Adsorption of Heavy Metal ions and Antibiotics from Aqueous Solution on Activated Carbons Prepared from Agricultural Waste

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Abstract. The contamination of water by heavy metal ions and antibiotics is presently a serious environmental challenge of the world. This work intends to use activated carbons made out of agricultural waste to alleviate the problem of water pollution. Commercialized coconut shell activated carbon was used for the experiment. Cadmium ions and chloramphenicol were selected as the model compounds for heavy metal and antibiotics in water solution. TOC analyzer and the atomic absorption spectrophotometry were used to determine the concentration of antibiotics and metal ions in solution, respectively. The coconut shell activated carbon turned out to be efficient in the adsorption of metal ions (removal efficiency up to 90% when concentration is 1mg/L) and chloramphenicol (removal efficiency up to 40% when concentration is 1ml/L). The rates of adsorption of both cadmium ions and chloramphenicol were high at first but declined as the contact time increases. The competitive adsorption was investigated in this study by using a mixed solution of cadmium nitrate and chloramphenicol. It was found that the adsorption capacity of chloramphenicol of activated carbon remains the same while the adsorption capacity of metal ions sharply dropped by 44%, indicating that Cadmium ions have no obvious effect on the adsorption of chloramphenicol, whereas chloramphenicol hinders the adsorption of cadmium ions.

Keywords: Chloramphenicol, Cadmium ion, Activated carbon, Adsorption.

1. Introduction
Heavy metals are persistent contaminants in water due to their non-biodegradable behavior, bioaccumulation even at trace levels [1]. Cadmium is a type of heavy metal that usually occurs along with zinc and is widely used in a variety of fields [2]. With the rapid development of the electroplating industry, electronics industry, and chemical industry, cadmium production has increased a lot, which then results in a more serious condition of cadmium pollution. A large amount of cadmium enters the environment through exhausted gas and wastewater from metallurgical plants, electroplating factories, and catalyst factories using cadmium compounds as raw materials. Under normal conditions, cadmium has no effect on our health. However, when the environment is contaminated by cadmium, this element tends to gather in the body of creatures and causes chronic intoxication through the chain of
food and water systems. Once the concentration of cadmium in one’s body reaches a high level, some serious diseases, such as osteomalacia, renal tubular damage, etc., are likely to occur [3, 4].

While heavy metal pollution is paid full attention to, problems caused by antibiotics are sometimes left unconcerned. Antibiotics are applied primarily in the pharmaceutical industry, as well as the aquaculture industry and stock farming industry. Since it is almost impossible for humans and animals to absorb antibiotics completely, a large amount of these chemicals is discharged into the environment, which can lead to intoxication and the emergence of resistant bacteria. Given that this kind of contamination is newly-emerged, a refined treatment has not yet been developed.

When heavy metal ions and antibiotics enter water bodies, they can cause serious pollution, especially when water is consumed by animals and humans. However, both the adsorption of both heavy metal ions and antibiotics is difficult to some extent due to their fundamental characteristics [5]. Therefore, it is necessary to investigate about adsorption methods of these substances.

Activated carbon has been widely applied to the aqueous-phase adsorption of both organic and inorganic compounds [6]. According to Chuah, activated carbon is successful in the removal of certain heavy metals and dyes from wastewater [7]. Compared to other methods, including physical filtration, neutralization, and biological treatment, activated carbon adsorption is often preferred for its versatile nature for a wide variety of compounds [8]. Coconut shell activated carbon has been a commercialized material for water treatment. Certain unique characteristics, such as large surface area, well-developed hole structure, tunable surface chemistry, and high chemical and thermal stability, enable it to be highly effective in water purification. Therefore, this work chooses coconut shell activated carbon to try absorbing cadmium ions and antibiotics in water.

2. Method

2.1. Materials
The activated carbon made out of coconut shell, which is one kind of mature commercialized activated carbon, was used in this experiment. This study chose cadmium nitrate as a representative of common metal pollutants, considering that nitrates play a considerable role in water pollution; chloramphenicol, as one type of broad-spectrum antibiotics, was chosen to represent antibiotics. Cadmium nitrate (purity: 99%, supplier: Nanjing Reagent co. LTD) and chloramphenicol (purity: 99%, supplier: Henan Xuanhang Industrial co. LTD) was used in this experiment.

2.2. Adsorption studies

2.2.1. Adsorption of metal ions or chloramphenicol from water. The commercialized coconut shell activated carbon, which has been introduced earlier, was used to conduct adsorption experiments. 0.1g granulated coconut shell activated carbon was put into 50ml cadmium nitrate solutions (100 mg/L) and 50ml chloramphenicol solutions (100 mg/L) separately, within the exact same condition. The solutions were stirred by magnetism mixers. After 60 minutes, the absorbance of the upper clear liquid of the two cadmium nitrate solutions was determined using an atomic spectrophotometer, and the concentration of chloramphenicol of the two antibiotic solutions was determined using TOC Analyzer. In addition, low concentration (1 mg/L) of cadmium solution was also prepared to investigate the effect of cadmium concentration on the adsorption performance of activated carbons.

2.2.2. Rate of adsorption. In order to explore how the rate of adsorption changes during the whole process, the concentration of solutes was measured every ten minutes after each adsorption mentioned previously started. The measurement ended after one hour, which means that the concentration would be measured for seven times, including the initial concentration. The adsorption experiment was conducted under the state of continuous stirring by the magnetism mixer, and the upper clear liquid was extracted every ten minutes within an hour to investigate the absorbance of the rest solution. For antibiotics, the same experiment, except for using a TOC Analyzer to determine the stage
concentration, was done. In this way, the influence of contacting time on the effect of adsorption can be studied.

2.2.3. Competitive adsorption of cadmium ions and chloramphenicol from water. Previously, the absorbance of 50ml cadmium nitrate solution (100 mg/L) and the TOC concentration of 50ml chloramphenicol solution (100 mg/L) were determined. During this part of the experiment, 0.1g coconut shell activated carbon was added to a 50ml mixture of the two solutions. After being stirred for 60 minutes, the upper clear liquid was extracted to determine the final absorbance and TOC concentration of the mixed solution, which were then compared with those of the separate solutions.

2.3. Characterization
The concentration of cadmium ions in solution was measured using atomic absorption spectrophotometry, and that of the chloramphenicol solution was measured using the total organic carbon analyzer (TOC Analyzer). Prior to the experiments, both pieces of equipment were calibrated by using standard solutions (100 mg/L for cadmium nitrate and 100 mg/L for chloramphenicol).

3. Results and Discussion

3.1. Characterization

| Parameters                        | Coconut shell AC |
|-----------------------------------|------------------|
| Particle size                     | 1.18mm-2.36mm    |
| Adsorption rate of benzene powder | 450mg/g          |
| Iodine value                      | 950mg/g          |
| Methylene blue value              | 170ml/g          |
| True density                      | 2.1g/cm³         |
| Bulk density                      | 0.37g/cm³        |
| Total porous volume               | 0.74cm³/g        |
| BET specific surface area         | 1211m²/g         |
| Ash content                       | 5%               |

In this study, the commercialized coconut shell activated carbon was used as adsorbents, which is a process of waste reclamation and potentially lowers the cost of water purification. The textural properties of these carbon adsorbents were shown in Table 1. It can be found that coconut shell derived activated carbon has a relatively high BET specific surface area (1211 m²/g) and total porous volume (0.74 cm³/g). This activated carbon would be used in the following experiments to explore the effects of adsorption.

3.2. Adsorption studies

3.2.1. Adsorption of metal ions. The study of adsorption kinetics is of importance to understanding the structure of activated carbon and the mechanism of contaminant removal. Adsorption experiments were carried out using two cadmium nitrate samples of different concentrations (100mg/L and 1mg/L) and coconut shell activated carbon at room temperature. 50ml of each cadmium nitrate sample was tested.
Table 2. Adsorption of Cd^{2+} by coconut shell activated carbons

| Concentration of Cd^{2+} (mg/L) | 1 mg/L | 100 mg/L |
|---------------------------------|--------|----------|
| Cd^{2+} (initial)               | 1.00   | 100.00   |
| Cd^{2+} (after adsorption)      | 0.11   | 84.86    |

The adsorption performance of the activated carbons was shown in Table 2 above. After 60 minutes, the coconut shell activated carbon adsorbed nearly 90% of the total metal ions in the 50ml solution when the initial concentration of cadmium ions is 1mg/L. The result indicates that the coconut shell activated carbon has a good adsorption efficiency when the cadmium concentration is relatively low, primarily due to its larger BET surface area and total porous volume, which provides more active sites for cadmium ions. When the concentration of cadmium ions increased to 100mg/L, and the volume of the solution remained at 50ml, the number of pollutants removed increased, but the removal efficiency sharply dropped regardless of the same amount of activated carbon (0.1g) was used. This indicates that when the concentration of cadmium ions is high, coconut shell activated carbon is unable to achieve a high adsorption efficiency. Figure 1 shows the adsorption quantity in both solutions, while Figure 2 shows the adsorption efficiency in both solutions.

Fig. 1 Cadmium ion adsorption quantity of AC vs. contact time
3.2.2. Adsorption of chloramphenicol

Table 3. Adsorption of chloramphenicol by activated carbons

|                      | Coconut shell adsorption |
|----------------------|---------------------------|
| Initial TOC (μmol/L) | 48.26                     |
| Final TOC (μmol/L)   | 28.16                     |

In the experiment, 0.1g of the coconut shell AC was added to 50ml chloramphenicol solution (100mg/L) at room temperature. Figure 3 shows that the coconut shell activated carbon was able to adsorb over 40% of the antibiotics.
The rate of adsorption of chloramphenicol was constantly high within the first 30 minutes and slowed down during the next 30 minutes, different from that of metal ions, which was extremely high only in the first ten minutes while quickly declined afterward. This suggests that chloramphenicol adsorption has a more lasting high adsorption rate than cadmium ions when the initial concentration is the same. Also, comparing the linear trendline of adsorption efficiency in both situations, we can see a smaller slope in 100mg/L cadmium ion adsorption (0.0022) than that in 100mg/L chloramphenicol adsorption (0.0103) in first forty minutes, which indicates a higher adsorption rate in the latter. However, the adsorption rate of chloramphenicol dropped to almost the same as that of cadmium ions in the next twenty minutes.
3.3. Competitive adsorption: cadmium vs. chloramphenicol

![Graph showing adsorption performance of activated carbons](image)

**Fig. 4** Adsorption performance of activated carbons in a mixed solution containing cadmium ions and chloramphenicol and simple-component solutions

The competitive adsorption study is carried out in purpose to explore whether an adsorption priority exists between metal ions and chloramphenicol and the possible influence they may have on the adsorption of each other. The experiment was conducted at room temperature, using a 50ml mixed solution of the two adsorbates (100mg/L and 25ml each) with 0.1g coconut shell activated carbon. The result is compared with the adsorption performance of the same amount of AC in 50ml cadmium ion solution of 100mg/L and 50ml chloramphenicol solution of 100mg/L within the same conditions. From Figure 4, it is reasonable to conclude that the chloramphenicol adsorption capacity of activated carbon remains the same, while the metal ions adsorption capacity sharply dropped by 30.14%. The results indicate that metal ions have almost no effect on the adsorption of chloramphenicol, while the chloramphenicol significantly hinders the adsorption of cadmium ions. This phenomenon reveals that chloramphenicol is prior to cadmium ions in the competitive adsorption. On the one hand, considering the irregular-shaped holes, it is possible for chloramphenicol molecules, which are relatively large molecules, to block up the holes and, as a result, make the cadmium ions unable to enter the holes. On the other hand, there may be active sites where both chloramphenicol and cadmium ions can be adsorbed. According to the results from section 3.2, the adsorption rate of chloramphenicol is faster than cadmium, so it becomes difficult for cadmium ions to be adsorbed. In this way, the adsorption efficiency of cadmium ions declines significantly in the competition, whereas that of chloramphenicol remains constant. It indicates that the antibiotics will be adsorbed preferentially absorbed by the carbon-based adsorbents in practical application.

4. Conclusion

In this study, commercialized coconut activated carbons were used to adsorb cadmium ions and chloramphenicol from water solution. It turns out that this type of activated carbon has a high adsorption efficiency when the cadmium ion concentration is relatively low, which attributes to its high surface area and pore volume. A larger quantity of metal ions can be adsorbed when the cadmium...
ion concentration is higher, but adsorption efficiency would decrease instead. The adsorption of cadmium ions and chloramphenicol showed a two-step process, and adsorption rate was high at first and dropped as time went by. The adsorption rate of chloramphenicol was faster than that of cadmium ions in the first forty minutes, but the gap closed in the final twenty minutes. Later, the competitive adsorption was studied using the mixed solution; the result indicates that chloramphenicol has a priority to cadmium ions and has a negative effect on the adsorption efficiency of cadmium ions.

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References
[1] Aydin, H., Bulut, Y., Yerlikaya, C., 2008. Removal of copper(II) from aqueous solution by adsorption onto low-cost adsorbents. J. Environ. Manag. 87, 37-45.
[2] Chuah, T.G., Jumasiah, A., Azni, I., Katayon, S., Thomas Choong, S.Y., 2005. Rice husk as a potentially low-cost biosorbent for heavy metal and dye removal: an overview. Desalination 175, 305-316.
[3] Edidiong Asuquo, Alastair Martin, Petrus Nzerem, Flor Siperstein, Xiaolei Fan, 2017. Adsorption of Cd(II) and Pb(II) ions from aqueous solutions using mesoporous activated carbon adsorbent: Equilibrium, kinetics and characterization studies. Journal of Environmental Chemical Engineering 5, 679-698.
[4] Issabayeva, G., Aroua, M.K., Sulaiman, N.M.N., 2006. Removal of lead from aqueous solutions on palm shell activated carbon. Bioresource Technology 97, 2350-2355.
[5] Joana M. Dias, Maria C.M. Alvim-Ferraz, Manuel F. Almeida, Jose Rivera-Utrilla, Manuel Sanchez-Polo, 2007. Waste materials for activated carbon preparation and its use in aqueous-phase treatment: A review. Journal of Environmental Management 85, 833-846.
[6] Madhava Rao, M., Ramesh, A., Purna Chandra Rao, G., Sesaiah, K., 2006. Removal of copper and cadmium from the aqueous solutions by activated carbon derived from Ceiba pentandra hulls. Journal of Hazardous Materials 129, 123-129.
[7] Meidl, J.A., 1997. Responding to changing conditions: how powdered activated carbon systems can provide the operational flexibility necessary to treat contaminated groundwater and industrial wastes. Carbon 35, 1207-1216.
[8] Zhang, F.-S., Nriagu, J.O., Itoh, H., 2005. Mercury removal from water using activated carbons derived from organic sewage sludge. Water Research 39, 389-395.