

Removal of Ciprofloxacin and Carbamazepine by Adsorption on Functionalized Mesoporous Silicates

Patiparn Punyapalukul and Thitikamon Sitthisorn

Abstract—Ciprofloxacin (CIP) and Carbamazepine (CBZ), non-biodegradable pharmaceutical residues, were become emerging pollutants in several aquatic environments. The objectives of this research were to study the possibility to recover these pharmaceuticals residues from pharmaceutical wastewater by increasing the selective adsorption on synthesized functionalized porous silicate, comparing with powdered activated carbon (PAC). Hexagonal mesoporous silicate (HMS), functionalized HMSs (3-aminopropyltriethoxy, 3-mercaptopropyltrimethoxy and n-octyldimethyl) were synthesized and characterized physico-chemical characteristics. Obtained adsorption kinetics and isotherms showed that 3-mercaptopropyltrimethoxy functional groups grafted on HMS provided highest CIP and CBZ adsorption capacities; however, it was still lower than that of PAC. The kinetic results were compatible with pseudo-second order. The hydrophobicity and hydrogen bonding might play a key role on the adsorption. Furthermore, the capacities were affected by varying pH values due to the strength of hydrogen bonding between targeted compounds and adsorbents. Electrostatic interaction might not affect the adsorption capacities.

Keywords—Adsorption, Carbamazepine, Ciprofloxacin, Mesoporous Silicates, Surface functional groups

I. INTRODUCTION

CIPROFLOXACIN (CIP) is one of the antibiotics in fluoroquinolone group, which is widely used for infectious symptoms treatment. CIP can be detected with the wide range of concentrations (0.2 ppb-30 ppm) from several sources, for example, hospital sewage, pharmaceutical production plant, and even in effluent of wastewater treatment plant [1] – [4]. CIP can affect to aquatic microorganisms and plant even in very low concentration [5], [6] due to its characteristics, including persistency and low biodegradability [7]. It should be noted that ionic molecular form of CIP is depend on pH of the solution. In recent years, various methods have been studied for removing CIP from water, for

instance, biodegradation and advance oxidation processes [7], however, the removal efficiencies was not high enough and effect of degradation by-products still have not been reported yet. Adsorption is the widely used chemical process for removing chemicals that cannot be eliminated by conventional treatment process.

Carbamazepine (CBZ) is a worldwide drug belongs to epileptic group. It is widely used for remediation several diseases or symptoms such as alcoholism [8], opiate withdrawal [9], relieve depressant [10], and epileptic [11]. CBZ was frequently detected in the environment including water and soil phase, particular in the sandy soil. [12] reported that no microbial degradation in sandy sediment. Moreover, several reports indicated that CBZ cannot be eliminate or partly removed approximately less than 10% in wastewater treatment [13]-[15].

Hexagonal mesoporous silicate (HMS) having been studied extensively in adsorption and catalysis fields has mesoscale pore and silanol as surface functional group. HMS surface can be modified by various methods to enhance specific characteristics (e.g., organic ligand modification). The objective of this study is to investigate the effects of surface functional groups of adsorbents on CIP and CBZ adsorption capacities. Batch adsorption experiments were carried out with various types of inorganic materials with different surface functional groups of HMS, comparing with powdered activated carbon (Shirasagi S-10, Japan EnvironChemicals Ltd.). Three methods of organic-ligand grafting on HMS with 3-aminopropyltriethoxy, 3-mercaptopropyltrimethoxy and n-octyldimethyl functional group were also employed to investigate the effects of physico-chemical characteristics on CIP and CSZ adsorption capacities.

II. MATERIALS AND METHODS

HMS synthesis

HMS was prepared by mixing 29.6 mol of water with 0.27 mol of dodecylamine and 9.09 mol of ethanol to form as organic template of HMS. Add 1.0 mol of tetraethoxysilane (TEOS) in the mixture and were then mixed under vigorous stirring. The reaction mixture was aged at an ambient temperature for 18 h. The resulting mixture was filtered and air-dried on a glass plate. The product was calcined in air

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under static condition at 650 °C for 4 h to remove organic template (Tanev et al., 1996).

Synthesis of functionalized HMS

3-aminopropyltriethoxy-functionalized HMS (A-HMS) was prepared by mixing 50 mol of water with 0.25 mol of dodecylamine and 10.25 mol of ethanol to form as organic template of HMS. Add 1.0 mol of tetraethoxysilane (TEOS) in the mixture and were then mixed under vigorous stirring for 30 min. Then 0.25 mol of 3-aminopropyltriethoxysilane (APTES) was added in the mixture. The reaction mixture was vigorously stirred for 20 h at ambient temperature and the resulting were filtered and air-dried on a glass plate for 24 h. Residual organosilane and organic template were removed by solvent extraction for 72 h with ethanol. [16]

3-mercaptopropyltrimethoxy-functionalized HMS (M-HMS) was prepared by mixing 50 mol of water with 0.25 mol of dodecylamine and 10.25 mol of ethanol to form as organic template of HMS. Add 1.0 mol of tetraethoxysilane (TEOS) in the mixture and were then mixed under vigorous stirring for 30 min. Then 0.25 mol of 3-mercaptopropyltrimethoxysilane (MPTMS) was added in the mixture. The reaction mixture was vigorously stirred for 20 h at ambient temperature and the resulting were filtered and air-dried on a glass plate for 24 h. Residual organosilane and organic template were removed by solvent extraction for 72 h with ethanol. [16]

Octyldimethyl-functional HMS (OD-HMS) was prepared by these following method: drying 5 g of HMS was put in a 250 ml three-neck round flash which containing 140 ml of dichloromethane and stirrer bead. The mixture is stirred, and then 1.8 g of 1-methyl-2-pyrrolidine and 3.6 g of n-octyldimethylchlorosilane were added under N₂ flow. The mixture was maintained stirred under reflux at 60°C for 4 hr, after that, filtrated and wash with 50 ml of chloroform twice and 50 ml of ethanol. The sample was drying under vacuum at 40 °C for 4 hr; the OD-HMS was obtained.

Characterization of adsorbents

Powder X-ray diffraction (XRD) patterns of synthesized adsorbents were recorded on a powder diffractometer equipped with Cu K α radiation (Bruker AXS Model D8 Discover). BET specific surface area was calculated from nitrogen adsorption isotherms at relative pressure between 0.04 and 0.20 measured at 77 K by a ASAP 2020 micromeritic surface area and porosity analyzer. Pore diameter and mesopore volume were calculated by D-H method. Surface functional groups were investigated after drying at 105 oC for 4 hours by FT-IR spectrophotometer (Nicolet Impact 410). Surface charges of all adsorbents were determined by acid-base titration with HCl and NaOH as in the methods previously described by Patiparn et al. [17].

Adsorption experiments

Adsorption kinetics and isotherms were conducted by adding to a glass vial with a stopper, and 20 ml of synthetic CIP and CBZ solution with known concentrations was added.

The adsorption experiments were processed at 25 + 2 °C under shaking at 220 rpm (Green SSeriker II) until the equilibrium concentration was reached. The mixture was filtered through GF/C glass filter (pore diameter 0.47 μ m). The filtrate was analyzed by a UV-spectrophotometer at 271 nm (Shimadzu UV 1601) for residual CIP concentration. Adsorption experiments were conducted at pH 5, 7, and 9 for both HMSs and PAC with 0.01 M ionic strength.

The pseudo-first-order and pseudo-second-order kinetic models are expressed as Equations 1, 2 and 3, respectively.

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (1)$$

$$\frac{t}{q_t} = \frac{1}{2k_2 q_e^2} + \frac{t}{q_e} \quad (2)$$

$$h = k_2 q_e^2 \quad (3)$$

Where k_1 is Lagergren rate constant (hr^{-1}); k_2 is pseudo second -order rate constant ($\text{g mg}^{-1} \text{hr}^{-1}$); q_e and q_t are amount of pollutant sorbed at equilibrium and at time t (hr), respectively, and h is initial adsorption rate (mg/g.h).

The Langmuir and Freundlich adsorption isotherm are calculated by Equations (5) and (6).

$$q = \frac{q_m b C_e}{1 + b C_e} \quad (5)$$

$$q = k C_e^{(1/n)} \quad (6)$$

Where q_m is the maximum adsorption capacity; b is Langmuir coefficient; k and n are parameters in Freundlich Isotherm

III. RESULTS AND DISCUSSION

Physico-chemical characteristics of adsorbents

The characteristics of synthesized adsorbents are shown in Table 1. PAC and M-HMS contained larger specific area comparing with the other adsorbents. Pore sizes of synthesized HMSs were in mesoporous scale. A-HMS had largest pore size which might be caused by collapse of it own silicate structure and surface area detected by XRD pattern. FT-IR spectra (data was not shown), can confirmed the presence of grafted organic functional groups on synthesized HMSs including, inaccessible silanol group on every silicate adsorbents. Pristine HMS and A-HMS was hydrophilic (water-like) due to hydrogen bonding caused by silently and amino functional groups on the surfaces. However, M-HMS, OD-HMS and PAC, which have non-polar organic functional groups and high complexity of surface of PAC, had highly hydrophobic. Moreover, pH_{zpc} of adsorbents were also shown in Table 1.

TABLE I PHYSICO-CHEMICAL CHARACTERISTICS OF ADSORBENTS

Adsorbents	Surface area (m ² /g)	Pore size (nm)	Water affinity	pH _{zpc}
HMS	712	2.60	Hydrophilic	5.5
A-HMS	262	3.95	Hydrophilic	9.5
M-HMS	912	2.48	Hydrophobic	6.2
OD-HMS	477	2.36	Hydrophobic	4.4
PAC	980	1.90	Hydrophobic	9.5

Adsorption kinetics

CIP and CBZ adsorption kinetics of HMSs and PAC were conducted at pH 7 with initial concentration of 6 and 9 mg/L, respectively. As shown in Figure 1 and 2, CIP and CBZ concentrations were dramatically decrease in 30 and 120 min, respectively and then achieve the saturation at approximately 9 hr, except for A-HMS. These obtained results were fitted well with a pseudo-second order model in every tested adsorbent as shown in Table 2 and 3.

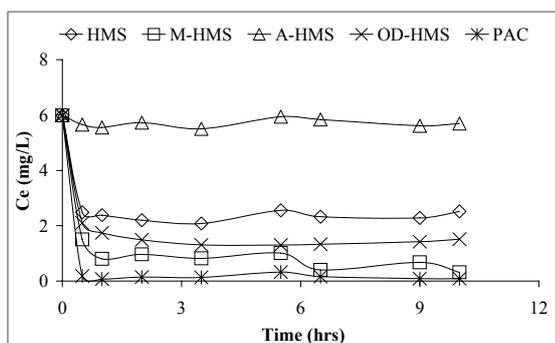


Fig. 1 Adsorption kinetic of CIP on HMSs and PAC at initial concentration 6 mg/L with pH 7, 25 ± 2 °C

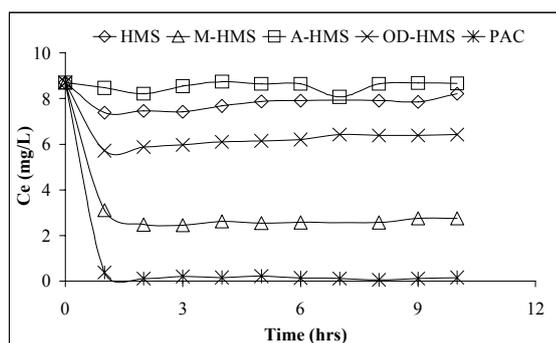


Fig. 2 Adsorption kinetic of CBZ on HMSs and PAC at initial concentration 9 mg/L with pH 7, 25 ± 2 °C

TABLE II KINETICS VALUES CALCULATED FOR CIP ADSORPTION ONTO HMS, FUNCTIONALIZED HMSS AND PAC

	Pseudo-second order			Experiment q _e (μg/g)	h (μg/g h)
	R ²	k ₂ (g/μg h)	Cal q _e (μg/g)		
HMS	0.9997	0.776	1.760	1.953	2.40
A-HMS	0.9978	0.013	0.171	0.242	0.04
M-HMS	0.9995	1.194	2.860	2.847	0.103
OD-HMS	0.999	3.124	2.280	2.340	16.23
PAC	1	0.059	2.953	2.956	0.52

TABLE III KINETICS VALUES CALCULATED FOR CBZ ADSORPTION ONTO HMS, FUNCTIONALIZED HMSS AND PAC

	Pseudo-second order			Experiment q _e (μg/g)	h (μg/g h)
	R ²	k ₂ (g/μg h)	Cal q _e (μg/g)		
HMS	0.9952	0.229	0.541	0.654	0.067
A-HMS	0.9999	3.731	0.205	0.244	0.156
M-HMS	0.9886	0.211	3.050	3.118	1.966
OD-HMS	0.9987	1.550	2.427	2.957	9.124
PAC	1	0.634	4.234	4.279	11.364

Adsorption Isotherms

The adsorption studies of CIP and CBZ were conducted at pH 6.8 – 7.2 with 0.01 M ionic strength controlled by phosphate buffer. CIP, which has pK_a at 6.10 (carboxyl group) and 8.70 (amine group) [18], and CBZ, which contained pK_a at 2.30 (ketone group) and 13.90 (amine group), were in neutral charge species. These two compounds had two pK_a values since they can be dissociate at two different functional groups depending on pH of solution. At this pH range, PAC and A-HMS provided the positively charged surface, while HMS, M-HMS and OD-HMS expressed the negative charge. The neutral species of CIP and CBZ were expected to have low electrostatic attraction with the charged adsorbents and can be neglected.

From Fig. 3, it was found that hydrophobic adsorbents (PAC, M-HMS and OD-HMS) provided higher adsorption capacity than the hydrophilic one (HMS and A-HMS). Note that the molecule dimensions of CIP (0.57 nm in width and 0.95 nm in length) and CBZ (0.72 nm in width and 1.35 nm in length) were smaller than pore size of all adsorbents; therefore, the effects of adsorbents' pore size can be neglected. As mentioned above, the adsorption mechanisms of CIP on the adsorbents' surface tend to be the results of water affinity of adsorbents as well as hydrogen bonding. It should be noted that adsorption of CIP on pristine HMS due to interaction between silanol groups on surface and intermolecular hydrogen bonding part of CIP molecule might be stronger than hydrogen bonding interacted with amino functional on A-HMS surface. Moreover, in case of M-HMS, hydrogen bonding caused by mercapto functional groups should be suggested to enhance the adsorption capacity comparing with OD-HMS.

In case of CBZ adsorption, the capacities obtained from adsorbents used in this study had a similar trend with CIP adsorption. Hydrophobicity of materials might play a key role

on the adsorption. Moreover, hydrogen bonding between amide groups ($-NH_2$) on the targeted compound surface that can interact with the surface functional group of materials was mainly responsible for this adsorption. It can be noticed from Fig 4 that CBZ interaction between silanol group on HMS and CBZ might be stronger than hydrogen bonding interacted with amino functional group on A-HMS surface. In addition, CBZ can also interact with mercapto group on M-HMS comparing with the hydrophobic OD-HMS.

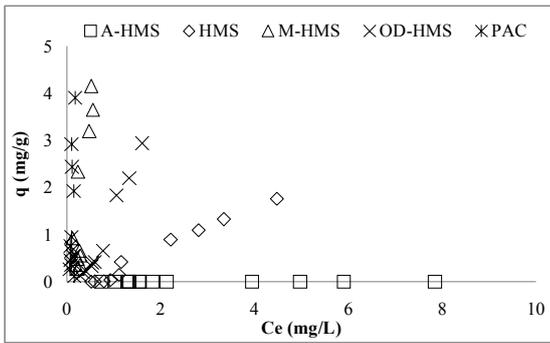


Fig. 3 Adsorption capacity of CIP with different surface functional groups at pH 7 and 25 ± 2 °C

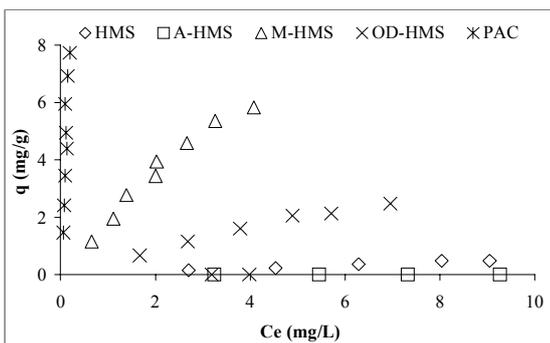


Fig. 4 Adsorption capacity of CBZ with different surface functional groups at pH 7 and 25 ± 2 °C

Effect of pH on CIP adsorption capacities

Fig 5-9 show the CIP adsorption capacities of studied adsorbent at varying pH for 5, 7, and 9. It can be firstly seen that the capacities were affected by pH change, except for A-HMS and PAC. From Fig 5, the highest adsorption capacity between HMS and CIP occur at pH 5 following by pH 7 and 9. Therefore, it can be concluded from this case that the electrostatic interaction might not affect the adsorption capacity of CIP on HMS as well as M-HMS, OD-HMS, A-HMS. In case of PAC, the adsorption capacity of CIP on PAC was not affected by changing of pH value as can be seen from Fig 9. The main adsorption mechanism might be hydrogen bonding between CIP and adsorbents, which was weaker at high pH since the increasing of pH might affect to the carboxylic group of CIP [19] resulting in decreasing of hydrogen bonding between CIP and surface functional group

of the adsorbents. In case of A-HMS, charge density surface can be ionized to be positive at pH around 9; where CIP contained negatively charged, but the effect of attractive interaction between positive surface and negative molecule of CIP still cannot be detected significantly.

The results of adsorption capacities of applied adsorbents at pH 5, 7, and 9 were fitted with Langmuir and Freundlich isotherm model by linear regression in order to describe the adsorption mechanism occurred in this study. It was found that the obtained experimental data had no relationship with Freundlich isotherm. On the other hand, Langmuir isotherm can be fitted to the results with very high correlation coefficients.

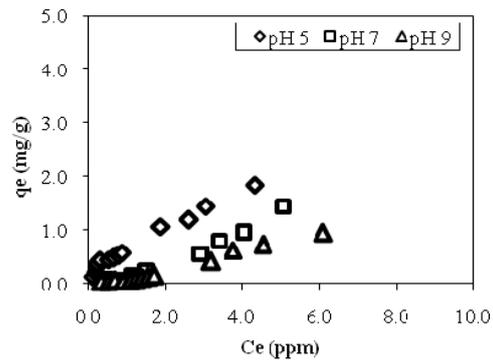


Fig. 5 Adsorption isotherms of CIP on pristine HMS at pH 5, 7 and 9 (25 ± 2 °C)

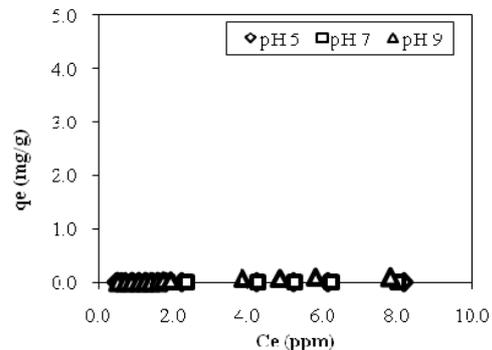


Fig. 6 Adsorption isotherms of CIP on pristine A-HMS at pH 5, 7 and 9 (25 ± 2 °C)

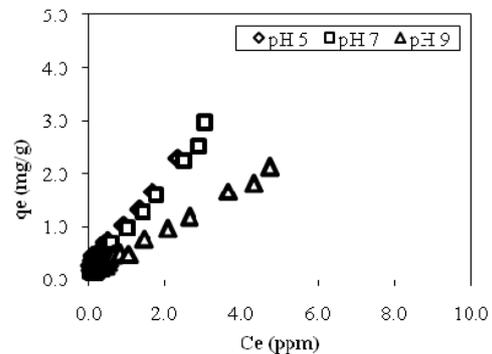


Fig. 7 Adsorption isotherms of CIP on pristine M-HMS at pH 5, 7

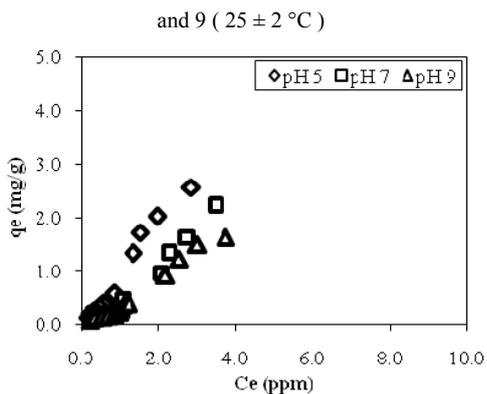


Fig. 8 Adsorption isotherms of CIP on pristine OD-HMS at pH 5, 7 and 9 (25 ± 2 °C)

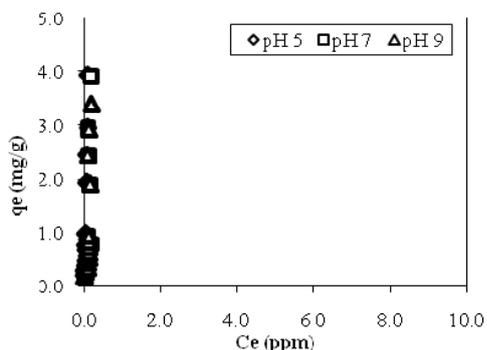


Fig. 9 Adsorption isotherms of CIP on pristine PAC at pH 5, 7 and 9 (25 ± 2 °C)

IV. CONCLUSION

Ciprofloxacin and Carbamazepine, non-biodegradable pharmaceutical residues, can be recovered from synthetic wastewater by adsorption on 3-mercaptopropyltrimethoxy groups functionalized hexagonal mesoporous silicate due to hydrophobicity and hydrogen bonding. The adsorption kinetics and isotherms results were compatible with pseudo-second order model and Langmuir equation, respectively. The adsorption capacities were affected by varying pH values due to the strength of hydrogen bonding between targeted compounds and adsorbents. Electrostatic interaction might not affect the adsorption capacities.

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