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Article

Retention of Carbamate Pesticides by Different Surfactant-Modified Sorbents: a Comparative Study

Prapha Arnnok and Rodjana Burakham*

Materials Chemistry Research Center, Department of Chemistry and Center for Innovation in Chemistry, Faculty of Science, Khon Kaen University, 40002 Khon Kaen, Thailand

Diferentes sorventes sólidos modificados com surfactantes foram investigados comparativamente para a retenção de pesticidas carbamato em solução aquosa. Três sorventes modificados, incluindo alumina tratada com dodecil sulfato de sódio (SDS), sílica revestida com brometo de cetil trimetil amônio (CTAB) e zeólita revestida com CTAB foram preparados usando diferentes concentrações de surfactante. Os pesticidas carbamato estudados incluíram oxamil, metomil, aldicarb, carbofurano, carbaril, isoprocarb, metiocarb, promecarb e carbosulfano e foram analisados por cromatografia líquida de alta eficiência (HPLC) com UV. A adsorção de pesticidas carbamato (faixa de concentração de 0,5-5,0 mg L^{-1}) nos sorventes modificados com surfactante, seguiu regressão linear com os coeficientes de correlação na faixa de 0,857-0,995. A zeólita modificada com CTAB apresentou alta captação para carbofurano, carbaril, metiocarb e carbosulfano. Alumina modificada com SDS demonstrou alta captação de carbaril, isoprocarb, metiocarb, promecarb e carbosulfano. Sílica modificada com CTAB apresentou alta captação de metiocarb, promecarb e carbosulfano. A dessorção dos pesticidas de carbamato dos sorventes modificados com surfactantes usando metanol foram melhores que as obtidas dos sorventes não modificados. O estudo provou que os sorventes modificados com surfactantes são efetivos para a extração de pesticidas carbamato.

Different surfactant-modified solid sorbents have been comparatively investigated for retention of carbamate pesticides in aqueous solution. Three modified-sorbents, including sodium dodecyl sulfate (SDS) treated alumina, cetyltrimethyl ammonium bromide (CTAB) coated silica and CTAB coated zeolite, were created using different surfactant concentrations. The studied carbamate pesticides including oxamyl, methomyl, aldicarb, carbofuran, carbaryl, isoprocarb, methiocarb, promecarb and carbosulfan were analyzed by HPLC/UV. Adsorption of all carbamate pesticides (concentration range between 0.5-5.0 mg L^{-1}) onto surfactant-modified sorbents followed linear regressions with the correlation coefficients in the range of 0.857-0.995. CTAB-modified zeolite showed high uptake values for carbofuran, carbaryl, methiocarb and carbosulfan. SDS-modified alumina demonstrated high uptake values for carbaryl, isoprocarb, methiocarb, promecarb and carbosulfan. CTAB-modified silica gave high uptake values for methiocarb, promecarb and carbosulfan. Desorption of carbamate pesticides from surfactant-modified sorbents using methanol were better than that obtained from unmodified sorbents. The study clearly proved that the surfactant-modified sorbents are effective for carbamate pesticides extraction.

Keywords: surfactant-modified sorbent, carbamate pesticides, sorption, retention

Introduction

Carbamates are one of the major persistent organic pesticides widely used in agriculture to protect a variety of crops. They are suspected carcinogens and mutagens since they are acetylcholinesterase inhibitor, which is the enzyme responsible for the hydrolysis of acetylcholine.[1] Solid phase extraction (SPE) using a variety of solid sorbents, i.e., C18, graphene-based magnetic nanocomposite, has been reported for preconcentration of carbamate pesticides prior to their analysis.[2-4] However, development or modification of new solid sorbents with the possibility of extracting the target compounds with high capacity, quantitative sorption and elution, regenerability and cost effectiveness, is of great interest.

Recently, surfactants have been frequently used to modify several solid sorbents, such as clay,[5] alumina,[6-9] zeolite,[10-12] silica[13-15] and magnetic nanoparticle,[16,17]

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*e-mail: rodjbu@kku.ac.th

since it can form self-aggregates on solid surfaces. At surfactant concentration below its critical micelle concentration (CMC), monolayers or hemimicelles are formed, while bilayers or admicelles are formed when surfactant concentration is higher than the CMC. Hemimicelles, admicelles or mixed hemimicelles/admicelles are created on solid surfaces depending on surfactant concentration.[8,18,19] The modification of sorbent with surfactant has been performed to alter sorption ability of sorbent. The surfactant-modified sorbents are widely applied for organic compound sorption, as their surfactant aggregates are able to solubilize a wide variety of organic compounds.[19-21]

Anionic surfactant-modified alumina has been widely studied since alumina has high surface area with positive charge at the solution pH below its point of zero charge, and anionic surfactants such as sodium dodecyl sulfate (SDS) can adsorb onto alumina surface. Unmodified alumina has low sorption ability for organic compounds due to its low hydrophobicity. The affinity for organic compounds is increased when it is coated with SDS. SDS-γ-alumina admicelles have been investigated for concentrating traces of chlorophenols in water. It pointed out that chlorophenols were concentrated onto the admicelles. The sorption capability of chlorophenols found was also increased with increasing their hydrophobicity.[6] Application of SDS-treated alumina for removal of herbicides from water has also been reported, and the enhancement in sorption of herbicides on surfactant treated alumina was observed.[9]

The cationic surfactant is effectively adsorbed onto silica surface because of negative charges on silica surface; therefore, silica gel was used as sorbent for removal of cationic surfactant from industrial waste water.[22] Furthermore, surfactant was used to modify properties of silica surface. The property of silica nanoparticles modified with cationic surfactant has been studied. It has been demonstrated that cationic surfactant formed bilayers on the silica surface.[13] Surfactant-coated silica has been applied for phenanthrene partitioning.[15] It was investigated for protein purification and found to be efficient media for protein separation as well.[14]

Cetyltrimethyl ammonium bromide (CTAB) is regularly used since the CTAB-modified zeolite can have both hydrophilic and hydrophobic phases, thus, it can be applied to wildly groups of target compounds. For example, CTAB-modified zeolite was proposed for sorption of perchloroethylene. Perchloroethylene sorption was affected by the bound surfactant molecule configuration and the faction organic carbon content.[10] Also, surfactant-modified zeolite has been employed for removal of water contaminants, including nitrate, humic acid, ionizable phenolic compounds and non-ionizable organic compounds.[11,12,23,24]

In this study, inorganic solid supports, which normally are used as sorbent materials, including silica, alumina and zeolite, were modified with surfactants to improve their sorption capability for organic compounds. Selection of surfactants depended on the nature of solid surfaces. We selected surfactant-sorbent systems that have been reported for sorption of organic substances. Anywise, application of these systems for pesticide residues should be remarked. Mixture of nine carbamate pesticides was used as model analytes since we intended analysis of pesticide residues in environmental samples. Adsorption and desorption of carbamate pesticides onto surfactant-modified sorbents were investigated. Three different surfactant-modified sorbents were prepared, including SDS-modified alumina, CTAB-modified silica and CTAB-modified zeolite. The effect of surfactant concentration on pesticide sorption was studied as well. The performance of three sorbents for retention of each carbamate was comparatively investigated. To the best of our knowledge, it is for the first time that surfactant-modified mineral oxide sorbents is studied for sorption of carbamate pesticides. We attempt the introduction of these surfactant-modified sorbents to the preconcentration of carbamate pesticides prior to instrumental analysis.

Experimental

Materials

SDS was obtained from VWR International Ltd. (Poole, England). CTAB was purchased from Sigma-Aldrich (St. Louis, USA). Their properties are presented in Table 1. All solid sorbents used were supplied by Merck KGaA (Darmstadt, Germany). The average particle diameters of solid sorbents used in this work are as follow: zeolite (molecular sieve 0.3 nm), beads 2.00 mm; alumina, 0.063-0.200 mm; silica, 0.040-0.063 mm. All standard carbamate pesticides were of analytical standard grade. Carbofuran (CBF, log K_{ow} 2.32), promecarb (PMC, log K_{ow} 3.05), methomyl (MTM, log K_{ow} 1.70) and isoprocarb (IPC, log K_{ow} 2.63) were purchased from Sigma-Aldrich Chemie GmbH (Steinheim, Germany). Methiocarb (MTC, log K_{ow} 3.06) was purchased from ChemService (West Chester, USA). Oxamyl (OXM, logK_{ow} 1.12), carbosulfan (CBS, log K_{ow} 4.61), aldicarb (ADC, log K_{ow} 1.88) and carbaryl (CBR, log K_{ow} 2.65) were purchased from AccuStandard (New Haven, USA). A stock solution containing 1000 mg L^{-1} of each pesticide was prepared in methanol. The working solution was obtained by diluting the stock solution with water. HPLC-grade methanol was obtained from Merck KGaA (Darmstadt, Germany). Other reagents used were of analytical grade. Ultrapure water ($18.2\ M\Omega$ cm) used in all experiments was prepared by a Simplicity water purification system from Millipore (Massachusetts, USA).

Preparation and characterization of surfactant-modified sorbents

Three solid sorbents, including silica, alumina and zeolite, were studied in this work. The cationic surfactant (CTAB) and anionic surfactant (SDS) were used to modify the solid sorbents. Zeolite and silica were treated with CTAB, while alumina was coated with SDS. The solid sorbents were modified using various initial concentrations of surfactant solutions, including at the CMC, less than the CMC (< CMC) and greater than the CMC (> CMC). For the < CMC treatment, zeolite and silica were treated with 0.5 mmol L^{-1} CTAB; alumina was coated with 5.0 mmol L^{-1} SDS. For the > CMC treatment, 10.0 mmol L^{-1} CTAB and 90.0 mmol L^{-1} SDS were used. A 20 mL of surfactant solution was added to a 50 mL Erlenmeyer flask containing 0.5 g of each solid sorbent. Only for the SDS-alumina system, pH of the solution was adjusted to 2 with 1 mol L^{-1} HCl. The mixture was shaken mechanically for 24 h at 150 rpm. After decanting the supernatant, 10 mL of deionized water was added to sorbent. The mixture was then shaken for 10 min at 150 rpm. The supernatant was decanted again. This washing step was repeated twice to ensure that excess or loosely bound surfactants were removed. Then the sorbents were air-dried and stored in closed bottles for subsequent uses.

In order to characterize the obtained surfactant-modified sorbents, a morphology study was performed using a Hitachi S3000N scanning electron microscope (Hitachi, Tokyo, Japan). For Fourier transform infrared spectroscopy (FT-IR) analysis, the sorbent was pounded, well mixed with KBr (1:10) and pressed into disk before measuring with a Spectrum One FT-IR spectrometer (PerkinElmer, Massachusetts, USA). Unmodified sorbents and surfactants were also investigated to prove the modification.

Adsorption and desorption of carbamate pesticides

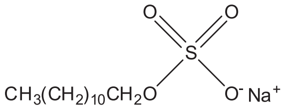
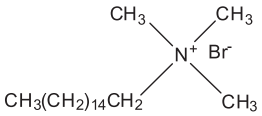
The studied carbamate pesticides used in this study include OXM, MTM, ADC, CBF, CBR, IPC, MTC, PMC and CBS. Adsorption and desorption experiments were carried out in batch systems. To study the adsorption, 5.00 mL of carbamate solution and 0.1 g of solid sorbent were mixed in a 15 mL polypropylene tube with cap. The mixture was mechanically shaken for 15 min at 200 rpm, and then centrifuged at 3,000 rpm for 10 min. The supernatant was filtered through 0.45 µm nylon membrane filter before analysis. All experiments were performed in triplicate. Blank solutions containing solid sorbents and deionized water were treated in the same manner as the carbamate pesticide solution. Selection of initial concentrations of each pesticide was based on their detection sensitivities.

Desorption experiments were studied by adding 1.00 mL of methanol to the sorbent after adsorption process as described above. After that, the mixture was put in ultrasonic bath for 5 min, and centrifuged at 3000 rpm for 10 min. The supernatant was filtered through 0.45 µm nylon membrane filter before analysis by HPLC.

Analysis of carbamate pesticides

Carbamate pesticides in the solution were analyzed with a Waters Tiger LC System (Waters, Massachusetts, USA) using a LichroCART RP-18 column (4 mm id × 100 mm, 5 µm). Manual injections were conducted with a Rheodyne injector equipped with a 20 µL loop. Separations were carried out using gradient elution of methanol and 0.1% acetic acid, as follows: started with 30% methanol, ramped to 50% methanol (0-3 min), ramped to 75% methanol (3-7 min), changed to 50% methanol (7-9 min), changed to 20% methanol (9-11 min), ramped to 100% methanol

Table 1. Properties of the studied surfactants

Surfactant	Molecular formula	Molecular structure	CMC at 25 °C[a] / (mmol L^{-1})
Sodium dodecyl sulfate (SDS)	$CH_3(CH_2)_{11}SO_4Na$		8.2
Cetyltrimethyl ammonium bromide (CTAB)	$C_{19}H_{42}BrN$		0.9

[a]The CMCs at 25 °C were obtained from the manufacturers.

(11-12 min) and held for 4 min before returning to 30% methanol (16-18 min) and holding for 2 min. A flow rate of 1.0 mL min^{-1} was used. All of studied pesticides were detected at 270 nm using a UV detector. The Clarity software (Waters, Massachusetts, USA) was used for data acquisition.

Results and Discussion

Characterization of sorbents

The surface morphology of unmodified and surfactant-modified sorbents was obtained from the scanning electron microscopy (SEM) studies. Unfortunately, the SEM images, which collected at magnification of ×10k (Figure 1), were not adequate to confirm aggregation of surfactant molecules on sorbent surfaces. However, sorption of surfactant on sorbent surfaces has been studied by FT-IR. The FT-IR spectra of surfactants were demonstrated in Figure 3. The major bands of both surfactants appeared at 3467-2871 cm^{-1}, while the FT-IR spectra of all modified sorbents were different from raw support materials (Figure 2). Apart from characteristic signals of each material, the modified sorbents show the bands within the range of 2853-2934 cm^{-1} which are assigned to C–H stretching vibration mode of long chain carbon on surfactant molecules. These results clearly indicated the surfactant sorption to sorbent surfaces.

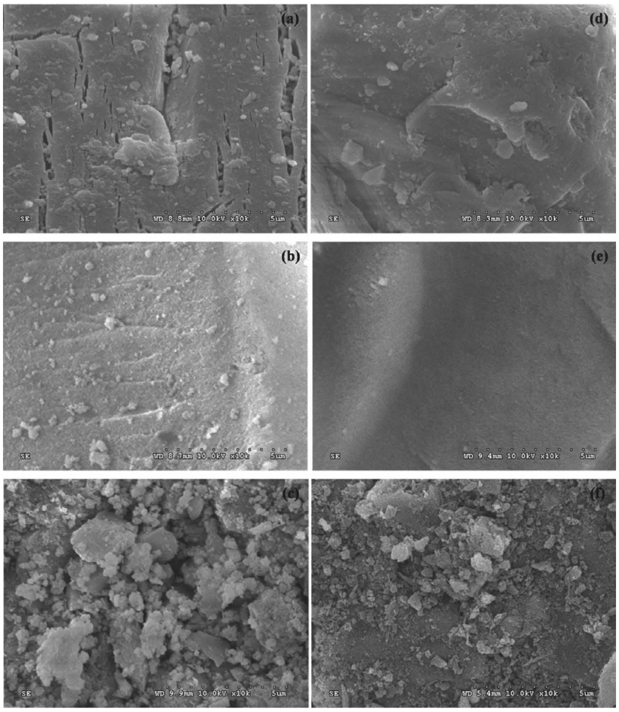


Figure 1. The SEM images of sorbents: (a) alumina; (b) silica; (c) zeolite; (d) alumina modified with 8.2 mmol L^{-1} SDS; (e) silica modified with 0.9 mmol L^{-1} CTAB; and (f) zeolite modified with 10.0 mmol L^{-1} CTAB.

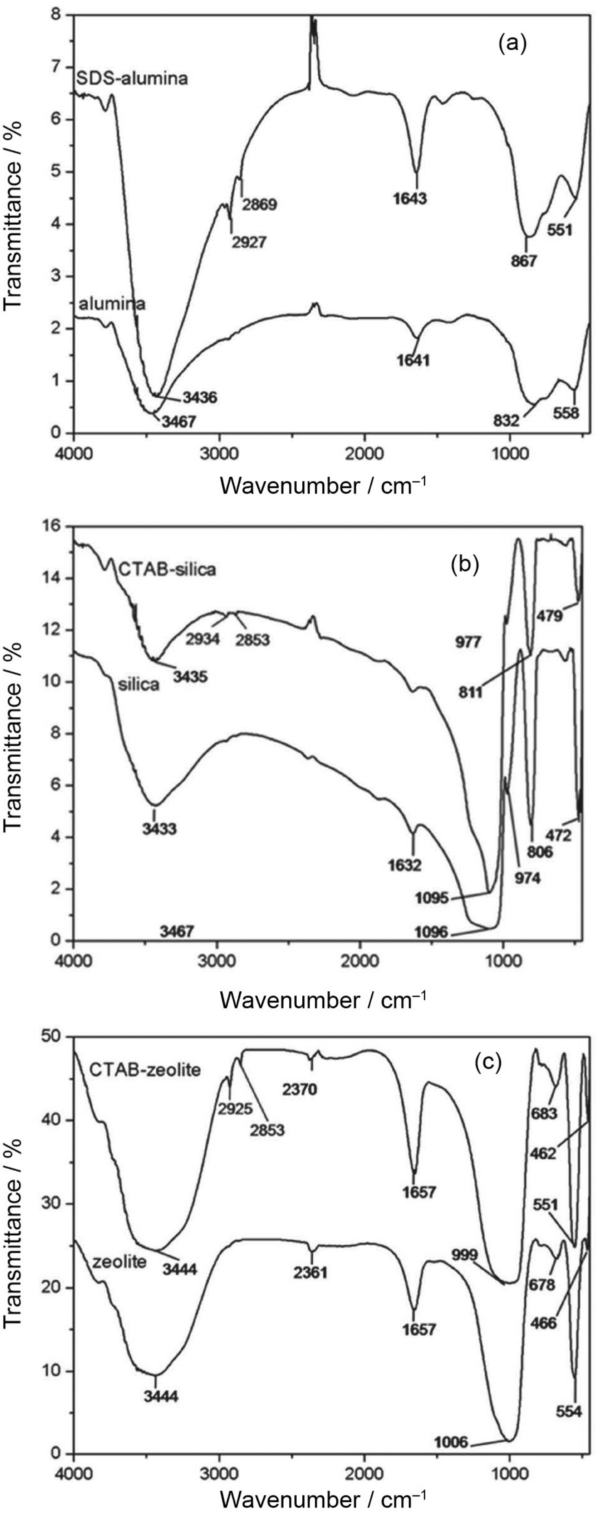


Figure 2. The FT-IR spectra: (a) alumina and alumina modified with 8.2 mmol L^{-1} SDS; (b) silica and silica modified with 0.9 mmol L^{-1} CTAB; and (c) zeolite and zeolite modified with 10.0 mmol L^{-1} CTAB.

Effect of surfactant concentration

According to general sorption model of ionic surfactant onto solid surface, various forms of surfactant aggregate:

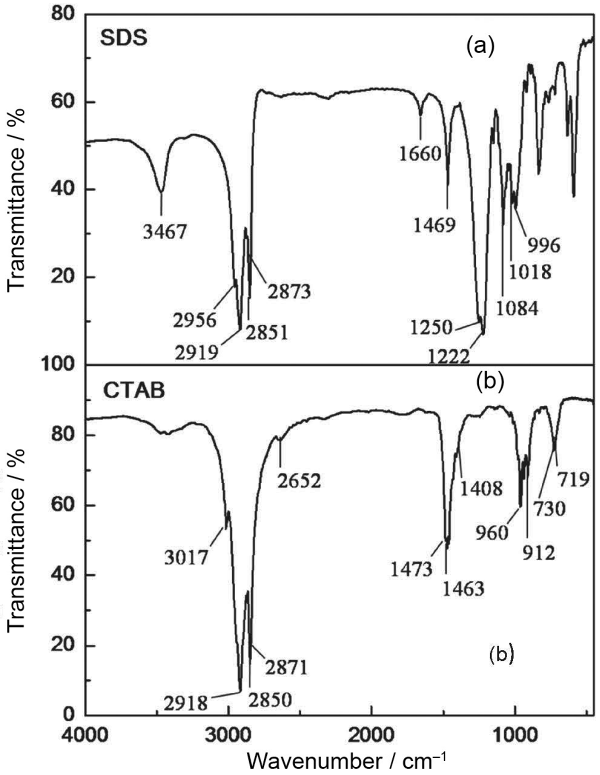


Figure 3. The FT-IR spectra of surfactants: (a) SDS and (b) CTAB.

monolayers, bilayers, or variations between two forms, are presented, as it is depended on surfactant concentration.[7,8,18,19] In addition, configuration of surfactant molecule as well as the fractional organic carbon content was found to effect the sorption of compounds.[10,21] Therefore, surfactant-modified sorbents using various surfactant concentrations were prepared and their adsorption capacities for carbamate pesticides were studied. The initial concentrations of each carbamate pesticides were 1.00 mg L^{-1} of OXM, ADC, CBF, CBR and MTC, and 5.00 mg L^{-1} of MTM, IPC, PMC and CBS. Adsorption of the analytes by unmodified sorbents was also examined. The results are summarized in Figure 4.

Some of the studied carbamate pesticides could be adsorbed onto the solid sorbents in the absence of surfactant. However, considerable enhancement in sorption of some pesticides on surfactant-modified sorbents was observed. For instance, SDS-modified alumina demonstrated higher adsorption percentage for ADC, IPC, MTC and PMC as compared to unmodified alumina. CTAB-modified silica showed enhancement of adsorption percentage for IPC, MTC and PMC. Improvement of adsorption percentage for MTM, ADC, CBR and MTC was observed using CTAB-modified zeolite. These could be due to the adsorbed surfactant molecules created an organic environment on sorbent surfaces which allowed more affinity for sorption of the analytes. The studied carbamate pesticides are non-polar to slightly polar compounds that adsorption on hydrophobic phase is more preferable than the hydrophilic phase, hence the surfactant-modified sorbents could improve sorption of these compounds as pesticide molecules could partition into surfactant aggregate.

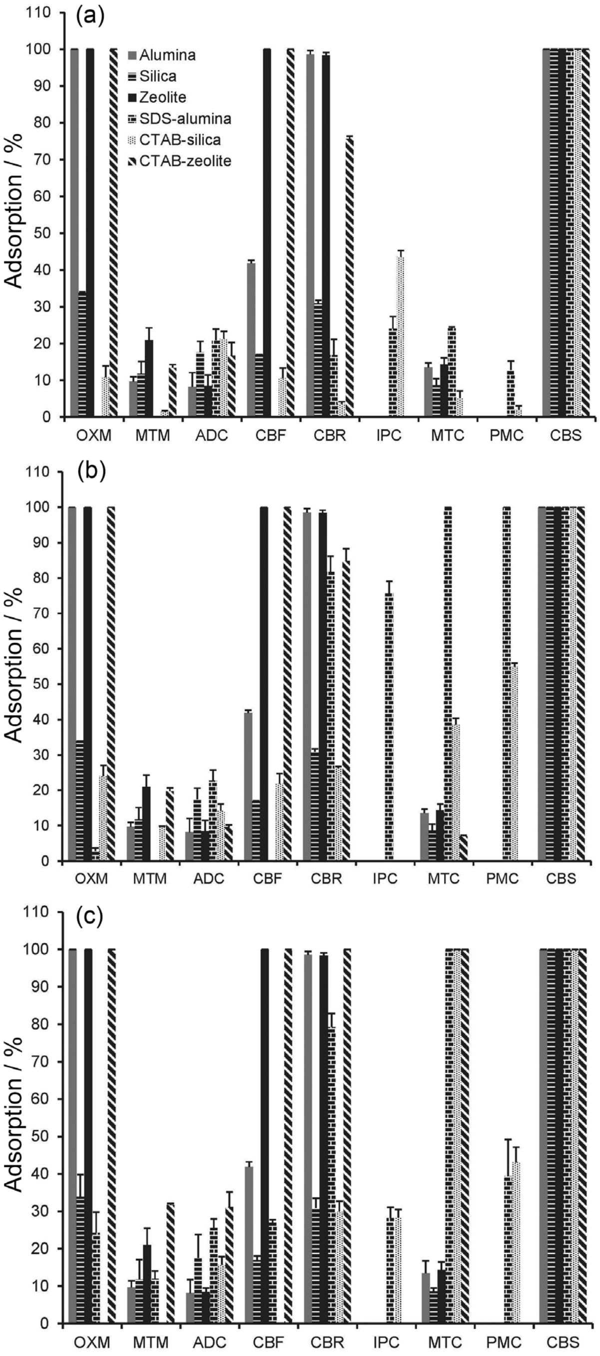


Figure 4. Adsorption of carbamate pesticides onto sorbents treated with different surfactant concentrations: (a) the < CMC treatment; (b) the CMC treatment; and (c) the > CMC treatment.

Considering the surfactant-modified sorbents prepared by different surfactant concentrations, low surface coverage of surfactant molecules on solid sorbent occurred when low concentration of surfactant was used. Coverage area increased with increasing amount of surfactant until the overall sorbent surfaces were overspread with monolayer of surfactant molecules (hemimicelles), then bilayer was formed (admicelles). For some of studied pesticides (i.e, OXM, MTM, ADC and CBF sorbed on SDS-alumina, CBF and MTC sorbed on CTAB silica, MTM and IPC sorbed on CTAB-zeolite), an enlargement of adsorbed amounts was observed when the surfactant concentration loaded onto the solid sorbents was increased. Nonetheless, when the amount of surfactant began to exceed, it formed micelles in aqueous solution and pesticides turned to solubilize into micelles in solution again which resulted in decreasing of the analytes adsorption on the modified sorbent. This could be observed in the cases of CBR, IPC, PMC sorbed on SDS-alumina and OXM, MTM, PMC sorbed on CTAB-silica.

Among various initial concentrations of surfactant, SDS-modified alumina and CTAB-modified silica treated at the CMC showed the highest sorption percentages for most of carbamate pesticides. At the CMC, surfactant molecules began to form micelles and sorbed on some area of sorbent surfaces to form admicelles; accordingly, the mixed hemimicelles/admicelles were created on sorbent surfaces. The mixed hemimicelles/admicelles provided both hydrophilic and hydrophobic phases. Therefore, interaction of cabarmate molecules and modified-sorbents occurred via both hydrophobic and hydrophilic interaction, resulted in high sorption of carbamate pesticides. However, the configuration of surfactant aggregate on solid surfaces found to be related to amount of surfactant, nature of surfactants and the characteristics of the solid surface.[25-27] In the present work, zeolite which had high sorption capacity for CTAB,[10] gave the greatest pesticide adsorption when using sorbent treated with surfactant at the concentration of higher than the CMC.

Form the results, SDS-modified alumina and CTAB-modified silica treated at the CMC, and CTAB-modified zeolite treated at higher than the CMC, were selected for further experiments.

Sorption of carbamate pesticides on surfactant-modified sorbents

Linear isotherm is often employed to interpret the sorption of organic compounds on solid sorbent. The equation used is $q_e = K_pC_e$, where, q_e is the amount of organic compounds sorbed *per* unit mass of sorbent at equilibrium, C_e is the equilibrium concentration of organic compound in solution, and K_p is the partition coefficient. This isotherm is equilibrium model, which offer a partitioning mechanism, thus, the experiment required time to establish the adsorption equilibrium. Generally, organic compound-solid sorbent system needs at least 24 h to reach the equilibrium condition.[10,11,21,24] However, application of the surfactant-modified sorbents for on-line extraction of carbamate pesticides in the flow manifold is expected. Therefore, experiments were desired by studying the adsorption efficiency only after 15 min of contact time.

Adsorption of carbamate pesticides onto the studied surfactant-modified sorbents, including SDS-modified alumina, CTAB-modified silica and CTAB-modified zeolite, are demonstrated in Figure 5. Linear regressions with the correlation coefficients in the range of 0.857-0.995 were revealed for all studied carbamates. The uptake of each pesticide on surfactant-modified sorbents was calculated from slope of the linear regression, as summarized in Table 2. All target compounds can adsorb onto surfactant-modified sorbents. The studied carbamate pesticides are slightly polar compounds (log K_{ow} > 1.1), except CBS which is non-polar compound having large log K_{ow} (log K_{ow} = 4.61).[28] CTAB-zeolite demonstrated high uptake values for CBF, CBR, MTC and CBS. High uptake levels of CBR, IPC, MTC, PMC and CBS were obtained using SDS-modified alumina. In the case of CTAB-modified silica, high uptake values of MTC, PMC and CBS were observed. The result showed that sorption of pesticides on CTAB-modified silica was lower when compared to the others, because of its high water-swelling. Great affinity of CBS on these surfactant-modified sorbents resulted from its low water-solubility, hence, the compound adsorbed on hydrophobic part of surfactant aggregate. It could be observed that the uptake levels of carbamate pesticides on SDS-modified alumina was in the order of CBS > PMC > MTC > IPC > CBR > ADC > MTM > OXM. It was corresponded to the order of elution analyzed by HPLC using reversed-phase C18 column (see Figure 6), which the lowest hydrophobic compound was appeared as the first peak. Figure 7 shows the relationship between uptake and log K_{ow} values of carbamate pesticides. Linear relationship between uptake levels and log K_{ow} was obtained using SDS-modified alumina (uptake value = 16.65 log K_{ow} - 20.88, r^2 = 0.9076). It indicated that the predominant factor for analytes to incorporate to the SDS-modified alumina sorbent was hydrophobic interaction. However, deviations from equilibration partition behavior have been observed in the case of CTAB-modified silica (uptake value = 14.12 log K_{ow} - 22.51, r^2 = 0.7446) and CTAB-modified zeolite (uptake value = 11.38 log K_{ow} - 0.54, r^2 = 0.4156). Based on using CTAB-modified silica as sorbent, carbamate compounds with low hydrophobicity have low uptake values (i.e., OXM, MTM, ADC, CBF and CBR), while more hydrophobic compounds could be more adsorbed onto the sorbent (i.e., MTC, PMC and CBS).

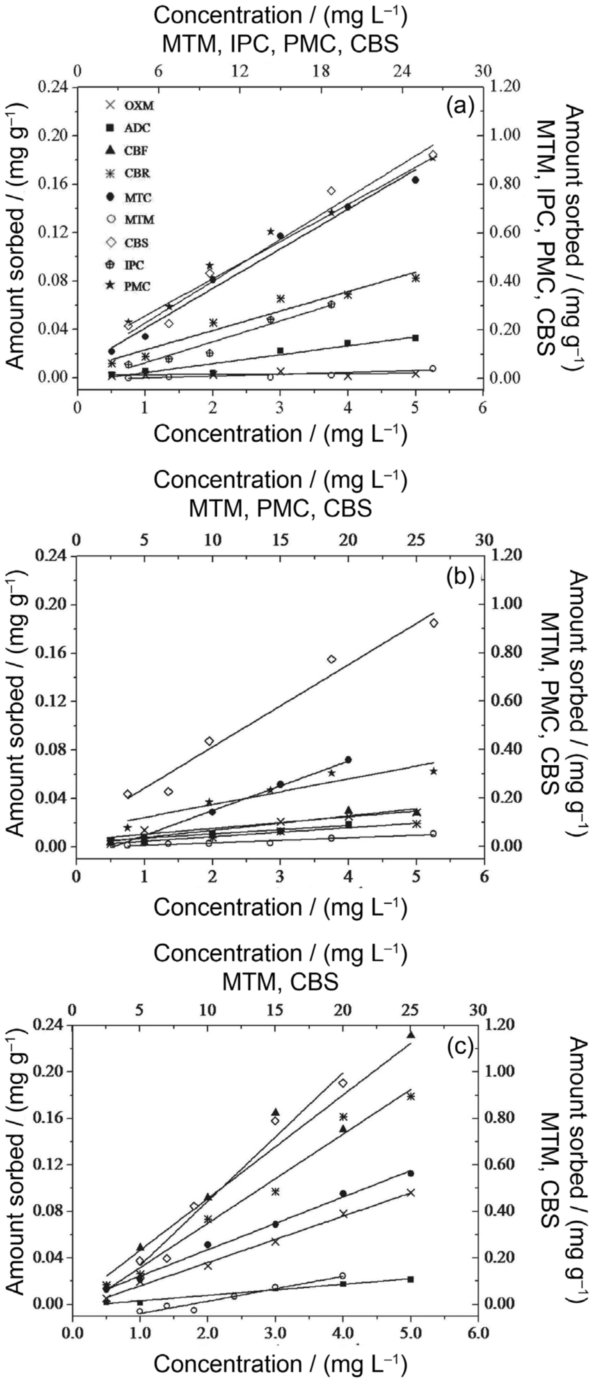


Figure 5. Carbamate pesticide sorption on (a) CTAB-modified alumina; (b) SDS-modified silica and (c) CTAB-modified zeolite.

Table 2. Sorption of carbamate pesticides

Carbamate	Uptake / (L kg^{-1})		
	SDS-alumina	CTAB-silica	CTAB-zeolite
OXM	1.5	4.8	20.0
MTM	2.4	3.3	10.3
ADC	7.0	3.5	4.7
CBF	–	6.0	44.5
CBR	16.1	3.7	38.3
IPC	28.0	–	–
MTC	32.7	20.5	22.7
PMC	36.8	12.9	–
CBS	53.1	53.1	53.1

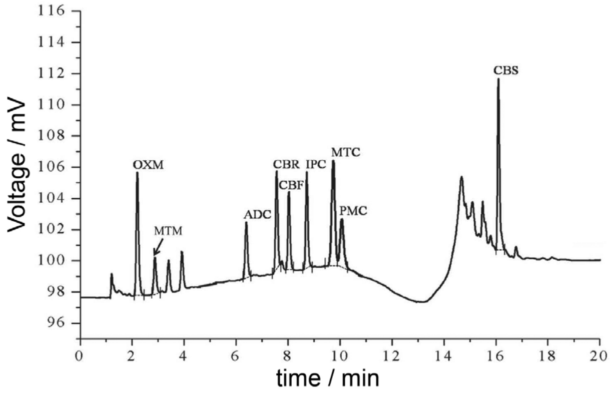


Figure 6. Chromatogram of carbamate pesticides.

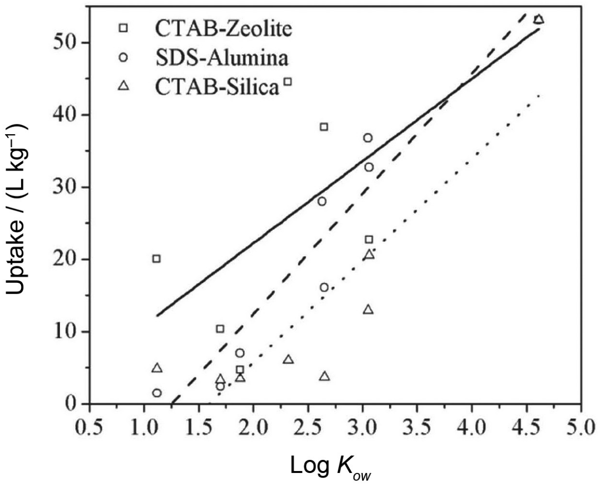


Figure 7. Relation of carbamate pesticide uptake on surfactant-modified sorbents and log K_{ow}.

Desorption of carbamate pesticides from surfactant-modified sorbents

Owing to aggregation of surfactants on solid surfaces, the chemistry of sorbent surfaces was greatly altered. The charge on the surfaces was changed and the organic-rich layer was formed. The organic-rich phase provided a partitioning medium for sorption of target analytes particularly non-polar compounds and also useable for slightly polar compounds. Retention of carbamate molecules on surfactant-modified sorbents mainly resulted from hydrophobic interaction of the analytes and the organic-rich phase. When proper solvent was added to the system, partition occurred again and the sorbed analytes were desorbed to liquid phase. In this work, methanol was chosen for desorption study. According to the results (Figure 8), the important finding of the study was that possibility of carbamate pesticide desorption from surfactant-modified sorbents was better than desorption from unmodified sorbents. Two slightly polar compounds, OXM and MTM, which have low K_{ow} values (K_{ow} = 1.12 and 1.70, respectively) were not desorbed from all studied sorbents. In contrast, CBS which is non-polar compound (K_{ow} = 4.16) demonstrated excellent desorption from all sorbents because of its solubility. However, most of the studied compounds revealed fair desorption using methanol as desorption solvent. As a result, other solvents should be involved in further study to optimize the proper desorption solvent.

Merit properties of surfactant-modified sorbent

Some properties of the new sorbent were evaluated to verify the applicability for SPE. According to the adsorption study, CTAB-modified zeolite with the CMC treatment presented the highest sorption capacity for all investigated pesticides. Thus it was chosen to study some merit properties which related to the performance of SPE, including its stability, sorbent-to-sorbent reproducibility, and comparison of its retention property with conventional materials. The obtained results were summarized in Table 3.

Seven independent batches of CTAB-modified zeolite were prepared for study the sorbent-to-sorbent reproducibility. After that, pesticides sorption was fulfilled via pesticide solution containing 1.0 mg L^{-1} of each carbamates. Likewise, pesticides sorption of conventional materials was performed using the same concentration of carbamates. The modification of sorbent showed reproducibility with %RSD of less than 11.8. Two conventional materials including polystyrene-divinylbenzene polymeric resin (Amberlite® XAD-4, 20-50 µm, Sigma-Aldrich, USA) and C18 material (Lichroprep® RP-18, 25-45 µm, Merck KGaA, Germany) which are widely used as sorbent for organic compounds were selected for the comparison of pesticides sorption. In terms of adsorption percentage, the new modified sorbent gave a comparable adsorption percentage to the conventional ones for almost studied pesticides such as OXM, CBF, CBR, MTC and CBS. Furthermore, it could be suggested that adsorption of MTM on the new modified sorbent was higher than that on both conventional materials. This might be a result of hydrophilic interaction of the slightly polar pesticide and charge of surfactant molecule on sorbent surface which enhanced retention of pesticides on the modified sorbent. In addition, high adsorption of other slightly polar pesticide was also observed, for instance, adsorption of OXM on the modified sorbent. Nevertheless, the proposed sorbent could not adsorb IPC, while this pesticide retained on both conventional materials. Again, PMC does not retain at all on all investigated sorbent.

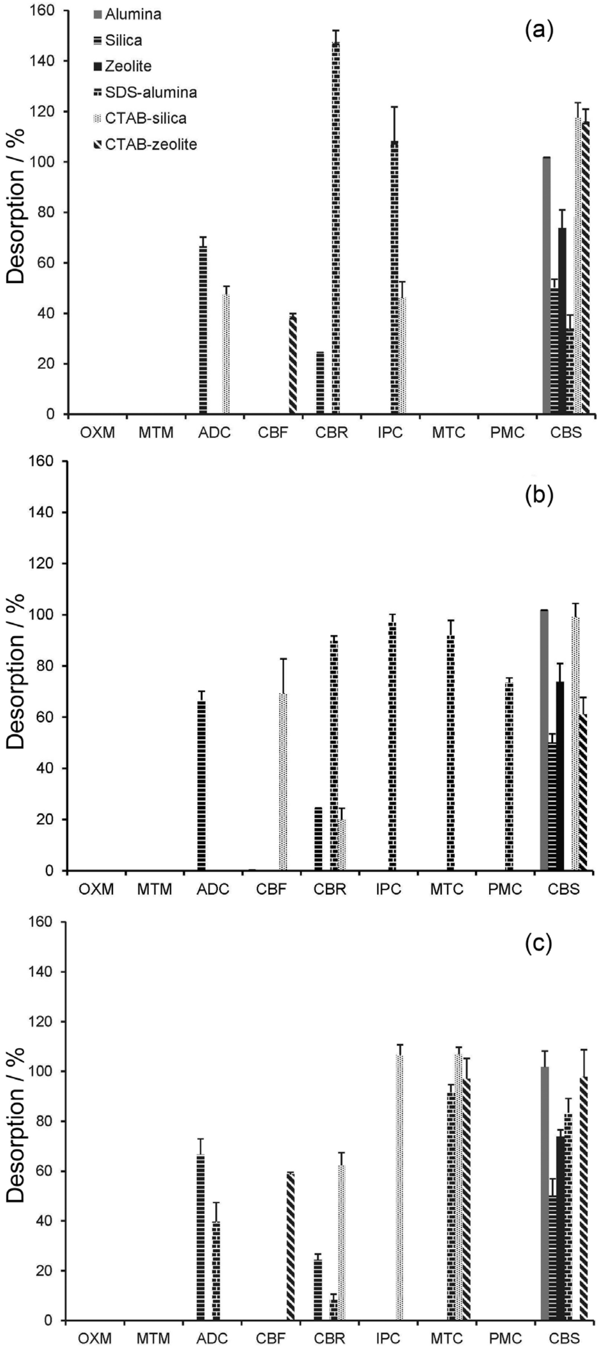


Figure 8. Desorption of carbamate pesticides from sorbents treated with different surfactant concentrations: (a) the < CMC treatment; (b) the CMC treatment; and (c) the > CMC treatment.

Table 3. Merit properties of surfactant-modified sorbent and comparison of its adsorption percentage with conventional materials

Carbamate	Adsorption / %[a]	RSD / %[b]	Reused cycles	Adsorption by convention materials / %[c] (RSD %)	
				PS-DVB resin	C18
OXM	96.5	10.6	0	100.0 (0.0)	72.5 (5.5)
MTM	35.5	6.0	8	16.1 (3.0)	12.0 (2.3)
ADC	34.0	9.4	5	36.6 (7.3)	83.5 (5.7)
CBF	96.8	9.9	7	100.0 (0.0)	98.5 (4.0)
CBR	94.7	10.2	8	58.5 (6.1)	91.5 (4.8)
IPC	–	–	–	52.1 (0.7)	99.0 (2.4)
MTC	94.8	11.8	> 10	75.6 (7.2)	99.5 (1.6)
PMC	–	–	–	–	–
CBS	100.0	0.0	2	100.0 (0.0)	100.0 (0.0)

[a]Average adsorption percentage of 7 independent modified sorbents; [b]%RSD of 7 independent modified sorbents; [c]average adsorption percentage and %RSD of 6 replicates.

To study the stability, the preliminary study showed that some of surfactant molecules lost from support materials during elution process. Hence, re-coating of surfactant for the next adsorption process was recommended. In order to express the stability of the new modified sorbent, solid support was re-coated and used for pesticides sorption again. After the first extraction cycle, coating step was carried out by adding 10 mL of 10 mmol L^{-1} CTAB to the remained solid support, then it was mechanically shaken at 200 rpm for 1 h. The re-coated material was rinsed twice with deionized water and ready for the next adsorption step. Experiments were repeated several times and the stability of sorbent was reported by the number of reused cycles that provided the decreasing of adsorption percentage for each pesticide of less than 5%. The number of reused cycles for each carbamate was summarized in Table 3. As the results, the sorbent could be efficiently reused for MTM, ADC, CBF, CBR and MTC. Unfortunately it effectively retained CBS only for 2 re-coating cycles and could not be reused for OXM which rapidly eluted from the sorbent.

Conclusion

The present study clearly demonstrated that the surfactant-modified sorbents are effective for the extraction of carbamate pesticides in aqueous solution. A great adsorption performance for carbamate pesticides is observed by using CTAB-modified zeolite and SDS-modified alumina due to hydrophobic property of surfactant aggregate on solid surface. Desorption of carbamates from the modified sorbents was made using methanol. Based on the findings, these surfactant-modified sorbents could be proposed for preconcentration of trace carbamate pesticides before instrumental analysis.

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