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Adsorptive removal of residual amoxicillin antibiotic using cationic surfactant cetyltrimethylamonium bromide modified nanosilica rice husk

Thi Diu Dinh[1], Minh Nguyen Phan[1], Thi Ngoc Mai Pham[1], Tien Duc Pham[1,*]

[1]Faculty of Chemistry, University of Science, Vietnam National University – Hanoi, 19 Le Thanh Tong, Hoan Kiem, Hanoi 100000, Vietnam
**Email: tienducpham@hus.edu.vn*

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ABSTRACT

Amoxicillin (AMX) is a highly antibiotic resistance so that many studies focus on the removal of AMX in water environment. The present study investigated adsorptive removal of beta-lactam antibiotic AMX using a cationic surfactant, cetyltrimethylamonium bromide (CTAB) modified nanosilica (CMNS). The CTAB adsorption on nanosilica was independent of ionic strength, indicating that both electrostatic and hydrophobic interaction induced adsorption. Effective conditions for AMX removal using CMNS were systematically studied. The AMX removal using 10 mg/ mL CMNS reached 99 % at pH 9. Adsorption isotherms of AMX on CMNS at two salt concentrations were in good agreement with Langmuir model than Freundlich model. Adsorption isotherms at different ionic strengths and the surface modification by Fourier transform infrared (FT-IR) spectroscopy demonstrate that AMX adsorption on CMNS was mainly controlled by electrostatic interaction.

Introduction

Antibiotics are important pharmaceutical products that are widely used to treat bacterial infections for both people and animals. Nevertheless, residual antibiotics in water environment can cause a serious problem due to antibiotic resistant bacteria [1]. Therefore, removal of antibiotics has attracted numerous studies [2]. Among many techniques are used for the removal of antibiotics, adsorption is one of the most effective method and suitable for developing countries when using cheap adsorbents [3].

Silica fabricated from rice husk is a low-cost material because rice husk is a very common agricultural sub-product. However, nanosilica rice has low charge density material that is low effectiveness in removal of charged adsorbate such as antibiotic. Thus, to enhance removal efficiency of antibiotic, surface modification of structural denaturation is necessary. In our previously published papers, we successfully modified nanosilica surface by different polycations [3,4], or protein [5] or coated with CeO_2 [6] to increase the removal of some antibiotics from aqueous solutions.

Amoxicillin (AMX) is one of the most widely used beta-lactam antibiotic for treating bacterial infections [7]. Although AMX residual in hospital waste water at ultra-trace level (part per billion), the influence on antibiotic resistance is serious. Due to the complicated structure with three pKa values, adsorptive removal of AMX is low efficiency when using nanosilica although surface modification is applied [8]. Interestingly, the interaction between surfactant and AMX can be utilize to enhance

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its removal. Cationic surfactant, cetyltrimethylamonium bromide (CTAB) was used to modify adsorbent for treating organic dyes [9,10]. Nevertheless, CTAB modified nanosilica rice husk for AMX removal has not been investigated.

In the present work, we study adsorptive removal of AMX using a new adsorbent based on CTAB modified nanosilica (CMNS). Adsorption of CTAB on nanosilica was investigated to find the suitable condition to modify nanosilica surface. Adsorption of AMX on CMNS at different pH and adsorbent dosage was thoroughly studied. Adsorption isotherms of AMX on CMNS at different ionic strengths are fitted by Freundlich and Langmuir models. Adsorption mechanisms are also suggested on the basis of the surface modification by Fourier transform infrared (FT-IR) spectroscopy and adsorption isotherms.

Experimental

Materials

Nanosilica was fabricated from rice husk according to our previously published paper [4]. Amoxicillin trihydrate with purity greater than 98% (HPLC grade) was purchased from AK Scientific (USA). Cationic surfactant, cetyltrimethyl amonium bromide (CTAB) with purity > 98 % was supplied by Tokyo chemical industry, TCI (Japan). Other chemicals are analytical reagents that are delivered from Merck (Germany). All solutions which were prepared with pure water from the ultrapure water system (Thermo Scientific, USA) with a resistivity of 18.2 MΩcm. All solution pH was measured using an HI 2215 pH meter (Hanna, USA).

Characterization and analytical methods

The FT-IR spectra were recorded at room temperature using Affinity-1S spectrometer (Shimadzu, Kyoto, Japan) with a resolution of 4 cm-1. Concentrations of CTAB were determined by UV-Vis spectroscopy using ion paired formation at a wavelength of 375 nm in the presence of 0.2 mL of 0.1% picric acid in 2 mM NaOH extracted by 1,2-dichloroethane. All AMX concentrations in aqueous solution were also quantified by UV-Vis spectroscopy using a spectrophotometer (UV-1650 PC, Shimadzu, Japan) at a wavelength of 229 nm.

Adsorption studies

All adsorption experiments were carried out in 15mL centrifuging tubes at room temperature. Contact time of 90 min was kept as for all adsorption studies. The influences of pH and adsorbent dosage on AMX removal were investigated. Adsorption capacity of CTAB onto nanosilica and AMX onto CMNS were obtained using Equation (1):

$$\Gamma = \frac{C_i - C_e}{m} \times 1000 \quad (1)$$

where Ci is initial concentration (mg/L), Ce is equilibrium concentration of CTAB or AMX (mg/L), and m (mg/mL) is adsorbent dosage.

To evaluate AMX removal using CMNS, initial concentration of 10 mg/L AMX was fixed while other parameters were changed to find optimum conditions. The AMX removal using CMNS was calculated by Equation (2).

$$Removal\ (\%R) = \frac{C_i - C_e}{C_i} \times 100\% \quad (2)$$

The adsorption isotherms of AMX on CMNS were fitted by Langmuir [11] and Freundlich models [12]. The AMX concentration were ranged from 10 to 280 mg/L under optimum conditions to find maximum adsorption capacity. The linear adsorption isotherm of Langmuir and Freundlich models were Equations (3) and (4), respectively:

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \frac{1}{q_{max}K_L} \quad (3)$$

$$\mathrm{Ln}q_e = \mathrm{Ln}K_F + \frac{1}{n_F}\mathrm{Ln}C_e \quad (4)$$

Where qe (mg/g) is the AMX adsorption capacity at equilibrium time, qmax (mg/g) is the maximum AMX adsorption capacity and KL (L/g) is the Langmuir constant while K_F ($mg^{n-1}L^n/g$) is the Freundlich constant, and $1/n_F$ is the adsorption intensity.

Results and discussion

Adsorption of CTAB on nanosilica

Adsorption of CTAB on nanosilica was conducted at pH 10 in which nanosilica has high negative charge while charging behavior of CTAB is independent on pH. Figure 1 shows adsorption capacity of AMX on nanosilca at two KCl concentrations.

Figure 1 shows that adsorption isotherms of CTAB arenot influenced by ionic strength. Surfactant adsorption decreases with increasing ionic strength when adsorption is mostly controlled by electrostatic attraction between oppositely charged interaction [13]. On the other hand, hydrophobic interaction plays important role if surfactant adsorption increases with an increase of ionic strength [14]. In our case, CTAB adsorption changed insignificantly at 1 and 10 mM KCl, indicating that both electrostatic and hydrophobic interactions induced adsorption. Adsorption capacity of CTAB reached a maximum when CTAB initial concentration was 3 mM. To create a high performance adsorbent, 3 mM CTAB was selected for modification of nanosilica surface.

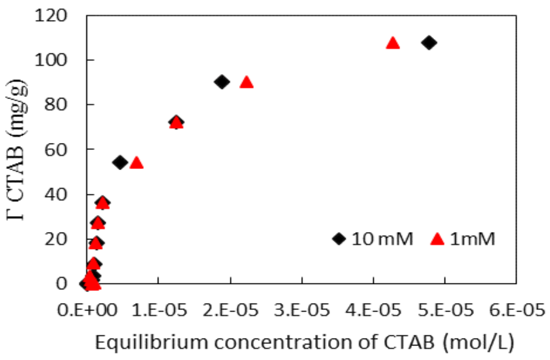

Figure 1: Adsorption isotherms of CTAB on nanosilica at 1 and 10 mM KCl

Adsorption of AMX on CTAB modified nanosilica

Influence of pH

Among many parameters influencing AMX removal, pH plays one of the most important role because pH strongly affects charging behavior of AMX.

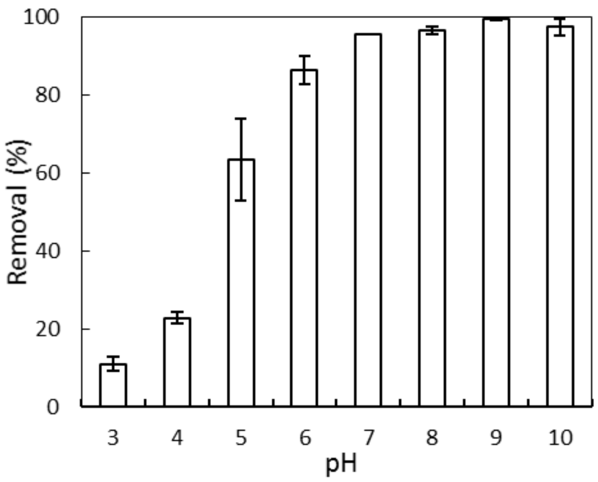

Fig 2: Influence of pH to AMX removal using CTAB modified nanosilica ($C_{i,AMX}$ = 10 mg/L, adsorbent dosage 10 mg/mL, and 1 mM KCl). Error bars show standard deviations of three replicates

Figure 2 indicates that AMX removal using CMNS increases with increasing pH because the negatively charged AMX species are dominant at high pH while surface charge of CMNS is independent on pH. This trend is similar to AMX removal using polycation modified nanosilica [4]. At pH 10, AMX removal was slightly decreased because of silica dissolution at high basic media. The highest AMX removal of 99 % was achieved at pH 9. Thus, pH 9 is was kept for further study.

Influence of adsorbent dosage

The influence of adsorbent dosage is an effective parameter because it strongly induces surface area and charge density.

Figure 3 shows that AMX removal grew up dramatically with increasing adsorbent dosage from 1 to 10 mg/mL due to an increase in total site and charge of CMNS [3]. However, AMX removal decreased with a higher adsorbent dosage than 10 mg/mL because of the fast aggregation of high concentration of nanosilica in the presence of organic molecules [15]. The best CMNS dosage for AMX removal was found to be 10 mg/mL

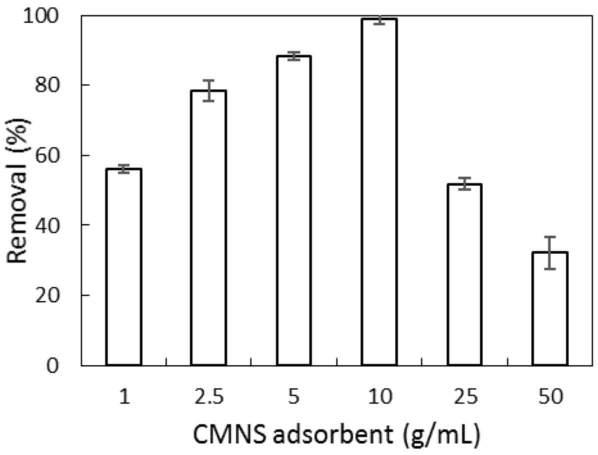

Figure 3: Influence of adsorbent dosage to AMX removal using CTAB modified nanosilica ($C_{i,AMX}$ = 10 mg/L, pH 9, and 1 mM KCl). Error bars show standard deviations of three replicates

Adsorption isotherms

Adsorption isotherms are important to evaluate the effect of ionic strength. In this study, we use Langmuir and Freundlich models to fit adsorption isotherms of AMX onto CMNS (Figures 4 and 5).

Figures 4 and 5 show that both Langmuir and Freundlich models can represent AMX adsorption isotherms on CMNS.

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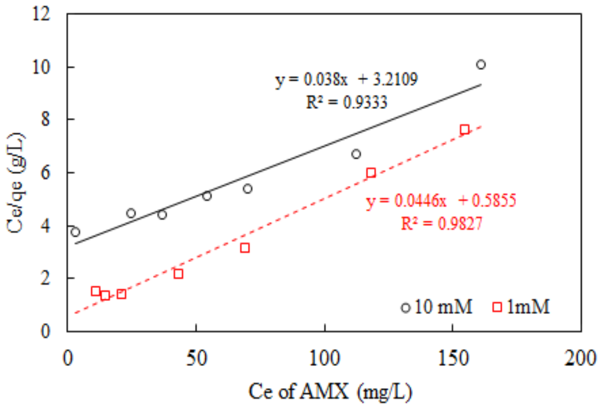

Figure 4: Adsorption isotherms of AMX on CMNS at different KCl concentrations fitted by Langmuir model

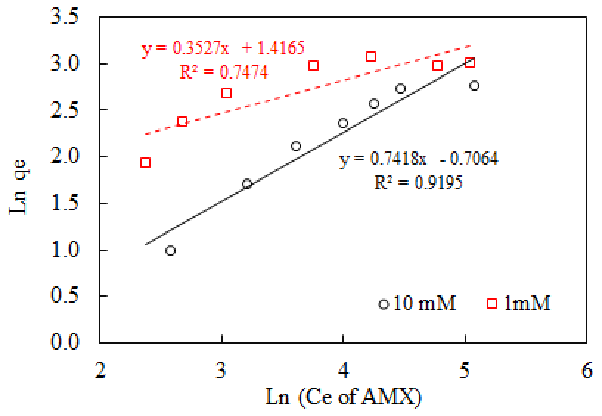

Figure 5: Adsorption isotherms of AMX on CMNS at different KCl concentrations fitted by Freundlich model

However, Langmuir model achieved a much higher correlation coefficient (R^2>0.98) than Freundichl model (R^2 <0.75) at 1 mM KCl. This suggests that AMX adsorption on CMNS is followed by monolayer than multilayer. Our result is similar to AMX adsorption on core-shell $CeO_2@SiO_2$ nanoparticles in which adsorption isotherm fitted well by Langmuir model [6]. The maximum adsorption capacity of AMX on CMNS was found by Langmuir model to be 26.32 mg/g that was much higher than that of activated carbon nanoparticles [16] or organobentonite [17]. It implies that CMNS is a novel adsorbent for AMX removal from aqueous solution.

Adsorption mechanisms

Adsorption mechanism of AMX on CMNS is proposed on the basis of adsorption isotherms and the change in functional group by FT-IR spectroscopy.

Figure 6 indicates FT-IR spectra of nanosilica with CTAB modification after AMX adsorption. As can be seen, FT-IR spectra were similar to the spectra of CMNS in which two small peaks at the wavenumbers of 2852 and 2922 cm^{-1} assigned for alkyl chain of CTAB molecules did not change. On the other hand, a wavenumber at 1477 cm^{-1} assigned for –COOH decreased dramatically and a boarding peak at 1037 cm^{-1} for –NH vibration of AMX could be clearly seen [18].

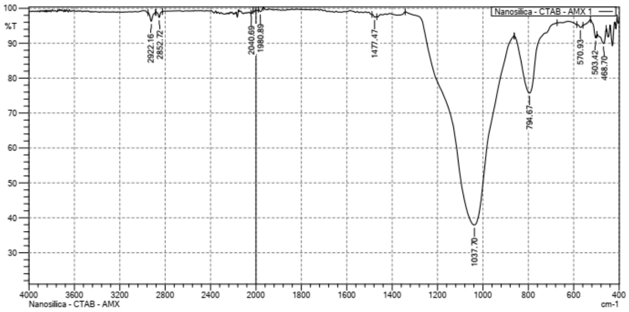

Figure 6: FT-IR spectra of CTAB modified nanosilica after AMX adsorption

It suggests that AMX adsorption on CMNS was promoted by the interaction between positively amine group of CTAB and carboxyl group of AMX molecule. This result agreed well with adsorption isotherms in which adsorption decreased with increasing ionic strength due to the screened electrostatic attraction with an increase in salt concentration. Based on the change in functional groups after AMX adsorption and adsorption isotherms, we indicate that AMX adsorption on CMNS surface is mainly controlled by electrostatic interaction and the chemi-adsorption is dominant.

Conclusion

We have investigated adsorptive removal of Amoxicillin (AMX) using cationic surfactant CTAB modified nanosilica (CMNS). Adsorption of CTAB on nanosilica was induced by both electrostatic and hydrophobic interactions. The optimum parameters for AMX removal using CMNS were pH 9, adsorbent dosage 10 mg/mL. Maximum adsorption capacity and removal efficiency were found as 26.32 mg/g and 99 %, respectively that were much higher than many other adsorbents. Adsorption isotherms of AMX on CMNS by Langmuir model was better than Freundlich model. Based on adsorption isotherm and the change in FT-IR spectra of CMNS after AMX adsorption, we demonstrate that AMX adsorption on CMNS was mainly controlled by electrostatic interaction between negatively charged AMX species and positively charged CMNS surface.

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