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Combined effect of co-existing heavy metals and organophosphate pesticide on adsorption of atrazine to river sediments

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Abstract−Adsorption characteristics of atrazine (AT) onto the surfacial sediments (natural surface coating samples) were investigated via thermal adsorption in the presence of pollutants malathion (Ma) and heavy metals (cadmium and copper). The results indicate that cadmium and Ma both have synergetic effect during the adsorption of AT; at the same time, copper caused antagonistic effect on the adsorption of AT. Ma could facilitate the adsorption of AT, no matter that Ma was added after the adsorption of AT or simultaneous adsorption of AT with Ma present. However, Ma inhibited the adsorption of AT when it was added before the adsorption of AT. The adsorption of AT was also enhanced when both cadmium and Ma were present; however, it was inhibited strongly when both copper and Ma were present. The infrared spectra of the surfacial sediments (natural surface coating samples), after the adsorption of AT in the presence of co-existing pollutants, indicated that organic functional groups, such as O-H or N-H and C=O, play important roles on sorption of AT to river sediments.

Key words: Atrazine, Cadmium/Copper, Malathion, Adsorption, Combined Pollution, River Sediments

INTRODUCTION

Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine, AT), which is one of the triazines, is widely used as a selective herbicide for the control of grassy and broadleaf weeds in maize, sorghum, rangeland, sugarcane, and other crops, as well as a nonselective herbicide in noncropland situations [1]. Because AT is highly persistent in soil and has a long half-life (60 to >100 days) [2], it has a high potential to contaminate surface water and soil despite its moderate aqueous solubility. It is prone to leaching to groundwater and surface runoff from soils and sediments. Atrazine has been frequently detected as a contaminant in soils, surface water, and groundwater in many countries [3-7]. More importantly, AT is classified as a possible human carcinogen by the US Environmental Protection Agency, and it is a known endocrine disrupting substance posing a potential health risk to humans [8,9] and wildlife [10]. It has been included in the priority substances list of the European Commission (EC) [11]. The surfacial sediments (SSs) and natural surface coating samples (NSCSs) are often considered as main carriers and potential sources of both organic and inorganic pollutants in aquatic environments [12-14]. They are playing a significant role in the adsorption of pollutants owing to their abundant internal surface area and high sorption intensity [15,16].

A large amount of agrochemicals, such as pesticides and fertilizers, may be leaked and released into aqueous systems, resulting in aquatic environmental contamination. Mobility and toxicity of co-existing chemicals are always involved. Some combinations of pollutants have shown additive effects, while others have shown less than additive (antagonistic) or greater than additive (synergetic) toxicity [17]. Recently, synergistic toxicity has been noted for binary mixtures of AT and other organophosphate pesticide [18,19]; therefore, a study on combined pollution is not only helpful for a comprehensive understanding of the transportation of co-existing pollutants, but also significant for the prediction of the water quality and management of the aquatic environment. Heavy metals enter the environment from both natural and anthropogenic sources, and the latter is even more serious. Anthropogenic sources of metals include wasters from industrial, mining and agricultural activities and accumulate in the ecosystem. While coexisting with organic contaminants at many polluted sites [20,21], metals can affect the adsorption of organic pesticides which may be involved in the formation of complexes with the metals [22]. Heavy metals have the potential to impose various effects on adsorption of pesticides to soil/sediments. It has been previously reported that the existence of cadmium could enhance the adsorption of AT but copper would suppress the process [23,24]. Previous works focused on the influence of heavy metals [23-25] and organic pollutants [26,27] on the adsorption of AT onto sediments or soils in binary systems especially. However, it becomes much more complicated when AT, heavy metals and other pesticides are all involved. The object of this study was to investigate the adsorption of AT onto sediments and to examine the combination effects of heavy metals (cadmium or copper) and organophosphate pesticide (malathion) on the sorption of AT.

MATERIALS AND METHODS

1. Chemicals

AT used was 99.9% pure in the experiments and it was supplied by Agro-environmental Protection Institute of Ministry of Agriculture in China. Methanol with HPLC grade was purchased from Fisher Co., USA. Malathion (Ma, 99.5%, Dr. Ehrenstofer Gmbh) was se-

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lected as the competing absorbent. All other chemicals were of analytical grade. Deionized water was used for all experiments.

2. Collection and Preparation of SSs (NSCSs)

The SSs (approximately 5 cm in depth from the surface) were collected in the Songhua River (near the Guofangyuan Square in Jilin, China) with a plastic scoop and stored in polyethylene bags. The SSs were puce, containing plenty of river water, stone and branches. During collection of SSs, 4 sub-samples approximately 20 cm from each other were obtained and mixed to one homogeneous sample. Shingles in the near bank of the river were taken out of the water [28], and NSCSs attached to the shingles were scraped using plastic scoop into plastic container which contained minimal mineral salts (MMS) solution [29]. There was a layer of algae on the surface of the NSCSs and zooplankton in NSCSs. Prior to collection, plastic container and apparatus were pre-cleaned with detergent, soaked for 24 h in soap solution, washed with acid 6 : 1 (v/v) H_2O : HNO_3 for 24 h, and then rinsed in distilled-deionized water (ddH_2O). Then the samples were brought to the laboratory and dried with air. The agglomerates in the samples were grounded using a mortar, the resulted powder was sieved, and those particles larger than 0.076 mm were discharged. All SSs and NSCSs samples, which have sizes 0.076 mm or less, were used for further analyses.

3. Batch Adsorption Experiments

Batch experiments were conducted to investigate adsorption behaviors of AT. In the binary system of experiments, an appropriate amount of solute was added to the 100 ml conical flasks with glass caps, which contained 0.5000 g of air-dried SSs (NSCSs) in 20 ml MMS solution, given levels of AT and Ma containing 100 mg/L NaN_3 as a biocide. The solution concentrations of AT were 0.5, 1.0, 2.0, 4.0, 6.0, 8.0 and 10.0 mg/L, and those of Ma were 1.45, 5.80 and 11.6 mg/L respectively. The suspensions were stirred continuously in the dark for 48 h at room temperature (25 °C) using a shaker. All

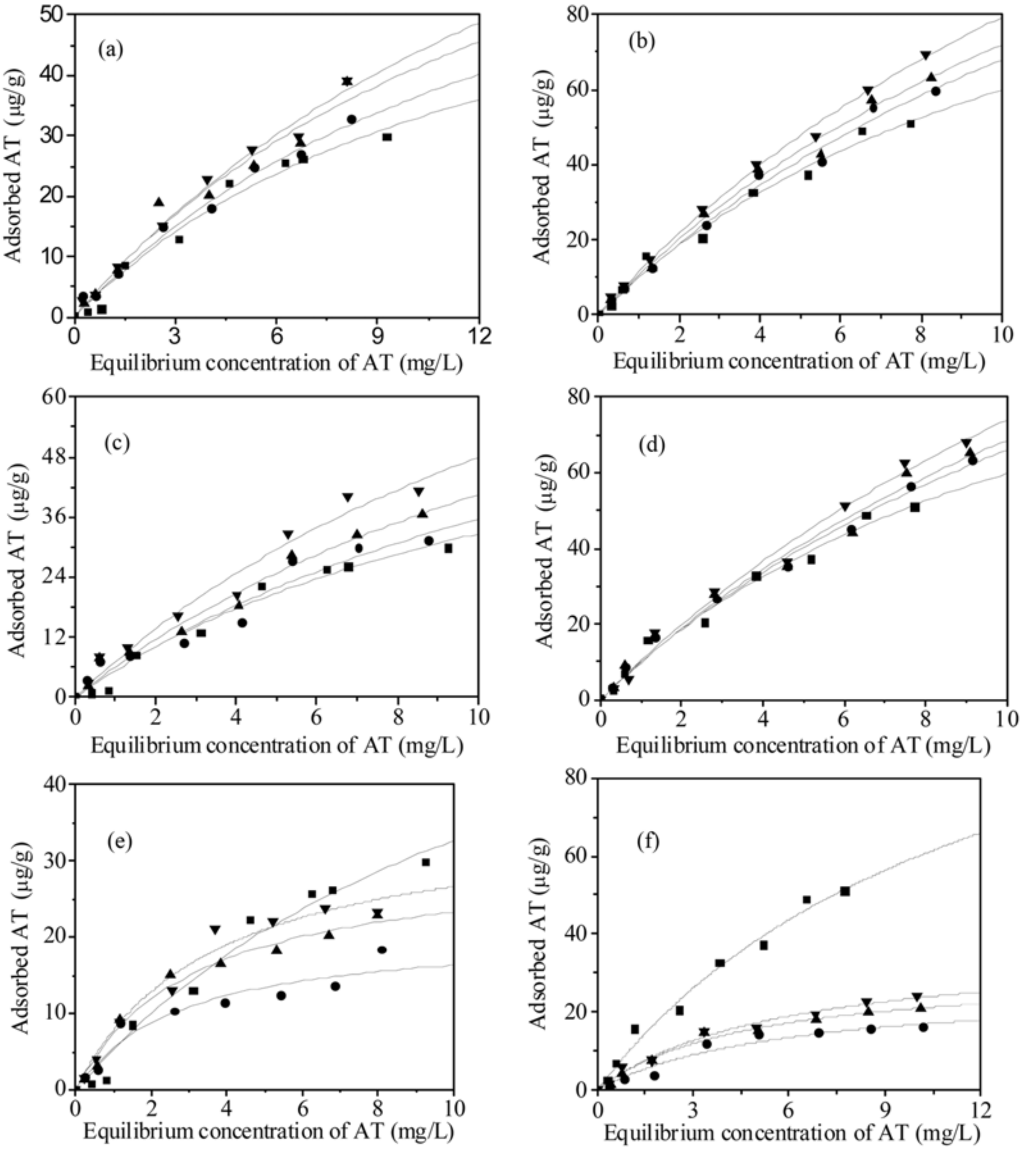

Fig. 1. Adsorption isotherms of AT on SSs (NSCSs) in the presence of Ma (a)/(b) simultaneous absorption of AT and Ma on SSs (NSCSs); (c)/(d) AT adsorption on SSs (NSCSs) in the co-existed Ma system after preloading with AT; (e)/(f) AT adsorption on SSs (NSCSs) in the Ma preloading system. Ma: ■ 0 mg/L ● 1.45 mg/L ▲ 5.80 mg/L ▼ 11.6 mg/L.

sorption experiments were performed in duplicate and the equilibration suspensions were filtrated through membrane filter with 0.45-μm pore size.

In the ternary system of the experiment, when Ma and cadmium/copper presented as the co-existing chemicals, Ma (1.45 mg/L), cadmium (2.0 mg/L) or copper (35.5 mg/L) were added in the above MMS solutions. The amount of AT adsorbed was calculated based on the concentration of AT in the solutions before and after the adsorption. The concentrations of AT and Ma in the supernatant were determined by an LC-10AD HPLC (high performance liquid chromatography, Shimadzu, Japan). A reversed-phase TC-C18 column (150 mm×4.6 mm×5 μm) (Agilent, USA) was used for analysis of AT and Ma at 30 °C. The mobile phase was obtained with methanol/water (70/30, v/v), and the flow rate, the injection volume and detection wavelength was 0.8 mL/min, 10 μL and 220 nm, respectively [30].

4. FTIR Measurements

Infrared spectra of the pollutants-loaded SSs (NSCSs) obtained before and after adsorption experiments were recorded by a Nicolet FTIR spectrometer in the range from 500 cm^{-1} to 4,000 cm^{-1}. Pressed pellets were prepared by grinding the powder specimens with IR grade KBr in an agate mortar.

RESULTS AND DISCUSSION

1. Adsorption of AT in the Binary Systems

To describe the behaviors of combined effect of co-existing AT and Ma, adsorption experiments of AT were conducted with Ma present, including (1) simultaneous adsorption of AT and Ma when both of them are present, (2) adsorption of Ma followed by AT contact (Ma preloading), and (3) adsorption of AT followed by sequential Ma contact (AT preloading).

Fig. 1 shows the simultaneous adsorption isotherms of AT on SSs (NSCSs) in the presence of Ma at various levels in the binary systems. Langmuir equations are used to simulate AT adsorption isotherms on SSs (NSCSs). The thermodynamic adsorption parameters are estimated and listed in Table 1. The co-existing Ma enhances AT adsorption on SSs and NSCSs, and AT adsorption on NSCSs is greater than that on SSs in the binary system. The maximum AT adsorption increases gradually with increase of Ma levels. When Ma (11.6 mg/L) was added, the maximum adsorption reached 126.0 μg/g on SSs and 233.2 μg/g on NSCSs, respectively. The increase percentages are 67.6% on SSs and 73.7% on NSCSs, respectively, compared to the adsorption of AT when Ma was absent. Ma was more tightly retained by various soils than AT. This is consistent with the fact that there is an interaction between Ma and soil fractions of the organic materials and clay. A possible reason is that it has polar groups in its structure [31]. Ma is easily degraded in aquatic environments, and the hydrolysis of Ma is one of the main processes for the degradation. An -OH group in water may be a nucleophilic group during the hydrolysis [32]. It may be suggested that hydrogen bonds are formed between oxygens of Ma and active hydrogens of AT. This is an explanation for the fact that the presence of Ma in the binary systems enhances the adsorption of AT. It was found that the adsorption of Ma decreased by the increase of particle sizes of fly ash [33]. The particle size of NSCSs is much

Table 1. Estimated Langmuir parameters for AT adsorption on SSs (NSCSs) in different procedures

Procedures	Ma/ (mg/L)	SSs			NSCSs		
		Γ_{max}/(μg/g)	K	r	Γ_{max}/(μg/g)	K	r
Simultaneous adsorption of AT and Ma^a	0.0	75.15±2.89	0.0768	0.986	134.3±1.6	0.0803	0.984
	1.45	90.89±3.66	0.0660	0.988	191.9±1.3	0.0547	0.989
	5.80	104.5±5.9	0.0644	0.966	200.4±0.5	0.0559	0.991
	11.6	126.0±9.7	0.0524	0.989	233.2±9.7	0.0514	0.996
AT preloading^a	0.0	75.15±2.89	0.0768	0.986	134.3±1.6	0.0803	0.984
	1.45	96.03±9.21	0.0590	0.937	183.5±5.5	0.0562	0.990
	5.80	108.2±9.5	0.0596	0.970	201.0±4.1	0.0517	0.978
	11.6	127.2±9.9	0.0604	0.966	231.6±5.6	0.0469	0.989
Ma preloading^a	0.0	75.15±2.89	0.0768	0.986	134.3±1.6	0.0803	0.984
	1.45	20.82±0.46	0.3645	0.909	26.65±0.85	0.1710	0.950
	5.80	30.43±0.95	0.3231	0.981	31.03±0.76	0.2082	0.981
	11.6	36.31±0.73	0.2748	0.972	37.27±0.98	0.1723	0.981

Table 2. Selected characteristics and textures of SSs and NSCSs

	pH	MC^a (%)	Clay (%)	Loam (%)	Sand (%)	Fe oxides/(μmol/g)		Mn oxides/(μmol/g)		OMs/(μmol/g)^b	
						Total amount	Extractable amount	Total amount	Extractable amount	Total amount	Extractable amount
SSs	5.95	3.13	19.61	61.73	18.65	554.5	174.0	9.15	6.09	1841	1841
NSCSs	6.53	2.85	24.09	56.00	19.92	528.1	168.6	10.91	7.84	2236	2236

^{a}Moisture content

^{b}Organic materials content

smaller than that of SSs. Sorption of atrazine on SSs and NSCSs was dependent largely on the quantity and quality of Fe oxides, clay minerals, and organic materials [34]. The content of clay (<0.002 mm) in NSCSs was 24.09%, larger than that in SSs (19.61%), the content of organic materials in NSCSs was also higher than that in SSs, and the content of Fe oxides in NSCSs and in SSs was nearly at the same level (Table 2). As a result, the affinity and sorption capacity of NSCSs to AT is significantly higher than that of SSs. There is synergism of Ma to AT adsorption on NSCSs but none on SSs.

Preloading with AT yielded a similar positive effect on AT adsorption. The maximum adsorption of AT on SSs (NSCSs) increases with the increase of concentration of Ma. The maximum adsorptions of AT in the two systems are almost identical in the presence of the same concentration of Ma but with different AT addition orders. The results suggest that the impact of malathion on AT adsorption is insignificant. The combined effect of Ma on AT adsorption might occur when Ma is added as the secondary solute; thus, AT adsorption is enhanced by the increase of Ma adsorbed on SSs (NSCSs).

AT adsorption of SSs (NSCSs) preloaded with Ma shows a completely different adsorption characteristic, compared with the simultaneous adsorption and the absorption of SSs (NSCSs) preloaded with AT. The AT adsorption was all suppressed when Ma was added, and the inhibition was significant at the beginning but saturated when Ma concentrations were very high. When the initial concentrations of Ma increased from 0 mg/L to 11.6 mg/L, the maximum adsorptions of AT were reduced from 75.15 μg/g to 36.31 μg/g (on SSs) and 134.3 μg/g to 37.27 μg/g (on NSCSs), respectively. The inhibition percentages are 51.7% (on SSs) and 72.2% (on NSCSs), respectively. It is possible that if Ma is preloaded in the system, it will occupy many more adsorption sites and inhibit the AT adsorption, resulting in the decline of the maximum adsorption of AT. Moreover, the results suggest that Ma is more likely to be absorbed on SSs (NSCSs) than AT. It might be because Ma and AT are both hydrophobic pesticides; their adsorption amounts are correlated to organic material content. The logarithm of octanol-water partition coefficient of Ma (2.89) is larger than that of AT, though it is much easier to be absorbed by SSs (NSCSs). The results above also indicate that absorption capacity of NSCSs for AT is inhibited much greater by the addition of Ma than that of SSs. Ma is a poor inhibitor of acetylcholinesterase (ACHe), whereas some oxo-analogs of Ma are highly potent ACHe inhibitors [35]. The contents of organic materials in NSCSs are much higher than those in SSs. The organic materials can have the polycarbonate bands [36]. Therefore, Ma has a greater effect on AT adsorption for NSCSs than that for SSs.

2. Adsorption of AT in the Ternary Systems

To investigate adsorption characteristics of AT, the following experiments were carried out: (1) adsorption of AT without any additive; (2) adsorption of AT in the presence of either Ma, cadmium, or copper, and (3) adsorption of AT in the presence of all Ma, cadmium and copper. The adsorption isotherms of AT in the ternary

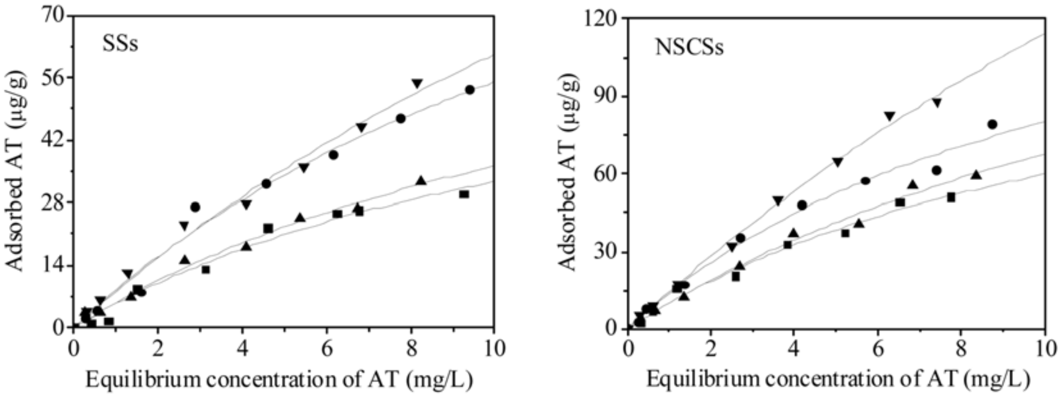

Fig. 2. Adsorption isotherms of AT on SSs (NSCSs) in the ternary system of AT-Cd-Ma. ■ AT ● AT-Cd ▲ AT-Ma ▼ AT-Cd-Ma.

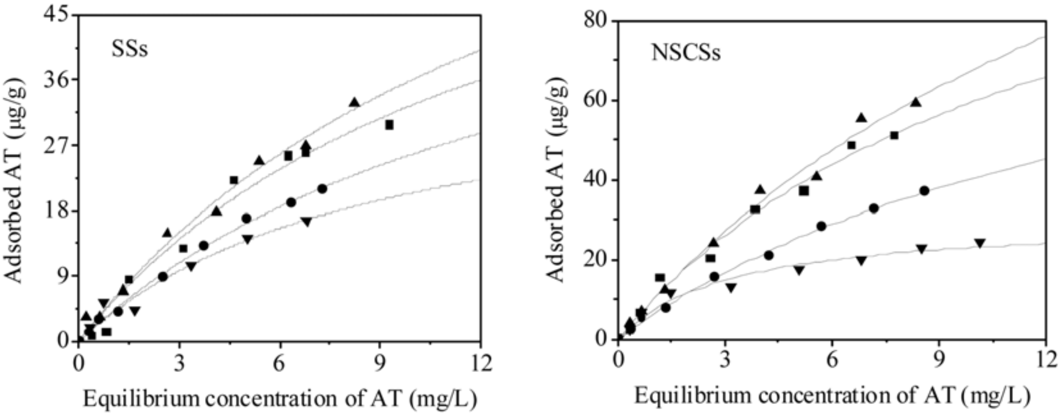

Fig. 3. Adsorption isotherms of AT on SSs (NSCSs) in the ternary system of AT-Cu-Ma. ■ AT ● AT-Cu ▲ AT-Ma ▼ AT-Cu-Ma.

Table 3. Estimated Langmuir parameters for AT adsorption on SSs (NSCSs) in different co-exciting systems

System	SSs			NSCSs		
	Γ_{max}/(μg/g)	K	r	Γ_{max}/(μg/g)	K	r
AT	75.15±2.89	0.0768	0.986	134.3±1.6	0.0803	0.984
AT-Cd	142.9±4.6	0.0623	0.980	167.3±6.3	0.0915	0.987
AT-Ma	90.89±8.92	0.0660	0.988	191.9±1.3	0.05472	0.989
AT-Cd-Ma	223.1±8.1	0.0379	0.988	484.0±9.6	0.0310	0.995
AT	75.15±2.89	0.0768	0.986	134.3±1.6	0.0803	0.984
AT-Cu	63.29±8.41	0.0690	0.998	105.9±4.1	0.0622	0.992
AT-Ma	90.89±5.36	0.0660	0.988	191.9±3.8	0.0547	0.989
AT-Cu-Ma	38.93±6.76	0.1113	0.982	30.43±0.62	0.3150	0.969

systems are shown in Figs. 2 and 3, and the fitted Langmuir parameters are estimated and listed in Table 3.

As shown in Fig. 2 and Table 3, co-existing cadmium and Ma yield additive effects on adsorption of AT in the ternary system AT-cadmium-Ma, and the maximum adsorption of AT has reached to 223.1 μg/g (on SSs) and 484.0 μg/g (on NSCSs), respectively. The value of 223.1 μg/g (on SSs) is 2.97, 1.56 and 2.45 times greater than that in the systems of single AT present, AT-cadmium coexisting, and AT-Ma coexisting, respectively. Similarly, the value of 484.0 μg/g (on NSCSs) is 3.61, 2.89 and 2.52 times greater than those three systems shown above, respectively. It should be noted that the promotion effect from co-existing cadmium and Ma to AT adsorption on NSCSs is much greater than that on SSs, probably due to the more active components and groups in NSCSs than SSs.

As can be seen in Fig. 3 and Table 3, adsorption characteristics of AT in the ternary system of AT-copper-Ma are quite different from those in the system of AT-cadmium-Ma. The co-existing copper and Ma evidently restrained AT adsorption on SSs (NSCSs). The combined effect can be as an antagonistic effect, that is, because of the presence of copper and Ma, the maximum AT adsorptions reduce to 38.93 μg/g (on SSs) and 30.43 μg/g (on NSCSs), which equal 51.8% (on SSs) and 22.7% (on NSCSs) of AT absorptions for the systems of AT only, 61.5% (on SSs) and 28.7% (on NSCSs) of AT absorptions for the systems of AT present with copper, and 42.8% (on SSs) and 15.9% (on NSCSs) of AT absorptions for the systems of AT present with Ma, respectively. The data indicate that the inhibition effect of copper is much stronger than the promotion effect of Ma on adsorption of AT in the ternary system. Effect of copper is the most significant on AT adsorption among the co-existing organic and inorganic pollutants employed. The interference effects of the two heavy metals are different from each other in the ternary systems. The two metals have different binding sites on SSs (NSCSs). The main adsorption site for cadmium on SSs (NSCSs) has been found to be Fe oxides [37]. It has been proven that binding of copper should involve organic materials, with which copper binds more tightly than other metals [38-40]. The copper is the only metal that has inner-sphere chelation with organic materials at lower pH. The organic materials exerted the greatest influence on copper binding but not Fe oxides. Therefore, copper tends to bind organic pollutants first and restrain adsorption of organic materials onto SSs (NSCSs), and it has antagonistic effect on AT adsorption in the combined process in the presence of Ma.

3. Adsorption Mechanisms of Atrazine on SSs and NSCSs in the Presence of Cadmium/Copper and Ma

The FTIR spectra of SSs and NSCSs are presented in Fig. 4 before and after the absorption of AT. Listed in Table 4 are the relevant absorption bands of the functional groups and shift circumstances. As shown, the characteristic absorption peaks of AT in SSs and NSCSs are similar in shape but different in wave numbers, suggesting that SSs and NSCSs are structurally different.

Hydroxyl group is present in metal oxides in SSs and NSCSs, such as Fe-OH [41]. The IR absorbance of the hydroxyl group (O-H) is at about 3,426 cm^{-1} in both SSs and NSCSs. For the treated SSs and NSCSs with AT, the IR wave numbers shifted to higher frequencies 3,432 cm^{-1} and 3,434 cm^{-1}, respectively, indicating that AT have been adsorbed onto metal oxides. Furthermore, the intensity of this absorption peak is also increased after AT adsorption. A possible explanation is that hydrogen bonds formed between Fe-OH groups and electron lone pairs on the oxygen atoms in AT molecules, and the intensity of O-H increases with increase of numbers of oxygen atoms.

The IR absorbance at about 2,926 cm^{-1} in NSCSs is consistent with the presence of alkyl groups. This absorbance was not seen in IR spectrum for SSs. The IR peaks at 1,632 cm^{-1} of SSs and 1,654 cm^{-1} of NSCSs indicate stretching vibration of carbonyl group C=O. After the adsorption of AT, the absorbance of C=O of NSCSs shifts significantly but that of SSs still remains the same, indicating that the C=O group plays an important role in AT adsorption. Furthermore, the IR peak of the C=O in NSCSs is much more intense than that of SSs, suggesting that there is higher content of organic materials in NSCSs. The FTIR spectra of SSs and NSCSs after adsorbing AT only are similar to those after adsorbing AT, Ma and cadmium/copper simultaneously without change in the peak shapes, indicating that adsorption of pollutants onto SSs and NSCSs does not break structures of the adsorbents. The absorbance of some peaks changed after the absorption of AT, suggesting that some groups in SSs and NSCSs interact with AT, cadmium/copper, and Ma. As the metals are in an oxide form, their interactions with organic pollutants such as AT or Ma in SSs (NSCSs) in the co-existing systems are probably weak; then, physisorption would be the main part of the adsorption mechanism, even though chemical reactions could also occur [42]. For the IR absorbance at 3,426 cm^{-1} of O-H or N-H in SSs in the systems, adsorption of AT without any additive, the adsorption of AT in the presence of cadmium has a strong intensity based on

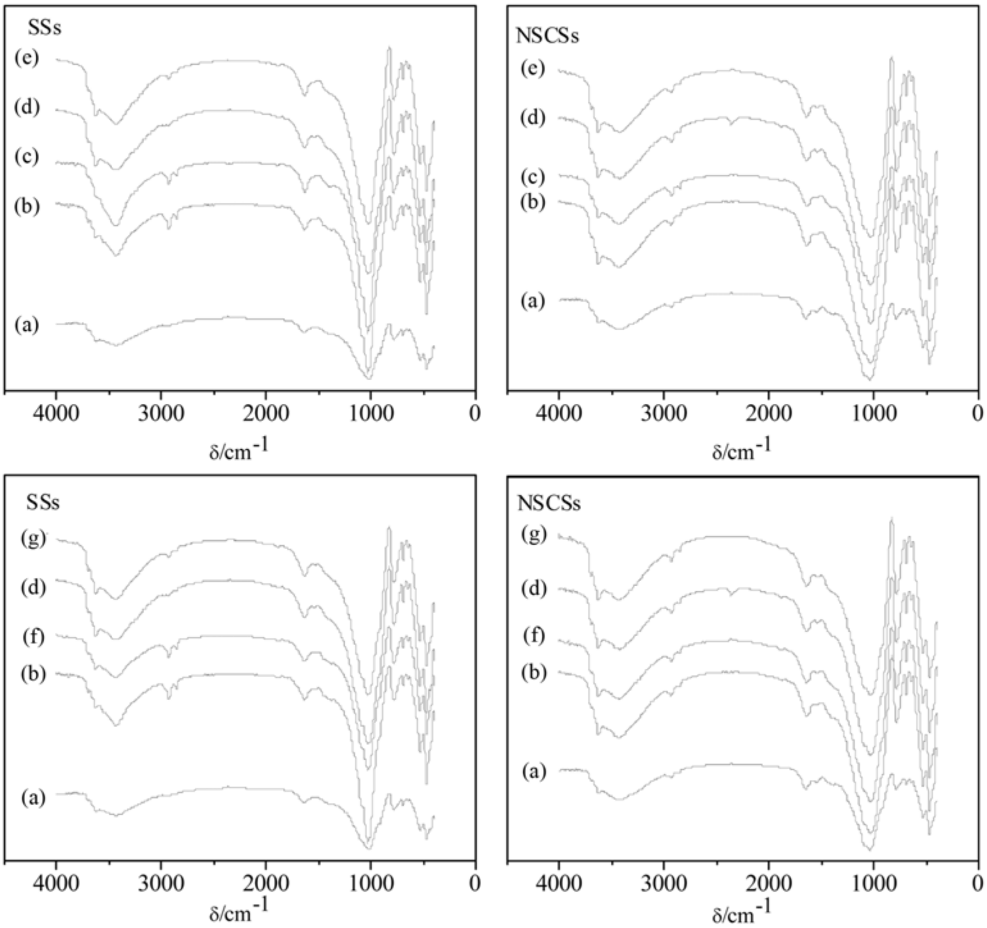

Fig. 4. FT-IR spectra of SSs (NSCSs) before and after AT, Cd, Cu and Ma adsorption. (a) original sample; (b) AT adsorption only; (c) simultaneous adsorption AT and Cd; (d) simultaneous adsorption AT and Ma; (e) simultaneous adsorption AT, Cd and Ma; *(f)* simultaneous adsorption AT and Cu adsorption; (g) simultaneous adsorption AT, Cu and Ma adsorption.

Table 4. Assignments of absorption bands in the FTIR spectra

Sample	Assignments	Frequency/cm^{-1}						
		Original	AT	AT-Cd	AT-Cu	AT-Ma	AT-Cd-Ma	AT-Cu-Ma
SSs	O-H or -NH	3426	3432	3430	3424	3428	3436	3634
		δ	6	4	-2	2	10	8
	C=O	1632	1632	1630	1632	1634	1628	1634
		δ	0	−2	0	2	−4	2
	C-O or Si-O	1032	1034	1032	1034	1032	1034	1034
		d	2	0	2	0	2	2
NSCSs	O-H or -NH	3426	3434	3420	3426	3420	3430	3426
		δ	8	−6	0	−6	4	0
	-CH	2926	2926	2924	2924	2926	2926	2928
		δ	0	−2	−2	0	0	2
	C=O	1654	1638	1636	1638	1640	1640	1640
		δ	−16	−18	−18	−14	−14	−14
	C-O or Si-O	1038	1034	1034	1034	1034	1036	1034
		δ	−4	−4	−4	−4	−2	−4

Fig. 4(a) and (b). The result suggests that the addition of cadmium enhances AT adsorption, and this is consistent with the results reported by Li et al. [20]. Moreover, for the band of either O-H or N-H shifts, the result suggests that either O-H or N-H plays an important role in AT adsorption processes. Cd can be bound to AT; the binding leads to the formation of a “bridge” between pollutants molecules and thereby enhances AT adsorption, whereas this phenomenon is not observed in the IR spectra of NSCSs. The absorbance of C=O group (1,632 cm^{-1}) in FTIR spectra of SSs shifts insignificantly but that of C=O group (1,654 cm^{-1}) in NSCSs shifts noticeably to the lower frequency, suggesting that the group C=O in NSCSs might be related to the AT adsorption and there is competition effect of AT with other pollutants.

CONCLUSIONS

Conclusions are summarized as follows:

(1) In the binary systems of AT-Ma, while AT is adsorbed without Ma or adsorbed simultaneously with Ma, the addition of Ma enhances AT adsorption on SSs (NSCSs) through forming hydrogen bonds between AT and Ma; when Ma is adsorbed after coating with AT, Ma inhibits AT adsorption mainly due to competitive adsorption.

(2) In the ternary systems of AT-cadmium/copper-Ma, co-existing cadmium and Ma have additive effect while co-existing copper and Ma have deductive effect on AT adsorption on SSs (NSCSs).

(3) The FTIR studies confirm that the bands of O-H or N-H and C=O have connections with AT adsorption and there are combination effects. The IR absorbance of group of O-H or N-H in SSs and NSCSs shifted to higher frequencies after AT adsorption. Furthermore, the absorbance of the group C=O in NSCSs shifts more significantly than that in SSs.

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