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Empirical models of kinetic rate for river treatment analysis of cellulosic materials

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ABSTRACT

The utilisation of cellulosic fibre in removing organic and nutrients pollutants in polluted river is becoming an increasingly popular alternative cost-effective and sustainable option. However, the related empirical models are yet to be fully comprehensive to study the adsorption mechanisms of natural adsorbents. This paper discusses developed empirical model used to estimate the mass transfer of organic pollutants into two natural fibres – coconut fibres and oil palm fibres to filter pollutant molecules in water. An empirical model was developed to estimate the mass transfer of organic pollutants in water onto the fibres in a fabricated physical model. The mass transfer relations were derived based on the substrates loading rates and the predicted accumulation rates of substrates in fibres along with the percentage of outflows. Matching empirical results with experimental results showed that the modified model was able to accurately predict the mass transfer rate. The higher adsorption rate of CF (91.02% COD) depicted greater global mass transfer rate (1.3696 d^{-1}) than OPF (82.35% COD) which only had 1.2768 d^{-1} of global mass transfer rate in 3% of COD outflow. The contribution of internal diffusion mechanism was significant due to the physical (porosity) and chemical (lignin and cellulosic content) characteristics of both CF and OPF. The study concluded that the performance of biological adsorption using CF and OPF is promising.

1. Introduction

River has been the source of life since billions of years ago. Early human civilization had mainly flourished at riverbanks, such as Egypt's Nile River, Indus River valley, and along major rivers in China. River forms a vital part of our ecosystem, providing food and shelter to many organisms, not to forget a mean of transportation for human [1]. In order to preserve its sustainability, it is important that river water bodies and riparian zones are maintained clean so that the delicate life balance is not disrupted. Ironically, as human civilization progresses by leaps and bounds throughout history, we are also stressing our river bodies through the tremendous amount of wastes generated. Many of these wastes are disposed irresponsibly into our river systems, overloading the rivers with excessive amount of nutrients that has resulted in harmful algal blooms, dead zones and fish killed [2].

The worsening pollution, fortunately, has also triggered vast amount of research being conducted on water treatment technologies and materials. However, the application of the water and wastewater treatment materials like alum, polymer flocculants, ferric chloride, and coal-prepared activated carbon remains a major challenge for the industry and agricultural sectors due to the high cost involved and the scarcity of equipment [3]. In order to reduce the treatment cost, efforts are now poured into exploring new and novel adsorbents. A notable example is the recycling of readily available agricultural and industrial by-products. These include fly ash bagasse [4], walnut shell [5], waste tires [6], and rice husk [7].

In this regard, coconut fibre (CF) and oil palm fibre (OPF) are natural residual products abundantly available as by-products from the agricultural industry, especially in Malaysia [8,9]. According to the Food and Agriculture Organization of the United Nations (FAU) in year

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Nomenclature

C_o	Initial concentration of organic pollutant (mg/L)
C_t	Concentration of organic pollutant in a day (mg/L)
k_{BA}	Adams-Bohart model's constant (L/mg d)
N_o	Sorption capacity (mg/L)
v	Linear flow velocity of water (m/d)
H	Bed depth (m)
q_t	Amount of adsorbed adsorbate into adsorbent at time (mg/g)
Q	Flow rate of water (L/s)
ρ	Density of adsorbents (g/L)
q_t acc	Accumulation of organic pollutant adsorbed per mass of cellulosic fibres (CF and OPF) (g/g)
k_f	Film mass transfer factor or external mass transfer factor (d^{-1})
k_g	Global mass transfer (d^{-1})
β	Elovich coefficient of desorption constant (g/mg)
k_d	Porous diffusion factor or internal mass transfer factor (d^{-1})
VLR	Volumetric loading rate (mg/Ls)

2013, the worldwide annual production of CF is approximately 650,000 t. This is mainly from India, Sri Lanka, Thailand, Indonesia, Malaysia, Vietnam, and the Philippines. In terms of OPF, approximately 29,091,000 t is being generated as waste annually in Malaysia [9]. The waste amounts are continuously increasing, but its utilization is marginal and yet to be fully tapped [10]. In fact, lignin and cellulose properties of coconut fibre are actively involved in chemical bonding and responsible for typical cation exchange characteristics [11]. It was discovered from previous findings that CF and OPF are expected in the direction of heavy metal ions, phenol and dye removal [12,13]. The examples of heavy metal ions and dyes removal using CF and OPF are such as chromium (VI), nickel (II), zinc (II), Copper (II), and Lead (II) ions [14–17]. While for the dyes and phenols that common been removed by CF and OPF are such as Methyelene blue, Malachite green blue, Cationic methylene blue, Anionic phenol red, Methylene Blue, Acid orange 7, Methylene blue, and *p*-chlorophenol [18–21].

However, overall observations are less comprehensive for research studies on natural organic matter and nutrients pollutants adsorption from water bodies using CF and OPF. Most of the time they were used as a precursor for activated carbon in contaminated water [22–25]. In fact, the natural adsorption properties of fibres is needed to further investigate especially on organic matter and nutrients removal. In view of this, this paper aims to present a potential utilization of both CF and OPF to remove organic matters (OM) from river water.

Other than the adsorption capacity of fibres, the existing literature has shown that the establishment of an appropriate adsorption correlation is essential prior to the application of the fibres as water treatment medium; this is to give reliable prediction of related parameters and adsorbents behaviour under various experimental conditions [26]. A variety of mathematical models have been developed for this reason to determine and describe the equilibrium isotherm, the adsorption kinetic isotherm, and the column dynamic behaviour. All the mathematical models are quite different in nature. In fact, the models are always constructed on the three basic consecutive steps that are external diffusion, internal diffusion and mass action [27]. However, most are restricted for activated carbon, chemical reaction kinetics and single solute applications only. The resistance of mass transfer during adsorption processes to remove pollutants from water using natural organic materials has by far been neglected. For example, pseudo-second-order rate equation was developed based on the chemical adsorption and not suitable to describe the physical organic pollutants adsorption by nonpolar adsorbents [28]. Therefore, it is significant to understand their boundary conditions and improve the current research on the adsorption kinetic modelling especially in organic pollutant adsorption by natural adsorbents.

With respect to this, this study had been conducted to focus on: (1) the physical and chemical characteristics of cellulosic fibres (CF and OPF); (2) its performance evaluation in treating OM from river water using a fabricated column model (FCM); and (3) the mass transfer resistance of OM through these fibres as predicted by a modified empirical model.

2. Methodology

2.1. Sampling location

The water sample was collected from a river located at one of the river catchments at Skudai, Johor Bahru, Malaysia. This river is severely polluted by domestic effluent discharged from four cells of oxidation ponds nearby. Other pollution sources include the discharge from residential and gardening areas and the surface runoff from rainy days. During the time of this study, fish kills and algal bloom have been observed even with the full operation of the waste stabilization pond nearby (see Fig. 1).

Fig. 1. Algal bloom and fish kills observed in river.