Study on simultaneous adsorption of Zn(II) and methylene blue on waste-derived activated carbon for efficient applications in wastewater treatment

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Abstract: Organic and inorganic pollutants often coexist in water bodies due to the influxes of pollutants from various pollution sources. The use of waste-derived adsorbents to remove pollutants is an economical and efficient method of wastewater treatment. The present study was designed to investigate the adsorption and cosorption of Zn and methylene blue (MB) on a capsicum straw derived activated carbon (CSAC), by determining equilibrium adsorption isotherms and simulation. The result showed that the Langmuir equation is more suitable for description of the adsorption isotherms of Zn2+ and MB than that of the Freundlich equation. The maximum adsorption amounts for both adsorbates were quite the same. The amount of Zn2+ adsorbed decreases with increasing MB and vice versa, suggesting the competitive rather than synergistic adsorption on the activated carbon. Cosorption of Zn(II) and MB on the CSAC showed MB to be preferentially adsorbed. The adsorption kinetic studies showed that the adsorption of Zn2+ comply with pseudo-second-order rate model rather than pseudo-first-order rate model. The findings of the present study helps to carry out an efficient application in waste treatment.

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Chongyang Yang has completed her Bachelor’s degree in Shanxi province of China at the age of 22 years from Shanxi University and now she is a Master degree student in Donghua University, School of Environmental Science and Engineering. Her research focuses on management and treatment of wastewater, specifically on adsorption and cosorption of inorganic metal and organic dyes wastewater by using different materials and novel technologies.

PUBLIC INTEREST STATEMENT
My research has focused primarily on understanding adsorption and cosorption of Zn(II) and methylene blue on waste-derived activated carbon for efficient applications in wastewater treatment. The field of wastewater treatment has expanded greatly due to the development of high-throughput experimental methodologies, which has significant contribution in solving environmental-related problems that occur by different pollutants, from different sources especially from industries on the water resource. Nowadays, keeping the water quality is a requirement due to climate change, but currently, the demand in using water has been gradually increased in agriculture, industry, and domestic sectors, which consequently produces a large quantity of wastewater. Therefore, it needs urgent and effective action in order to maintain the quality of water for the sake of keeping our environment safe. Though adsorption and cosorption of Zn(II) and methylene blue on waste-derived activated carbon (absorbent), the efficiency and cost effectiveness of the approach have been investigated.
1. Introduction

Wastewater discharged by industries often contain different levels of harmful substances, which may be organic or inorganic and have negative effects on the water environment. Therefore, the water bodies receiving wastewater become complex systems. For example, heavy metals, which are inorganic and non-biodegradable, undergo transformations in the environment and have a large environmental, public health, and economic impacts (Muchuweti et al., 2006; Singh, Sharma, Agrawal, & Marshall, 2010). Moreover, organic dyes are applied in some industries such as dye manufacturing and textile industries; the presence of very small amounts of dyes in water (less than 1 ppm for some dyes) is highly visible and undesirable (Crini, 2006; Kannan & Sundaram, 2001).

Many metal-bearing wastewater containing dyes may reduce the metal and dye removal efficiencies and result in unacceptable concentrations of contaminants remaining in the effluent. The presence of heavy metal ions in industrial effluents is also relevant due to its toxicological profile and potential impacts on the human health and environment (Kyzas, Lazaridis, & Kostoglou, 2013). So, the need of the study of simultaneous removal of dyes and ions is obvious given the extended coexistence of both of them in large amounts of wastes (and mainly industrial effluents) (Kyzas, Siafaka, Pavlidou, Chrissafis, & Bikiaris, 2015). Various treatment technologies such as precipitation, ion-exchange, membrane separation, reverse osmosis, solvent extraction, filtration, oxidation, electrochemical methodology, and biological treatment have been employed to remove metal and dyes pollutants from aqueous solutions (Gupta & Suhas, 2009; Wan Ngah & Hanafiah, 2008). However, some methods are limited due to a number of side effects, such as a large amount production of sludge, high costs of materials, complicated and strict operational conditions. Activated carbon is well known by its effectiveness in removing not only organic chemicals from wastewater, but also inorganic and heavy metal pollutants (Monser & Adhoum, 2002). In general, activated carbon adsorption is considered to be particularly competitive and effective process for the removal of heavy metals and dyes due to its ease of operation and insensitivity to toxic substances (Kyzas, Fu, & Matis, 2013). Recently, the evaluation of waste-derived activated carbon is gaining attention all over the world, as it is renewable, widely available, cheap, and environmentally friendly (Karagoz, Tay, Ucar, & Erdem, 2008). Most importantly, the advantage of adsorption is that waste can be reused. A wide range of agricultural wastes have been treated as precursors in the production of activated carbon (Wei & Yushin, 2012).

The main purpose of this study is to investigate the adsorption and cosorption of metal ions and ionic dyes on waste-derived activated carbon in aqueous solutions. Zn(II) and methylene blue (MB) act as the typical pollutants. Zn is an essential trace element, but high levels also cause harmful health effects. The main water pollution sources for zinc, is the wastewater from pharmaceuticals, galvanizing, paints, pigments, insecticides, cosmetics, etc. (Bhattacharya, Mandal, & Das, 2006; Hameed, Din, & Ahmad, 2007). Methylene blue (MB) dye (Figure 1) may be used for coloring paper, temporary hair colorant, dyeing cottons, wools, and coating for paper stock. It is often serves as a model compound for removing organic contaminants from aqueous solutions (Kalavathy, Karthikeyan, Rajgopal, & Miranda, 2005; Vadivelan & Kumar, 2005). In this study, the effects of pH on the Zn(II) adsorption capacity were studied. Isotherm models, and adsorption kinetics were also investigated.

Figure 1. Molecular structure of methylene blue (MB).
2. Materials and methods

2.1. Materials
A Capsicum straw obtained from (Jiangxi China) was used as a raw material for preparation of activated carbon. It was carbonized at 450°C under nitrogen atmosphere for 0.5 h. A certain amount of produced char was then soaked with potassium hydroxide at an impregnation ratio of 3:1 (KOH:char). The mixture was set in a water bath at 80°C for 16 h, and then oven-dried at 100°C. The Samples were heated to 750°C in 60 min in a tubular reactor furnace. After activation of samples, appropriate amounts of 0.1 M hydrochloric acid solution was added, followed by stirring, the solution in a continuous manner in order to neutralize the excess KOH, and then washing it with hot distilled water (80°C) for several times to remove residual chemicals. Finally, a mesh size of 200 was employed to form porous activated carbon powder by grinding and sieving. The activated carbon powder prepared from capsicum straw (hereafter CSAC) was the adsorbent used in this study.

Zinc nitrate and MB, which were used as adsorbate was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Stock solutions of Zn(II) (10 mmol/L) and MB (10 mmol/L) were prepared by dissolving exact quantities of Zn(NO₃)₂·6H₂O and MB using deionized water. The solution pHs were adjusted using nitric acid and sodium hydroxide. All of the reagents used in this experiment were analytical grade chemicals.

2.2. Batch sorption experiments
Batch sorption experiments were carried out at ambient temperature (20 ± 2°C) by adding 30 mg of CSAC to 30 mL pH-controlled solutions in polyethylene tubes, forming the suspension with a solid–liquid ratio of 1:1,000. The initial concentrations of Zn ions and MB in aqueous phases started at 0.76–5.4 and 0.16–3.1 mmol/L, respectively. They were mechanically shaken for 24 h to ensure adsorption equilibrium, and then filtered using 0.45 μm membranes for chemical analyses.

In cosorption experiments, the concentration of one of the adsorbates (Zn(II) or MB) in the initial was fixed, while that of another one was increased. The equilibrium concentrations for both adsorbates were simultaneously measured to investigate the adsorption on the CSAC.

Kinetic experiments for adsorption of Zn(II) from aqueous solutions using CSAC affected by MB were designed in 1.0 mmol-Zn(II)/L with and without 0.10 mmol-MB/L in contact times starting from 2 min to 24 h.

The concentration of MB in aqueous phase was determined at a wavelength of 669 nm by TU-1810 UV-vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd.). Acidic digestion with HNO₃ and H₂O₂ was employed to remove MB, the concentrations of Zn(II) in the filtrates was determined using Z-2000 SERIES Polarized Zeeman Atomic Absorption Spectrophotometer (Hitachi, Japan).

3. Results and discussion

3.1. Adsorptions of Zn(II) and MB
Solution pH is one of the most important factors influencing heavy metal adsorption (Kalavathy et al., 2005; Sheng, Ting, Chen, & Hong, 2004; Wang et al., 2010). To find out the best adsorption conditions, the performance of Zn(II) on the CSAC was first studied using a series of solutions with an unified initial concentration of 1.1 mmol-Zn(II)/L and different pH (2–6), and the equilibrium concentrations determined are shown in Figure 2. The effect of pH can be explained considering the surface charge on CSAC. At low pH (2–3), H⁺ ions occupy the surface of the CSAC, enhancing electrostatic repulsion that prevents Zn²⁺ ions near CSAC and hindering the removal of Zn²⁺. With increasing pH from 3 to 4, OH⁻ reacts with H⁺ to form H₂O. Electrostatic repulsion becomes weak with the decreased positive charge density, resulting in an enhancement of metal adsorption. At high pH (4–6), the removal of Zn²⁺ reaches the maximum. The adsorption capacity of 0.72 mmol-Zn(II)/g-CSAC was observed at pH of 6. Therefore, all the experiments were carried out at pH 6.0.
The adsorption isotherm can provide fundamental physiochemical data for evaluating the applicability of the sorption process as a unit operation (Vadivelan & Kumar, 2005). Figure 3 shows experimental results of Zn\(^{2+}\) (A) and MB (B), and the corresponding adsorption isotherms obtained by the simulation with Langmuir and Freundlich equations. It is observed that the experimental results of
Zn\(^{2+}\) and MB can be well simulated using Langmuir equation with the correlation coefficients (\(R^2\)) being 0.9667 and 1.0, respectively, both of which were slightly higher than that of using Freundlich equations, 0.9575 and 0.9264, respectively. Langmuir and Freundlich isotherm constants together with the corresponding (\(R^2\)) are calculated and given in Table 1. The Langmuir isotherm fits better than the Freundlich, suggesting a homogeneous nature and monolayer surface adsorption for Zn(II) and MB on the surface of the CSAC and the maximum adsorption capacities of 63.3 and 357 mg/g-CSAC (i.e. 0.97 and 1.1 mmol/g), respectively. The dimensionless parameter of the equilibrium or adsorption intensity (\(R_L\)) is calculated by using the adsorption constant (\(K_L\)) and the initial concentration (\(C_0\)) (Weber & Chakravorti, 1974) as follows:

\[
R_L = \frac{1}{1 + K_L C_0} \tag{1}
\]

The adsorption is unfavorable (\(R_L > 1\)), linear (=1), favorable (0 < \(R_L < 1\)), or irreversible (\(R_L = 0\)). In the present study, all the values were in the range between 0 and 1. This indicates that the adsorption process of Zn(II) and MB are favorable for all the CSAC samples prepared.

### 3.2. Cosorption of Zn(II) and MB

Cosorption experiments of Zn\(^{2+}\) and MB were also carried out by batch method, which specifically include: (1), the initial concentration of Zn\(^{2+}\) was set to be 0.93 mmol/L while that of MB was increased from 0 to 1.0 mmol/L; (2) is different from (1), the initial concentration of MB was 1.0 mmol/L and that of Zn\(^{2+}\) was from 0 to 0.96 mmol/L. The equilibrium concentrations of Zn\(^{2+}\) and MB were determined, and then the equilibrium adsorption amounts of Zn\(^{2+}\) and MB were calculated, the sum of both of which was hereinafter expressed as \([S]\). Both the measured and calculated results are showed in Figure 4(A) and (B), respectively.

These two batch experiments can be considered as continuous processes, in which the initial concentration of one adsorbate is fixed while another is gradually added. We collected aqueous samples and determined the concentrations of Zn\(^{2+}\) and MB at all adsorption equilibrium stages of interest. Figure 4(A) shows that with MB being added, Zn\(^{2+}\) ions were desorbed from the CSAC, causing the Zn\(^{2+}\) concentration increase in aqueous solutions. After MB added in the solution it reached a certain level, the equilibrium concentration of MB by itself also started to increase significantly. At the same time, the cosorption amount of Zn\(^{2+}\) and MB, i.e. \([S]\), shows a synchronous growth trend with the initial concentration of MB until near 0.9 mmol/g. Figure 4(B) shows that with Zn\(^{2+}\) ions being added, its equilibrium concentration increased nearly in a constant manner with increasing total input amount while the concentration of MB is quite low and varies irregularly. This is because most of MB is being adsorbed on CSAC and at the initial stage, Zn\(^{2+}\) added is too little to cause the significant desorption of MB. It is noteworthy that \([S]\) has been fluctuating between 0.8 and 0.9 mmol/g. Thus, it can be understood that the sum of total adsorption amounts of Zn\(^{2+}\) and MB on CSAC, \([S]\), has approached the maximum and is slightly lower than that achieved by the single adsorption of either Zn\(^{2+}\) or MB. By comparing the results of two batch experiments, it may be understood that MB is organic and more easily adsorbed than inorganic Zn\(^{2+}\) ions on CSAC. In other words, CSAC is more suitable for the removal of organic pollutants from wastewater than that of inorganic ones. The findings of experiments help to understand the competitive cosorption behavior of two adsorbates that are chemically different and do not react with each other.

### Table 1. Langmuir and Freundlich isotherm constants for Zn(II) and MB on CSAC

| Adsorbate | Langmuir equation \( Q_e = \frac{K_L C_e}{1 + a_L C_e} \) | Freundlich equation \( Q_e = a_f C_e^{b_f} \) |
|-----------|--------------------------------|---------------------------------|
| Zn(II)    | \( K_L \) = 2.07, \( a_L \) = 0.0327, \( R^2 \) = 0.9677 | \( a_f \) = 8.835, \( b_f \) = 0.3445, \( R^2 \) = 0.9575 |
| MB        | \( K_L \) = 98.0, \( a_L \) = 0.2745, \( R^2 \) = 0.9997 | \( a_f \) = 272, \( b_f \) = 0.0417, \( R^2 \) = 0.9264 |
3.3. Kinetic study of Zn$^{2+}$ adsorption of on CSAC as affected by MB

The adsorptions of Zn$^{2+}$ in the absence and presence of and MB on CSAC over time were investigated to examine the kinetic behavior of Zn$^{2+}$ and the influence by the presence of MB. Even if the adsorption progress is rapid in the first 60 minutes, in order to ensure the equilibrium, 24 hours was employed to be more consistent (Figure 5). The adsorption amounts are calculated from the concentrations of Zn$^{2+}$ at all stages of interest. The pseudo-first order and pseudo-second-order kinetic models were used to fit the time-elapsed adsorption amounts of Zn$^{2+}$ on CSAC in the first 60 mins (Equations (2) and (3))

Pseudo-first-order rate model equation: \[ \ln\left(\frac{q_e - q_t}{q_e}\right) = -k_1 t \]  

(2)

Pseudo-second-order rate model equation: \[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]  

(3)

where, \( q_t \) and \( q_e \): the adsorption amount at time of \( t \) (min) and the maximum on CSAC, mmol/g, respectively; \( k_1 \) and \( k_2 \): pseudo-first-order and pseudo-second-order constants in the unit of min$^{-1}$ and g mmol$^{-1}$ min$^{-1}$, respectively.
Figure 5. Time-elapsed adsorption amounts of Zn²⁺ onto CSAC in the absence (A) and presence (B) of MB (1.2 mmol/L) at 20°C and pH 6.0.

$k_1$, $k_2$, and the correlation coefficients $R^2$ are calculated and listed in Table 2. Results show that the pseudo-first-order kinetic curves do not give a good fit to kinetic data for the two experiments, which can be corroborated by lower $R^2$, i.e. 0.9112 and 0.9973. On the other side, $R^2$ of pseudo-second-order kinetic model are 0.9536 and 0.9998, respectively. Therefore, Zn²⁺ ions exhibit similar pseudo-second-order adsorption kinetic behavior on CSAC regardless of the absence or presence of MB, and due to the presence of MB (1.2 mmol/L), the maximum adsorption amount of Zn²⁺ ions decreased from 0.36 to 0.086 mmol/g.

| Table 2. Simulation of adsorption of Zn²⁺ in the absence and presence of MB |
|---------------------------------------------------------------|
| Kinetic models      | Parameters          | Adsorbate                                      |
|                    | $k_1$               | Zn²⁺  | Zn²⁺ in the presence of MB (1.2 mmol/L) |
| Pseudo-first-order rate model | $k_1$ | 0.0141 | 0.0575 |
|                     | $R^2$               |       | 0.9112 | 0.9973 |
| Pseudo-second-order rate model | $k_2$ | 2.291  | 9.612  |
|                     | $R^2$               |       | 0.9536 | 0.9998 |
4. Conclusion

In general, based on the results it could be concluded that the Langmuir equation is more suitable for description of the adsorption isotherms of Zn$^{2+}$ and MB than the Freundlich equation. The maximum sum adsorption capacity of both adsorbates remain fluctuating within an acceptable range. Moreover, the amount of Zn$^{2+}$ adsorbed decreases with the increasing MB and vice versa, suggesting the competitive rather than synergistic adsorption on the activated carbon. Within the cosorption process on the CSAC, MB appears to be preferentially adsorbed. The adsorption kinetic studies for Zn$^{2+}$ ions exhibit an adsorption complying with pseudo-second-order rate model rather than pseudo-first-order rate model. Finally, all the findings of the present study help to carry out an efficient application in wastewater treatment. CSAC can be used as a low-cost sorbent to remove organic dyes from wastewater and the following research effort can focus on the chemically modified waste-derived activated carbon which is to be most effective in removing inorganic metal Zn$^{2+}$ or organic and inorganic pollutants mixed wastewater.

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