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# Tetracycline adsorption onto rice husk ash, an agricultural waste: Its kinetic and thermodynamic studies

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ABSTRACT

As an agricultural waste, rice husk ash (RHA) has the potential to be a viable alternative adsorbent for the removal of tetracycline (TC) from aqueous solution. This study aims to explore its feasibility of RHA as a new adsorbent, and understand its adsorption mechanism for TC. Also assessed in this study are the influences of initial concentration of TC, adsorption time, solution pH and temperature on RHA adsorption performance. It is found that TC removal efficiency of RHA is related to the initial concentration of TC solution. TC concentration decreases sharply within the first 60 min in its adsorption process, and then only gradually, reaching the equilibrium within 600 min. RHA adsorption capacity is related to solution pH, temperature, and ion intensity, especially at a high pH value. A rise of 313 K in temperature caused the adsorption capacity to more than double. Furthermore, low-acid and high-alkaline solution can accelerate the adsorption of TC onto RHA. The highest adsorption capacity of 8.37 mg/g achieved in this study is much higher than other adsorbates reported in the literature, indicating the feasibility of RHA as a new adsorbent. The Langmuir isotherm model is the most reasonable in depicting the adsorption behavior. The pseudo second order model fits the experimental data nicely, suggesting a mostly physical and chemical control over the adsorption. Such findings can serve as a useful guide in expanding the applicability of RHA to new areas.


## 1. Introduction

Tetracyclines (TCs) are a group of broad spectrum antibiotics which have been applied vastly to human and veterinary medicine for disease control, and in livestock feed owing to their perceived therapeutic effects [1,2]. However TCs are very stable and poorly absorbed in the digestive tract. Only a small portion of ingested TCs is metabolized or absorbed, with approximately 50–80% of TCs excreted through feces and urine in the raw form [3]. After TCs are discharged into the environment, their presence in soil, sediments, surface water, and even in drinking water has been frequently detected [4,5]. Studies have indicated that TCs may pose a significant risk to ecosystems and human health [6], even at a very low, permissible concentration. TCs can develop allergies in humans and antibiotic resistance genes in bacteria [7], which is regarded as one of the greatest threats to human health in the 21st century by the World Health Organization [8].

TCs have a low degradability, and are lethal to most microorganisms due to their antibacterial nature, which adds difficulty to their effective removal in the activated sludge treatment processes [9]. Accordingly, the removal rate of TCs tends to be very low in general, and they cannot be completely eliminated from water in traditional wastewater treatment plants (WWTPs) that have become the dominant source of residual TCs [10]. Various physical and chemical treatment methods have been used to enhance the removal efficiency of TCs in WWTPs, such as photocatalytic oxidation [11], ozonation [12] and adsorption [13]. Adsorption of TCs by porous materials has been proved to be one of the most efficient methods, with various adsorbents studied, including activated carbon [14], bamboo charcoal [15], clays [16], polymers [17], aluminum oxide [18], nanomaterials and microparticles [19], and even resins [2]. Nevertheless, these adsorbents can be excessively expensive in practice, particularly if they are used in macroscale for water treatment. Therefore, there is a need to develop more economic and effective adsorbents for TCs. One possible candidate adsorbent is rice husk ash (RHA), an agricultural waste. Accounting for nearly one-fifth of the annual gross rice production of 545 million metric tons of the world, it is used mostly as a fuel in boiler furnaces [20]. Rice husk has been found to be an efficient adsorbent for the removal of both organic and inorganic pollutants from aqueous systems, including phenol [21], dye [22], nitrate [23], and toxic metals [24]. Crop residue-derived ashes have a demonstrated ability to adsorb TCs and sulfamethoxazole in soils [25], which suggests that RHA can be a potentially efficient adsorbent for TCs' removal from aqueous systems. This study attempts to determine

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the TC adsorption behaviors onto RHA, and aims at revealing the feasibility of applying RHA for TCs adsorption from aqueous environments, including the influences of initial TC concentration, adsorption time, and solution temperature and pH on adsorption efficiency. This study will be conducive to a better comprehension of the physicochemical adsorption processes of this new adsorbent of RHA.

## 2. Materials and methods

Analytical-grade tetracycline (TC) hydrochloride was acquired from Aladdin-reagent Co., Ltd. (China), and RHA was collected from Jiangsu Shengli Materials Co., Ltd. (China). To prepare for the tests, stock solution containing 50 mg/L of TC was prepared first with deionized water. The adsorption experiments were carried out in 50 mL polypropylene centrifuge tubes soaked in $HNO_3$ solution in advance for 12 h in a temperature-controlled orbital shaker (ZD-85A, Jintan Ronghua Instrument Manufacture Co., Ltd.). These centrifuge tubes were wrapped with aluminum foil to prevent light-induced decomposition during storage and adsorption processes [26]. All adsorption experiments were replicated three times, with the mean values considered as the final results.

Bach experiments were carried out using 2 g/L of RHA (0.04 g of RHA was added to 20 mL TC solution), and the initial concentration of TC was ranging from 5 to 20 mg/L. Samples were taken at predetermined time, and all the suspensions after adsorption experiments were filtered through 0.45 μm membrane. For the pH-effect experiments, the initial concentration of TC was 10 mg/L, and the solvent's pH values were calibrated with NaOH and HCl aqueous solutions to reach pH values of 2–12. To investigate the influence of adsorption temperature, the experiments were conducted at three different temperatures (283, 298, and 313 K) for 10 h. Prior to detection, samples' pH values were adjusted to 2.0 by adding concentrated HCl to improve the analytical results of TCs that were stable in the HCl solution [18]. The samples were detected by UV–vis spectrophotometer (UV-2550, Shimadzu, Japan). Full band ultraviolet scan of TC was performed to determine the maximum absorption wave length as being 356 nm (Fig. 1a). The calibration plot of absorbance versus TC concentration level exhibits a linear relationship between them over the 0–50 mg/L range (Fig. 1b).

The adsorption capacity of RHA ($Q_t$, mg/g) and its removal rate of TC ($r$, %) were counted using Eqs. (1) and (2), respectively [27].

$$Q_t = \frac{(C_0 - C_t) \times V}{m} \quad (1)$$

$$r = \frac{C_0 - C_t}{C_0} \times 100\% \quad (2)$$

where $C_0$ and $C_t$ represent the initial concentration and residual concentration of TC solution (mg/L) at a given time, respectively; $V$ stands for the volume of TC solution (20 mL); $m$ is the mass of RHA (g).

The structure of RHA was studied using X-ray diffractogram (XRD) obtained from an X-ray diffracto-meter (D/max 2500VL/PC, Rigaku, Japan) with CuKα as the radiation source. The scanning scope was $5° \le 2\theta \le 85°$ at room temperature. The XRD patterns of RHA (Fig. 2) are characterized by a very distinct peak at around 22° corresponding to crystalline silica.

## 3. Results and discussions

### 3.1. Effects of initial TC concentration and adsorption time

The effects of initial TC concentration and adsorption time on the adsorption of TC onto RHA were undertaken at durations ranging from 0 to 900 min in Fig. 3.

Obviously, the TC concentration of the solution decreases sharply within the first 60 min, followed by a gradual decrease. If the adsorption time is prolonged to over 600 min, the TC concentration does not change significantly, indicating the adsorption equilibrium for RHA. Namely, the amount of TC being adsorbed onto the adsorbent equals the quantity being desorbed from the adsorbent [28]. Therefore, 600 min was chosen to be the adsorption equilibrium time in all subsequent experiments. Moreover, the time needed to attain the equilibrium state hardly varies with the initial concentration of TC solution. The initial rapid decrease in the concentration of TC solution may be attributed to the presence of a large quantity of vacant area for adsorption at the surface of RHA; and the reduction in available surface area may contribute to the retarded decrease of TC. In addition, repulsive forces between TC molecules in the solution and those adsorbed on the surface of RHA may be responsible for the decreased adsorption [29]. In other words, the aggregation of TC molecules around RHA particles could hind the diffusion of TC molecules into the adsorbent structure [30].

As the initial concentration rises from 5 to 20 mg/L, the removal efficiency of TC solution ($r$) decreases from 60.93% to 34.40%, and the adsorption capacity of RHA ($Q_e$) increases from 1.51 to 3.41 mg/g (Table 1).

This is because a high concentration of TC solution facilitates a greater mass transfer driving force to allow more TC molecules to pass from the aqueous solution to the RHA particle surface, resulting in higher TC absorption [31,32]. However, the removal efficiency ($r$) decreases with the increase of initial TC concentration. There are lots of vacant sites in the surface of RHA at low TC concentration, and the vacant sites are saturated with TC concentration increased, resulting in a decrease in the removal efficiency [33].

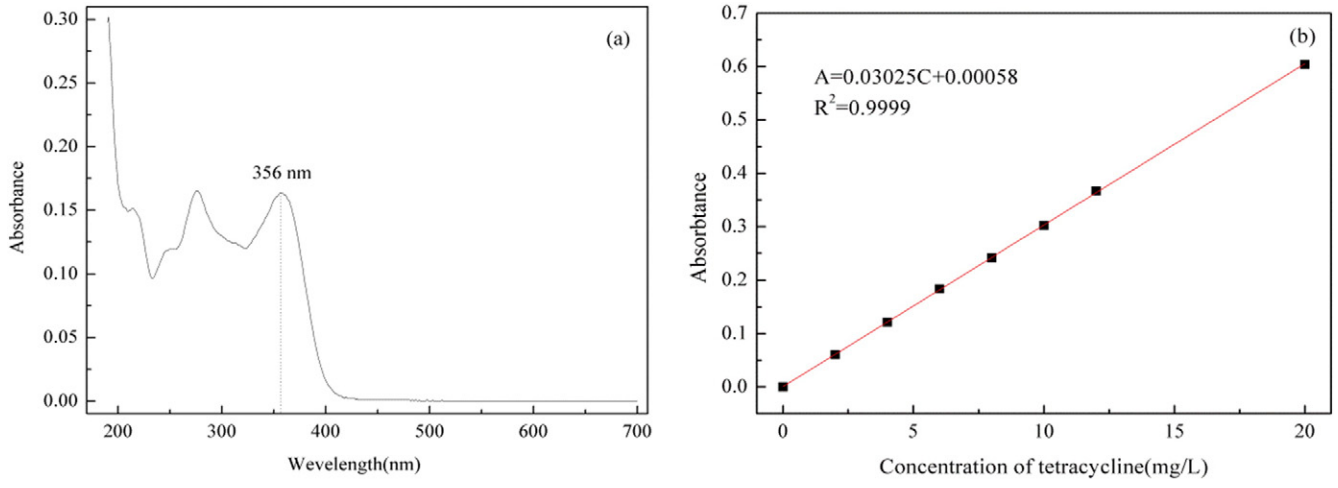


**Fig. 1.** Full band ultraviolet scan of tetracycline (a) and its standard curve (b).