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Adsorption characteristics of amoxicillin antibiotic on CeO_2-coated SiO_2 nanomaterials

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ABSTRACT

This study investigated adsorption of beta-lactam antibiotic Amoxicillin (AMX) on a new material of cerium oxide-coated nanosilica (CeO_2-coated SiO_2). The CeO_2-coated SiO_2 based on rice husk, was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). Adsorption behaviors of AMX on CeO_2-coated SiO_2 at different pH and ionic strength were thoroughly studied. The highest removal of AMX using CeO_2-coated SiO_2 reached 99.26 % at pH 4 while the maximum adsorption capacity was found to be greater than 11.0 mg/g. Adsorption isotherms of AMX on CeO_2-coated SiO_2 at different ionic strength were in accordance with Freundlich model. Adsorption of amphoteric AMX species on CeO_2-coated SiO_2 increased with a decrease of salt concentration indicating that adsorption was controlled by both electrostatic and non-electrostatic interactions.

Introduction

Metal oxides are important materials that are widely used in chemical engineering, such as adsorption technology. Cerium oxide (CeO_2) is high performance adsorbent for for removal of various pollutants [1-3]. However, due to high cost material, CeO_2 is not common metal for environmental remediation. On the one hand, silica (SiO_2) is a very common material for water and wastewater treatment[4]. The evident disadvantage of SiO_2 is easily dissolved in basic media.

Recently, the material is based on the combination between CeO_2 and SiO_2 to form a new material as CeO_2-coated SiO_2 attracted intense studies [5,6].. Different methods have been investigated to synthesize CeO_2-coated SiO_2,, for example chemical precipitation [1,6], soft fabrication in the presence of surface active agent [7], sol-gel [5], solvothermal [8] and dispersion with impregnation [9]. It implies that the chemical precipitation is the one of the simplest method to fabricate CeO_2-coated SiO_2.

In order to decrease the price of material, SiO_2 should be synthesized from agricultural sub-product such as rice husk. Nano-SiO_2 is easily produced from rice husk with simple procedure due to high amount of silica in its product [4]. To the best our knowledge, the CeO_2-coated SiO_2 material based on SiO_2 rice husk has not been studied.

Amoxicillin (AMX) is one of the most popular beta lactam antibiotic that causes a serious problem in antibiotic resistance genes [10] [11]. Among various techniques for removal of antibiotic, adsorption is known as an effective technique to remove antibiotic in water enviroment with high efficiency. This technique is also suitable for developing countries by using low-cost adsorbents such as minerals, industrial wastes or agricultural sub-product.

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In this work, for the first time, we investigated the adsorption of AMX on synthesized CeO_2-coated SiO_2 nanomaterials. The CeO_2-coated SiO_2 based on rice husk was characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), and Scanning electron microscopy (SEM). Adsorption of AMX at different pH and ionic strength was thoroughly studied. Adsorption mechanism was also studied on the basis of adsorption isotherm and the change in surface charge of CeO_2-coated SiO_2 after AMX adsorption.

Experimental

Materials

Amoxicillin trihydrate with purity 98% (HPLC grade) was purchased from Tokyo Chemical Industry (Tokyo, Japan). The chemical structure of AMX is indicated in Figure 1. Cerium (III) nitrate hexahydrate (99 %) was purchased from Shanghai Zhanyun Chemical. Nanosilica (SiO_2) was fabricatd from rice husk according to our previously published papers [4,12]. Ionic strength and pH were studied by using KCl with addition of HCl and KOH (p.A, Merck, Germany). All solutions which were prepared by pure water from ultrapure water system (Labconco, USA) with a resistivity of 18.2 MΩcm. The pH of solution was monitored by using an HI 2215 pH meter (Hanna, USA). Other chemicals with analytical grade were supplied from Merck.

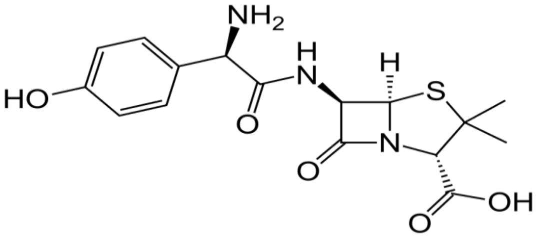

Figure 1: Structure of beta lactam Amoxicillin (AMX).

Synthesis of nano SiO_2 from rice husk

Nanosilica was synthesized from rice husk according to our previously published paper, [[12]. A 80 g of milled rice husk was placed in a 1 L beaker containing 386 g of ultrapure water and 14 g of concentrated H_2SO_4 and stirred for at least 3 h at 120 °C. After that, the pretreated rice husk was washed with ultrapure water until neutral pH was reached. Then, the rice husk was dried at 110 °C for 1 h and calcined in a thermal furnace at 800 °C for 12 h to obtain nanosilica. To purify nanosilica, diluted sulfuric acid (0.2M H_2SO_4) was used before washing with ultrapure water. Finally, nanosilica particles were re-heated at 800 °C for 24 h and then cooled to room temperature to obtain SiO_2 powder.

Synthesis of CeO_2-coated SiO_2 based on rice husk

The procedure was followed Dhmees et al. [1] with the modifications. First of all, 2.0 g SiO_2 fabricated from was dispersed in 100 mL ethanol. A 4.0 g $Ce(NO_3)_3$ was added to SiO_2 suspension. The pH was slowly adjusted to 10 by 2 M KOH. After 2h reaction, the yellow precipitation was separated by centrifuging and washed by pure water. The sample was heated for 2h before calcinating at 600 ℃ for 3h. Finally, the sample was cooled to room temperature in a desiccator.

Characterization methods

The CeO_2-coated SiO_2 was characterized by XRD, FT-IR and SEM measurements. The XRD pattern was conducted on a Bruker D8 Advance X-ray Diffactometer. The FT-IR spectra were recorded with an Affinity-1S spectrometer (Shimadzu, Kyoto, Japan) while SEM and TEM images were collected by Hitachi S4800, Japan and JEM- 2100, (Jeol, Japan)

To evaluate the change in surface charge after adsorption, the ζ potential measurements were used. The ζ potential was calculated from electrophoretic mobility with Smoluchowski's equation

$$\zeta = \frac{ue\ \eta}{\varepsilon rs\varepsilon 0} \quad (1)$$

where ζ is the ζ potential (mV), ue is the electrophoretic mobility (µm.cm/sV), η is the dynamic viscosity of the liquid (mPa.s), ε_{rs} is the relative permittivity constant of the electrolyte solution, and ε_0 is the electric permittivity of the vacuum (8.854 x 10^{-12} F/m).

Adsorption studies

All adsorption experiments were conducted in in 15mL Fancol tubes at room temperature controlled by an air conditioner at 25 ± 2℃.

The influence of pH and ionic strength on AMX adsorption were studied. The UV-Vis spectroscopy using a spectrophotometer (UV-1650 PC, Shimadzu, Japan) was used to determine all AMX concentrations at a wavelength of 229 nm.

The removal of AMX using CeO_2-coated SiO_2 was calculated by Equation(2).

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

where C_i (mg/L), Ce (mg/L) and C_f (mg/L) are the initial, the equilibrium and the final concentrations of AMX, respectively while m (g/L) is adsorbent dosage.

The adsorption isotherm is fitted by Freundlich model [13]:

$$Lnqe = LnK_F + \frac{1}{n_F} LnCe \qquad (3)$$

where K_F ($mg^{n-1}L^n/g$) is the Freundlich constant, qe is adsorption capacity and $1/n_F$ is the adsorption intensity.

Results and discussion

Characterizations of CeO_2-coated SiO_2 based on rice husk

The synthesized CeO_2-coated SiO_2 was characterized by XRD, FTIR, and SEM.

The XRD pattern of CeO_2-coated SiO_2 is indicated in Figure 2.

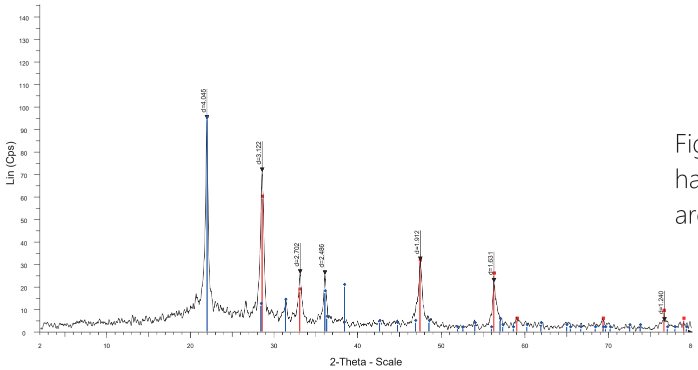

Figure 2: XRD pattern of CeO_2-coated SiO_2 nanomaterials.

Figure 2 shows that XRD pattern of CeO_2-coated SiO_2 appearred the specific peaks at 2θ 21.83°, 28.33°, 31.29°, and 36.00° for Cristobaline [14], while the peaks occurred at 28.6° , 33.1° , 47.5° and 56.4° indicates the structure of CeO_2 [6]. The CeO_2 was evident on SiO2 surface due to the appearances of both specific peaks of SiO_2 and CeO_2 with strong intensities.

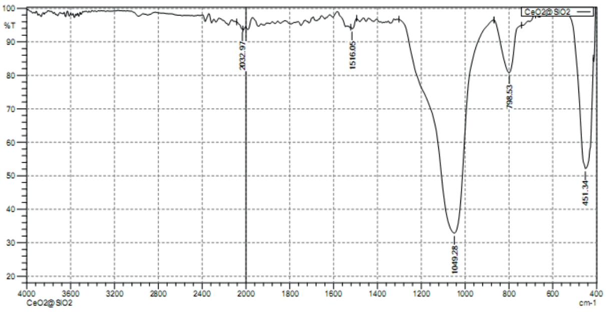

Figure 3: FT-IR spectra of CeO_2-coated SiO_2 nanomaterials

Figure 3 shows the FT-IR spectrum of CeO_2-coated SiO_2. The bands at 451.34 cm^{-1} and 798.53 cm^{-1} assigned for the Si-O bending and stretching vibrations of SiO_2, respectively. Furthermore, the Ce–O stretching appearred at the peaks of 451.34 [7]. The results of FT-IR spectrum confirmed the specific vibration of CeO_2-coated SiO_2.

The SEM image of CeO_2-coated SiO_2 in Figure. 4 show that CeO_2-coated SiO_2 has the average diameter of CeO_2-coated SiO_2 is about 30 nm.

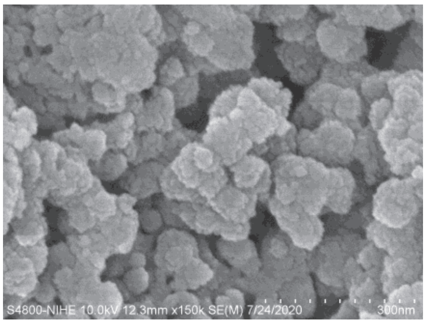

Figure 4: SEM image of CeO_2-coated SiO_2 nanomaterials

Figure 5 shows the TEM image of CeO_2-coated SiO_2 has cubic with the diameter of CeO_2-coated SiO_2 is aroundt 30 ± 10 nm.

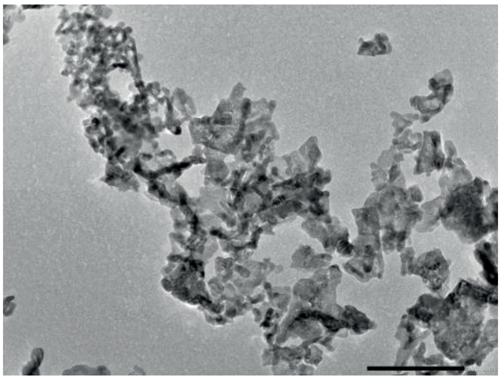

Figure 5: TEM image of CeO_2-coated SiO_2 nanomaterials

Based on XRD, FT-IR and SEM and TEM results, we indicate that CeO_2-coated SiO_2 nanomaterials successfully synthesized in the laboratory.

Adsorption of AMX on CeO_2-coated SiO_2 nanomaterials

Effect of pH

The pH of solution is one of the most effective parameter on AMX adsorption because pH induces the surface charge of CeO_2-coated SiO_2 nanomaterials and the charging AMX species.

Figure 6 shows that AMX removal using CeO_2-coated SiO_2 decreased with increasing pH that is similar to

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AMX adsorption on activated carbon nanoparticles synthesized from vine wood [15]. However at pH 3, a slighly decrease of AMX removal because of the dissolution of material at high acid media. When increasing pH from 4 to 10, the AMX removal reduced due to the decrease of positively charged CeO_2-coated SiO_2 surface while AMX occurred with amphoteric containing both negative and positive species. The removal of AMX decreased dramatically at pH > 6.0 at which the charge reversal of CeO_2-coated SiO_2 was taken place while the AMX changed to negative form. Therefore, pH 4 is the optimum solution condition and to be kept further study.

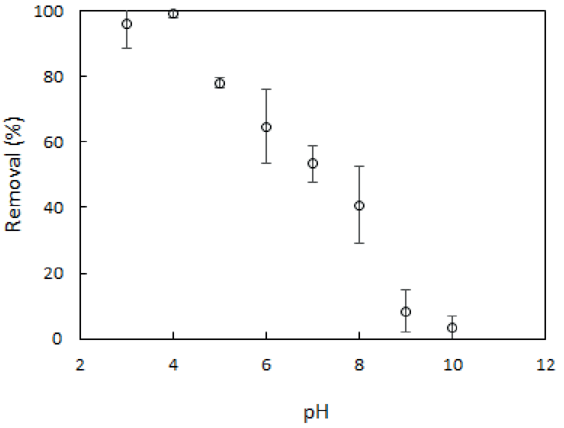

Figure 6: Effect of pH to AMX removal using CeO_2-coated SiO_2 nanomaterials ($C_{i,,AMX}$ = 2.5 mg/L, adsorbent dosage 5mg/mL, and 1 mM KCl). Error bars show standard deviations of three replicates

In order to emphasize the efficiency of CeO_2-coated SiO_2 in the AMX removal, we compare AMX removal using the SiO_2, CeO_2, and CeO_2-coated SiO_2 (Figure 7).

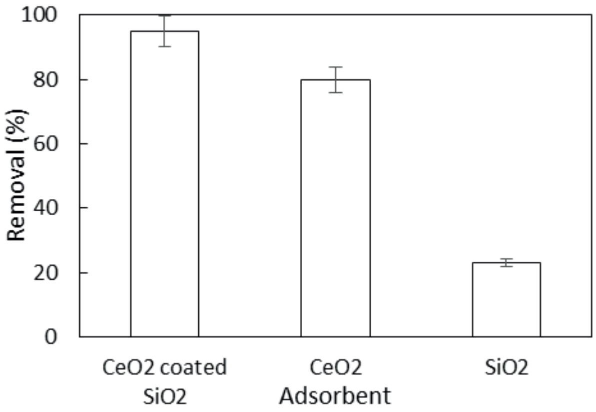

Figure 7: The AMX removal using CeO_2-coated SiO_2 CeO_2-coated SiO_2 and SiO_2 adsorbents ($C_{i,,AMX}$ = 2.5 mg/L, pH 4, adsorbent dosage 5 mg/mL, and 1 mM KCl). Error bars show standard deviations of three replicates

As can be seen in Figure 7, the AMX removal using CeO_2-coated SiO_2 was higher than CeO_2 and much higher than SiO_2. It implies that CeO_2-coated SiO_2 is the best adsorbent for AMX removal. The CeO_2 covering SiO_2 is necessary to enhance the removal efficiency.

Effect of ionic strength

The effect of ionic strength is clearly observed on the adsorption isotherms at different salt concentrations (Figure 6).

Figure 8 shows that the adsorption of AMX on CeO_2-coated SiO_2 increased with decreasing KCl concentrations from 1 to 100 mM. The Freundlich model can fit the isotherms well with R^2 > 0.971 that is much better than Langmuir isotherms with R^2< 0.820. In other words, adsorption of AMX on CeO_2-coated SiO_2 followed by multi-layer than mono-layer (n_F >2.2). The maximum adsorption capacity of AMX on CeO_2-coated SiO_2 was found to be 11 mg/g that was higher than using other adsorbent [4].

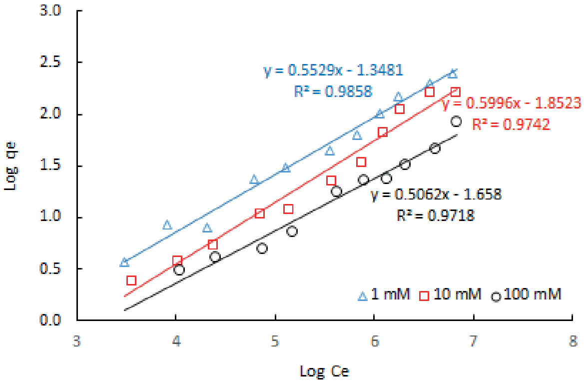

Figure 8: Adsorption isotherms of AMX on CeO_2-coated SiO_2 nanomaterials at different KCl concentrations fitted by the Freundlich model

Adsorption mechanisms

Adsorption mechanism of AMX on CeO_2-coated SiO_2 is suggested based on adsorption isotherms and the surface charge change by ζ potential measurements.

The surface charge change by ζ potential measurement

To determine the change in surface charge of CeO_2-coated SiO_2 after AMX adsorption, we measured the ζ potential using Smoluchowski's equation [16].

The ζ potentials of CeO_2-coated SiO_2 before and after AMX adsorption at pH 4 in 1 mM KCl are indicated in Figure 7.

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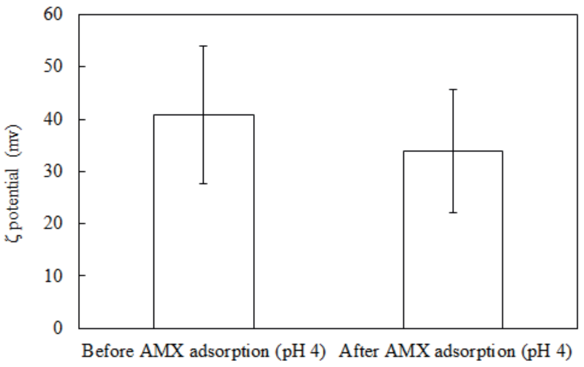

Figure 9: The ζ potential of CeO_2-coated SiO_2 before and after AMX adsorption at pH 4 in 1 mM KCl.

Figure 9 shows that at pH 4, after AMX adsorption the positive charge of CeO_2-coated SiO_2 decreased. At pH 4, adsorption of AMX was highest that induced the significant decrease in surface charge. Although, at pH 4, the zitterionic form of AMX is dominated because this pH is greater than pKa1 of AMX (2.67), the adsorption is higher Other interactions such as hydrogen bonding, hydrophobic interactions may induce the AMX adsorption but the main driving force is electrostatic attraction between negative AMX species and positvely charged CeO_2-coated SiO_2. The results were in good agreement with FT-IR spectra of CeO_2-coated SiO_2 after AMX adsorption (not shown here). After AMX adsorption, the wavenumber at about 1400 cm^{-1} for –COOH enhanced while the assigned peak at 1000 cm^{-1} for –NH vibration did not observe. The change in surface charge by ζ potential and surface vibration group change by FT-IR demonstrate that AMX adsorption on CeO_2-coated SiO_2 was mainly controlled by electrostatic interaction.

Conclusion

We have studied adsorption of Amoxicillin (AMX) on nano CeO_2-coated SiO_2. Nano CeO_2-coated SiO_2 which was fabricated by chemical precipitation method based on rice husk, was characterized by X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR), and Scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The nanometer-sized CeO_2-coated SiO_2 with average diameter was approximately 30 nm. The optimum solution conditions of AMX nano CeO_2-coated SiO_2 was found to be pH 4.0 and 1 mM KCl. Adsorption isotherms of AMX onto nano CeO_2-coated SiO_2 was well represented by Freundlich model. Based on adsorption isotherm and the change in surface charge by ζ potential measurment and FT-IR spectra of CeO_2-coated SiO_2 after AMX adsorption, we indicate that AMX adsorption on nano CeO_2-coated SiO_2 was controlled by both electrostatic and non-electrostatic interactions in which electrostatic one was dominant.

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