal efficiency of DCF was relatively higher by using the best performed MACCS from Section 3.2 as biosorbent in comparison to RHAC and MCS. The maximum achievable removal efficiency of MACCS, MCS and RHAC were 91%, 68% and 59%, respectively at the natural pH of 6.8. The high adsorption capacity of the MACCS were contributed by the high porosity of the activated carbon and the abundance availability of amine functional groups of the chitosan. These had further increased the surface area and the active sites of the biosorbent and hence enhanced its adsorption capability.

3.4 Effect of Solution pH

The best performed biosorbent (MACCS) was selected to study the influence of solution pH on the adsorption ability of the DCF as illustrated in figure 5. Acidic condition of pH 2.5 showed the highest adsorption of DCF with 94% of removal efficiency. On the other hand, the increment of alkalinity condition reduced the removal efficiency significantly. The \( pK_a \) value of DCF was experimentally found to be around pH 4.15 [15]. At pH values above its \( pK_a \), most of the DCF began to deprotonate and exhibit a negative charge. The deprotonated form of DCF would lower the interaction with the surface of the MACCS, and thus increased the repulsion force and decreased the adsorption at higher pH values. On the other hand, the solubility of DCF declined at pH below DCF's \( pK_a \), i.e. where DCF was presented in its unionized form. Consequently, the removal efficiency increased inversely with the solution's pH [16]. As a result, ‘van der Waals’ force was presumed to be responsible for the interaction between the DCF and the MACCS surface increased by physical adsorption process at low pH value. Besides, it is noteworthy to mention that the adsorption phase reached its equilibrium within the 10 to 20 min under acidic condition as shown in figure 5.
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**Figure 5.** Effect of solution pH on removal efficiency of DCF.

4. **Conclusion**

Biosorbent made up of rice husk activated carbon coated with chitosan and Fe$_3$O$_4$ nanoparticles was successfully produced as confirmed by FTIR and SEM analysis. The SEM image of RHAC exhibited large number of regular cavities, with high porosity on surface texture. Meanwhile, the perfect covering of chitosan onto the RHAC in SEM image of MACCS was also observed. MACCS showed improved adsorption efficiency as compared to the RHAC (pure activated carbon from rice husk) and MCS (Fe$_3$O$_4$ nanoparticles incorporated with chitosan). The best synthesis ratio of activated carbon and chitosan to produce MACCS was achieved at a ratio of 1:2. In addition, the solution pH was found to influence the structural stability of the DCF significantly and the maximum adsorption of DCF was identified in the acidic solution of pH 2.5.

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