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 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 environment 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 fabricated 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 other chemicals with analytical grade were purchased from Shanghai Zhanyun Chemical.

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$_2$SO$_4$ 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$_2$SO$_4$) 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 rice husk 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 °C 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 Difffactometer. 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

$$\zeta = \frac{ue \eta}{\varepsilon_0 rs}$$

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), $\varepsilon_r$ is the relative permittivity constant of the electrolyte solution, and $\varepsilon_0$ is the electric permittivity of the vacuum ($8.854 \times 10^{-12}$ 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°C.

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).

$$Removal \ (%R) = \frac{C_i - C_f}{C_i} \times 100\%$$

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where \( C_i \) (mg/L), \( C_e \) (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]:

\[
\ln q_e = \ln K_F + \frac{1}{n_F} \ln C_e
\]

where \( K_F \) (mgn\(^{-1}\)L/g) is the Freundlich constant, \( q_e \) 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 shows that XRD pattern of CeO\(_2\)-coated SiO\(_2\) appeared the specific peaks at 2\( \theta \) 21.83\(^\circ\), 28.33\(^\circ\), 31.29\(^\circ\), and 36.00\(^\circ\) for Cristobaline [14], while the peaks occurred at 28.6\(^\circ\), 33.1\(^\circ\), 47.5\(^\circ\) and 56.4\(^\circ\) indicates the structure of CeO\(_2\) [6]. The CeO\(_2\) was evident on SiO\(_2\) surface due to the appearances of both specific peaks of SiO\(_2\) and CeO\(_2\) with strong intensities.

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 appeared 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 around 30 ± 10 nm.

Figure 5: TEM image of 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 slightly 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.

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 8).

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].

Adsorption mechanisms

Adsorption mechanism of AMX on CeO$_2$-coated SiO$_2$ is suggested based on adsorption isotherms and the surface charge change by $\zeta$ potential measurements.

The surface charge change by $\zeta$ potential measurement

To determine the change in surface charge of CeO$_2$-coated SiO$_2$ after AMX adsorption, we measured the $\zeta$ potential using Smoluchowski’s equation [16].

The $\zeta$ potentials of CeO$_2$-coated SiO$_2$ before and after AMX adsorption at pH 4 in 1 mM KCl are indicated in Figure 7.
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, the zwitterionic 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 positively 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 measurement 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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References

1. Dhmees, A.S.; Rashad, A.M.; Eliwa, A.A.; Zawrah, M.F., Preparation and characterization of nano SiO$_2$@CeO$_2$ extracted from blast furnace slag and uranium extraction waste for wastewater treatment, Ceramics International, 45, (2019) 7309-7317. https://doi.org/10.1016/j.ceramint.2019.01.014
8. Nguyen, H.T.T.; Ohtani, M.; Kobiro, K., One-pot synthesis of SiO$_2$–CeO$_2$ nanoparticle composites

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