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Original Research

Interference Adsorption of Cadmium with a Variety of Pollutants in Sediments Based on Fractional Factorial Design (Resolution V)

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Abstract

The characteristics of composite cadmium contamination via adsorption onto the surficial sediments in a pesticide (dimethoate, metalaxyl, atrazine, malathion, and prometryn)/heavy metal (copper, zinc, lead, cadmium, and nickel) composite contamination system were examined. To do this, a confounding design-assisted resolution V of 2^{10-3} fractional factorial design method composed of a fixed effects model, a multiple linear regression model, and the best subset regression modeling methods was used to identify the main effects and second-order interaction effects of the aforementioned pollutants. Overall, 87.08% of the total contribution to cadmium adsorption derived from the main effect, and the main effects of copper, lead, zinc, and dimethoate had a significant antagonistic effect on cadmium adsorption on the sediments in the order of: copper (17.41%)>lead (13.09%)>zinc (10.06%)>dimethoate (5.03%), while the main effects of cadmium (41.49%) had a significant synergistic effect. Moreover, 12.92% of the total contribution to cadmium adsorption was attributed to second-order interaction effects (zinc*nickel and copper*zinc), with zinc*nickel (4.57%) having a significant antagonistic effect and copper*zinc (8.35%) having a significant synergistic effect on cadmium adsorption on the sediments. When compared with resolution IV of the 2^{10-5} fractional factorial design method, the freedom of resolution V of the 2^{10-3} fractional factorial design method increased from 21 to 45. This showed that resolution V of the 2^{10-3} fractional factorial design method can significantly distinguish the aliases of the second-order interaction effects related to the objective pollutant cadmium. Also, the total contribution to cadmium adsorption of the second-order interaction effects decreased from 61.48% to 12.92%, indicating that resolution IV of the 2^{10-5} fractional factorial design method overestimates the second-order interaction effect on cadmium adsorption on sediments.

Keywords: cadmium, heavy metals, pesticides, competitive adsorption, fractional factorial design

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Introduction

With the rapid development of agriculture and industry, pollution problems have become increasingly prominent [1]. Pesticides and heavy metals discharged into the environment accumulate [2] and later cause serious pollution to the atmosphere [3], water [4], and soil [5], while threatening the health of animals, plants, and humans [6-7]. There are few instances of only one pollutant or pollution source in the environment [8], and interactions between two types of pollutants often lead to further contamination by changing the environmental behavior and eco-toxicity, and forming a combined pollution [9].

Sediment is a type of small particle that can be moved by fluid flow and eventually become a layer of solid particles at the bottom of an aquatic system. Sediment is an important carrier leading to the migration of many pollutants in natural surfaces, as well as a major destination of pollutants in water [10]. Sediment can accumulate a variety of heavy metals, pesticides, and other pollutants from aquatic environments [11]. Scholars from various countries have conducted many studies regarding the adsorption behavior of heavy metals and pesticides in the water-sediment interface. These include investigations of pesticides and heavy metal contents of different geographical sediments [12-14], the mechanism of sediment adsorption on pollutants, and the mechanism of sediment adsorption on pollutants under combined pollution cases [15]. Guo et al. measured the effects of Cr (VI) and As (V) on lindane sorption and found that more lindane is adsorbed by biofilms than suspended particles and sediments on a total mass basis, whereas the sediments had a higher lindane sorption capacity per unit mass of organic carbon than suspended particles and biofilms. Co-occurring Cr (VI) or As (V) decreased the lindane sorption on the biofilms by about 48% [16].

Currently, the main difficulty in such studies is that there are many different types of pollutants in nature, making the combined fouling mechanism extremely complex. Cheng et al. used a resolution IV fractional factorial design method to explore the combined pollution rules of malathion and a variety of pollutants in sediment [17]. However, they could not solve the mixed phenomenon between the main effects and the second-order interaction.

Cadmium is a toxic heavy metal that is extremely harmful to humans and other mammalian species [18] and that is present in air, soil, sediments, water, and smoke. Following intake, cadmium accumulates in multiple organs and tissues – particularly the liver and kidneys [19]. In this study, we used a resolution V 2^{10-3} fractional factorial design method to reveal the composite contamination characteristics of cadmium adsorption onto the surficial sediments in a pesticide (dimethoate, metalaxyl, atrazine, malathion, and prometryn)/heavy metal (copper, zinc, lead, cadmium, and nickel) composite contamination system. This study provides theoretical support for revealing the combined pollution mechanism between pesticides and heavy metals.

Materials and Methods

Sediment Sample Collection and Pretreatment

Sediment samples were collected from the Songhua River in Jilin, China. Samples were collected from the surface layer to a depth of 5 cm using a digging type sampler. One sample was collected every 20 cm from around the sampling point, and four samples were collected and then composited into a single sample.

Experimental Methods and Designs

Five pesticides – dimethoate (A), metalaxyl (B), atrazine (C), malathion (D), and prometryn (E) – and five heavy metals – copper (F), cadmium (G), lead (H), zinc (J), and nickel (K) – were selected as experimental factors. The heavy metal Cd was the target pollutant, and the main effects and second-order interaction effects of pollutant adsorption on the sediments to the targets were investigated. The factor levels are shown in Table 1. In this experiment, a 2^{10-3} resolution V fractional factorial experiment with a minimum low-order mixture was used and 128 was treated as a unit and set parallel to the sample, resulting in a total of 384 group processing. Table 2 shows a 2^{10-3} fractional factorial experimental table established using statistical analysis software. Based on the principles of fractional factorial design in Minitab, the interactions of dimethoate (A), metalaxyl (B), atrazine (C), malathion (D), prometryn (E), Cd (G), and Cu (F), and the form of the generating element, the concentrations of Pb (H), Zn (J), and Ni (K) are determined as follows: H = ABCG, J = BCDE, and K = ACDF.

A mixed solution of 10 pollutants at different concentrations was prepared in accordance with Table 2. Next, 20 ml of each of the 384 mixed solutions was placed into a conical flask containing 0.1000±0.0001 g of sediment samples. Each solution was then oscillated at room temperature for 48 h, after which the solution was passed through filter paper with a pore size of 0.22 μm. Subsequently, the concentrations of pesticides and heavy metals in each solution were measured using HPLC and a flame atomic absorption spectrophotometer. In addition, the initial concentrations of the pollutants were measured. Finally, the amounts of pollutants adsorbed were determined by differential subtraction calculations.

According to the principle of the resolution V fractional factorial design method, the generators of the main effects and the second-order interaction effects were determined, and the aliases of the main effects and the second-order interaction effects were found to be as follows:

- Aliases of the main effects: A = BCGH = CDFK, B = ACGH = CDEJ, C = ABGH = ADFK = BDEJ, D = ACFK = BCEJ, E = BCDJ, F = ACDK, G = ABCH, H = ABCG, J = BCDE, K = ACDF.

Table 1. High and low levels of five heavy metals and five pesticides (μmol/L).

Level	Dimethoate	Metalaxyl	Atrazine	Malathion	Prometryn
Low (-)	10	10	10	10	10
High (+)	25	25	25	25	25
Level	Cu	Cd	Pb	Zn	Ni
Low (-)	60	60	60	60	60
High (+)	150	150	150	150	150

Table 2. 2^{10-3} fractional factorial design of 10 pollutants adsorbed onto the sediments.

	Dimethoate	Metalaxyl	Atrazine	Malathion	Prometryn	Cu	Cd	Pb	Zn	Ni
1	-	+	+	-	-	-	+	-	+	-
2	+	+	+	-	+	-	-	-	-	+
3	-	+	-	+	-	-	+	+	+	-
4	+	-	+	-	-	+	+	-	-	-
5	+	-	-	-	+	-	+	+	-	-
6	-	-	+	+	+	-	+	+	-	+
7	+	+	-	+	+	+	-	+	-	-
8	-	+	-	+	-	+	-	-	+	+
9	-	-	-	-	+	-	-	+	-	+
10	+	+	-	-	-	+	+	-	-	+
11	-	+	-	+	+	+	-	-	-	+
12	-	+	+	+	+	+	+	-	+	-
13	+	-	+	+	+	-	-	+	-	-
14	+	+	-	-	+	-	+	-	+	-
15	-	-	+	-	-	-	+	+	-	-
16	-	+	+	+	-	-	-	+	-	+
17	+	-	-	-	-	-	+	+	+	-
18	-	+	+	-	-	+	+	-	+	+
19	+	+	+	+	-	+	-	-	-	+
20	-	+	-	-	+	-	-	-	+	+
21	-	-	+	-	-	+	+	+	-	+
22	-	-	-	+	+	-	-	+	+	-
23	+	+	-	+	-	-	-	+	+	+
24	-	+	-	+	+	-	-	-	-	-
25	-	+	+	+	-	-	+	-	-	+
26	+	+	-	-	-	+	-	+	-	+
27	+	+	+	+	+	-	-	-	+	-
28	+	-	-	+	+	+	-	-	+	-
29	-	-	+	-	-	-	-	-	-	-
30	-	-	-	-	+	+	+	-	-	-
31	+	+	+	+	+	-	+	+	+	-

Table 2. Continued.

32	-	-	-	-	-	-	-	+	+	+
33	+	+	+	-	-	+	-	-	+	-
34	-	+	-	-	+	+	-	-	+	-
35	+	+	-	-	-	-	+	-	-	-
36	-	+	+	-	-	+	-	+	+	+
37	-	-	-	+	-	-	-	+	-	-
38	+	-	-	-	-	+	+	+	+	+
39	+	+	-	-	-	-	-	+	-	-
40	-	-	-	+	-	+	+	-	-	+
41	+	+	-	-	+	+	+	-	+	+
42	-	-	+	+	-	-	+	+	+	+
43	-	-	+	-	+	+	+	+	+	+
44	+	-	-	-	-	+	-	-	+	+
45	+	+	+	-	+	+	+	+	-	-
46	-	+	-	+	+	-	+	+	-	-
47	-	-	-	-	-	+	-	+	+	-
48	+	+	+	+	-	-	-	-	-	-
49	-	+	-	+	-	-	-	-	+	-
50	-	-	+	+	-	-	-	-	+	+
51	+	+	-	+	-	+	-	+	+	-
52	+	+	-	-	+	+	-	+	+	+
53	+	-	-	+	-	+	-	-	-	-
54	-	-	+	+	+	-	-	-	-	+
55	-	-	-	+	-	+	-	+	-	+
56	+	+	+	-	+	-	+	+	-	+
57	-	+	+	+	+	-	+	-	+	+
58	+	-	+	-	-	-	-	+	-	+
59	+	+	-	+	+	-	-	+	-	+
60	+	+	+	+	+	+	+	+	+	+
61	-	+	-	-	-	+	+	+	-	-
62	+	-	+	+	+	+	-	+	-	+
63	+	-	-	-	+	+	+	+	-	+
64	+	-	+	-	+	+	+	-	+	-
65	-	-	-	+	-	-	+	-	-	-
66	+	+	-	+	+	-	+	-	-	+
67	+	-	+	-	+	+	-	+	+	-
68	-	+	-	-	-	+	-	-	-	-
69	+	+	+	-	-	+	+	+	+	-
70	-	-	+	+	-	+	-	-	+	-
71	-	-	-	-	-	+	+	-	+	-
72	-	+	+	-	+	+	+	-	-	+

Table 2. Continued.

73	+	+	+	+	-	+	+	+	-	+
74	-	+	+	-	-	-	-	+	+	-
75	-	-	-	-	+	+	-	+	-	-
76	-	+	-	-	+	-	+	+	+	+
77	-	-	+	-	+	-	-	-	+	-
78	+	-	+	+	-	-	-	+	+	-
79	+	-	-	+	+	-	-	-	+	+
80	+	-	+	-	-	-	+	-	-	+
81	+	+	-	-	+	-	-	+	+	-
82	-	-	+	-	+	-	+	+	+	-
83	+	-	+	+	+	+	+	-	-	+
84	+	-	-	+	-	+	+	+	-	-
85	+	-	-	+	+	-	+	+	+	+
86	+	-	+	+	-	+	-	+	+	+
87	-	-	-	+	+	+	+	-	+	+
88	-	+	+	-	+	-	+	-	-	-
89	-	-	-	-	+	-	+	-	-	+
90	+	-	-	-	+	-	-	-	-	-
91	+	-	+	+	+	-	+	-	-	-
92	+	+	+	+	+	+	-	-	+	+
93	+	-	+	+	-	-	+	-	+	-
94	+	+	-	+	-	-	+	-	+	+
95	+	+	-	+	-	+	+	-	+	-
96	+	-	+	-	+	-	-	+	+	+
97	+	-	-	+	+	+	+	+	+	-
98	+	-	+	-	-	+	-	+	-	-
99	+	-	-	-	-	-	-	-	+	-
100	-	+	-	-	+	+	+	+	+	-
101	-	+	+	+	+	-	-	+	+	+
102	-	+	+	+	+	+	-	+	+	-
103	-	+	-	-	-	-	+	+	-	+
104	-	+	+	-	+	+	-	+	-	+
105	-	+	-	+	-	+	+	+	+	+
106	-	-	+	+	-	+	+	+	+	-
107	+	-	-	+	-	-	-	-	-	+
108	-	+	-	-	-	-	-	-	-	+
109	-	-	+	+	+	+	+	+	-	-
110	-	+	+	+	-	+	+	-	-	-
111	-	-	-	+	+	-	+	-	+	-
112	-	+	+	+	-	+	-	+	-	-
113	+	-	-	+	-	-	+	+	-	+

Table 2. Continued.

114	-	-	+	-	+	+	-	-	+	+
115	+	+	+	+	-	-	+	+	-	-
116	+	+	+	-	-	-	+	+	+	+
117	+	-	+	+	-	+	+	-	+	+
118	-	-	+	-	-	+	-	-	-	+
119	-	+	+	-	+	-	-	+	-	-
120	-	+	-	+	+	+	+	+	-	+
121	-	-	-	+	+	+	-	+	+	+
122	+	+	+	-	-	-	-	-	+	+
123	+	+	+	-	+	+	-	-	-	-
124	+	-	+	-	+	-	+	-	+	+
125	-	-	-	-	-	-	+	-	+	+
126	+	+	-	+	+	+	+	-	-	-
127	-	-	+	+	+	+	-	-	-	-
128	+	-	-	-	+	+	-	-	-	+

- Aliases of the second-order interaction effects: AB = CGH = EFJK, AC = BGH = DFK, AD = CFK = EGHJ, AE = BFJK = DGHJ, AF = CDK = BEJK, AG = BCH = DEHJ, AH = BCG = DEGJ, AJ = BEFK = DEGH, AK = CDF = BEFJ, BC = AGH = DEJ, BD = CEJ = FGHK, BE = CDJ = AFJK, BF = AEJK = DGHK, BG = ACH = DFHK, AK = CDF = BEFJ, BC = AGH = DEJ, BD = CEJ = FGHK, BE = CDJ = AFJK, BF = AEJK = DGHK, BG = ACH = DFHK, BH = ACG = DFGK, BJ = CDE = AEFK, BK = AEFJ = DFGH, CD = AFK = BEJ, CE = BDJ, CF = ADK, CG = ABH, CH = ABG, CJ = BDE, CK = ADF, DE = BCJ = AGHJ, DF = ACK = BGHK, DG = AEHJ = BFHK, DH = AEGJ = BFGK, DJ = BCE = AEGH, DK = ACF = BFGH, EF = ABJK, EG = ADHJ, EH = ADGJ, EJ = BCD = ABFK = ADGH, EK = ABFJ, FG = BDHK, FH = BDGK, EG = ADHJ, EH = ADGJ, EJ = BCD = ABFK = ADGH, EK = ABFJ, FG = BDHK, FH = BDGK, FJ = ABEK, FK = ACD = ABEJ = BDGH, GH = ABC = ADEJ = BDFK, GJ = ADEH, GK = BDFH, HJ = ADEG, HK = BDFG, JK = ABEF.

As shown above, the alias structure of interactions could be used to distinguish the main effects from the second-order interaction effects completely by fractional factorial design of resolution V. In addition, the response value of each main effect and the second-order interaction effect were estimated.

Data Processing and Analysis

Experimental design and statistical analysis were performed using the experimental design module in the Minitab software package (Design of Experiment). Before using a fixed effects model, a fit test (i.e., normal assumption, independence assumption of residuals, and homogeneity assumption of the variance) was carried out [20]. The model was only considered suitable if it met the above conditions. Next, we set the adsorption capacity of Cd onto the sediment as the dependent variable and the 10 types of main pollutant concentration effects and the second-order interaction effects as the independent variables. This was done to establish the multiple linear regression adsorption model and the best subset regression model.

Table 3. Analysis of variance of Cd adsorption effects.

Source	DF	SS	MS	F	P
Main effect	10	1,487.59	148.76	45.84	0.000
Second-order effect	45	211.37	4.70	1.45	0.080
Residual error	72	233.67	3.25		
Total	127	1,932.63			

Table 4. Estimates of main and second-order effects of pollutant concentrations affecting Cd in the sorption of heavy metals and the pesticide system.

Factor	Estimate of effect	Coefficient	T	P
Constant	9.568	0.1592	0.000	
Dimethoate	-0.706	-0.353	-2.22	0.030
Metalaxyl	-0.155	-0.078	-0.49	0.627
Atrazine	0.398	0.199	1.25	0.215
Malathion	0.432	0.216	1.36	0.179
Prometryn	-0.190	-0.095	-0.60	0.552
Cu	-2.442	-1.221	-7.67	0.000
Cd	5.821	2.910	18.28	0.000
Pb	-1.836	-0.918	-5.76	0.000
Zn	-1.412	-0.706	-4.43	0.000
Ni	-0.612	-0.306	-1.92	0.059
Dimethoate*Metalaxyl	-0.483	-0.242	-1.52	0.134
Dimethoate*Atrazine	0.283	0.141	0.89	0.378
Dimethoate*Malathion	0.144	0.072	0.45	0.653
Dimethoate*Prometryn	0.089	0.044	0.28	0.781
Dimethoate*Cu	0.127	0.063	0.40	0.692
Dimethoate*Cd	-0.340	-0.170	-1.07	0.290
Dimethoate*Pb	0.207	0.104	0.65	0.518
Dimethoate*Zn	-0.087	-0.043	-0.27	0.786
Dimethoate*Ni	0.422	0.211	1.33	0.189
Metalaxyl*Atrazine	-0.137	-0.068	-0.43	0.669
Metalaxyl*Malathion	-0.477	-0.238	-1.50	0.139
Metalaxyl*Prometryn	0.109	0.055	0.34	0.733
Metalaxyl*Cu	0.241	0.121	0.76	0.452
Metalaxyl*Cd	-0.219	-0.110	-0.69	0.493
Metalaxyl*Pb	0.170	0.085	0.53	0.595
Metalaxyl*Zn	-0.414	-0.207	-1.30	0.198
Metalaxyl*Ni	-0.173	-0.087	-0.54	0.588
Atrazine*Malathion	-0.299	-0.149	-0.94	0.351
Atrazine*Prometryn	0.415	0.207	1.30	0.197
Atrazine*Cu	-0.093	-0.047	-0.29	0.770
Atrazine*Cd	0.510	0.255	1.60	0.114
Atrazine*Pb	-0.128	-0.064	-0.40	0.690
Atrazine*Zn	-0.546	-0.273	-1.71	0.091
Atrazine*Ni	-0.311	-0.155	-0.98	0.332
Malathion*Prometryn	-0.319	-0.159	-1.00	0.320
Malathion*Cu	0.335	0.168	1.05	0.296
Malathion*Cd	0.081	0.041	0.26	0.799
Malathion*Pb	0.162	0.081	0.51	0.612

Table 4. Continued.

Malathion*Zn	-0.292	-0.146	-0.92	0.363
Malathion*Ni	-0.198	-0.099	-0.62	0.536
Prometryn*Cu	0.335	0.167	1.05	0.297
Prometryn*Cd	0.369	0.184	1.16	0.251
Prometryn*Pb	0.133	0.066	0.42	0.679
Prometryn*Zn	0.478	0.239	1.50	0.137
Prometryn*Ni	-0.367	-0.183	-1.15	0.253
Cu*Cd	-0.205	-0.103	-0.64	0.521
Cu*Pb	-0.512	-0.256	-1.61	0.112
Cu*Zn	1.171	0.585	3.68	0.000
Cu*Ni	-0.123	-0.061	-0.38	0.702
Cd*Pb	-0.588	-0.294	-1.85	0.069
Cd*Zn	-0.487	-0.244	-1.53	0.130
Cd*Ni	-0.538	-0.269	-1.69	0.096
Pb*Zn	0.625	0.313	1.96	0.053
Pb*Ni	0.062	0.031	0.19	0.846
Zn*Ni	-0.641	-0.321	-2.01	0.048

Analysis of Variance

Effect estimates and analysis of variance were employed to analyze the effects of the pollutant factor concentration in the heavy metal/pesticide coexistence system on the adsorption capacity of the sediment to Cd. Next, the significant impact factors were filtered out using $P < 0.05$ to indicate significance. The analysis of variance results are shown in Table 3, and the effect estimates are presented in Table 4.

As shown in Table 3, analysis of variance showed that the main effect was significant, while the second-order interaction effect was not, indicating that the main effects influenced the absorption of cadmium on sediment. When compared with resolution IV of the 2^{10-5} fractional factorial design method, the freedom increases from 21 to 45, and the alias structures of second-order interaction effects are broken in the resolution V experiment, showing that resolution V of the 2^{10-3} fractional factorial design method can distinguish the alias structure of the second-order interaction effect significantly [17].

As shown in Table 4, the main effects of Cd, as well as the second-order interaction effects of cadmium*Zn, had significant synergistic effects on cadmium adsorption in the sediment. The estimated effects were 5.821 and 1.171, respectively, while the main effects of factors that had significant antagonistic effects on Cd adsorption on the sediment were Cu = −2.442, Pb = −1.836, Zn = −1.412, dimethoate = −0.706, and Ni = −0.612, and the second-order interaction effect was Zn*nickel = 0.048.

Analysis of Contribution Rate

The contribution rate of the significant main effects and second-order interaction effects to Cd adsorption reflected the composite contamination characteristics of Cd adsorption directly. Combined pollution effects are shown in Table 5.

Table 5 lists the calculated values of the main effects and the second-order interaction effects based on a fixed effects model, as well as the contribution rate of synergism and antagonism. As shown in the table, the contribution of the main effects and second-order interaction effects to the adsorption of Cd were 87.08% and 12.92%, respectively, and the contribution rate of Cd was 41.49%. Ma et al. pre-

Table 5. Combined pollution effects of pollutant fact concentration of Cd adsorption.

Factor	Estimate of effect	Rate of contribution[%]	
		synergism	antagonism
Cd	5.821	41.49	
Cu	-2.442		17.41
Pb	-1.836		13.09
Zn	-1.412		10.06
Dimethoate	-0.706		5.03
Cu*Zn	1.171	8.35	
Zn*Ni	-0.641		4.57
Total	14.029	49.84	50.16

Table 6. Goodness of fit test for AT-MRAM (1).

MRAM	R^2	Adjust R^2	Forecast R^2
Value	87.91%	78.67%	61.79%

Table 7. T-test for AT-MRAM (1).

Factor	Coefficient	T	P
Constant	0.1592	0.000	
Dimethoate	-0.353	-2.22	0.030
Metalaxyl	-0.078	-0.49	0.627
Atrazine	0.199	1.25	0.215
Malathion	0.216	1.36	0.179
Prometryn	-0.095	-0.60	0.552
Cu	-1.221	-7.67	0.000
Cd	2.910	18.28	0.000
Pb	-0.918	-5.76	0.000
Zn	-0.706	-4.43	0.000
Ni	-0.306	-1.92	0.059
Dimethoate*Metalaxyl	-0.242	-1.52	0.134
Dimethoate*Atrazine	0.141	0.89	0.378
Dimethoate*Malathion	0.072	0.45	0.653
Dimethoate*Prometryn	0.044	0.28	0.781
Dimethoate*Cu	0.063	0.40	0.692
Dimethoate*Cd	-0.170	-1.07	0.290
Dimethoate*Pb	0.104	0.65	0.518
Dimethoate*Zn	-0.043	-0.27	0.786
Dimethoate*Ni	0.211	1.33	0.189
Metalaxyl*Atrazine	-0.068	-0.43	0.669
Metalaxyl*Malathion	-0.238	-1.50	0.139
Metalaxyl*Prometryn	0.055	0.34	0.733
Metalaxyl*Cu	0.121	0.76	0.452
Metalaxyl*Cd	-0.110	-0.69	0.493
Metalaxyl*Pb	0.085	0.53	0.595
Metalaxyl*Zn	-0.207	-1.30	0.198
Metalaxyl*Ni	-0.087	-0.54	0.588
Atrazine*Malathion	-0.149	-0.94	0.351
Atrazine*Prometryn	0.207	1.30	0.197
Atrazine*Cu	-0.047	-0.29	0.770
Atrazine*Cd	0.255	1.60	0.114
Atrazine*Pb	-0.064	-0.40	0.690
Atrazine*Zn	-0.273	-1.71	0.091
Atrazine*Ni	-0.155	-0.98	0.332
Malathion*Prometryn	-0.159	-1.00	0.320
Malathion*Cu	0.168	1.05	0.296
Malathion*Cd	0.041	0.26	0.799
Malathion*Pb	0.081	0.51	0.612
Malathion*Zn	-0.146	-0.92	0.363
Malathion*Ni	-0.099	-0.62	0.536
Prometryn*Cu	0.167	1.05	0.297
Prometryn*Cd	0.184	1.16	0.251
Prometryn*Pb	0.066	0.42	0.679
Prometryn*Zn	0.239	1.50	0.137
Prometryn*Ni	-0.183	-1.15	0.253
Cu*Cd	-0.103	-0.64	0.521
Cu*Pb	-0.256	-1.61	0.112
Cu*Zn	0.585	3.68	0.000
Cu*Ni	-0.061	-0.38	0.702
Cd*Pb	-0.294	-1.85	0.069
Cd*Zn	-0.244	-1.53	0.130
Cd*Ni	-0.269	-1.69	0.096
Pb*Zn	0.313	1.96	0.053
Pb*Ni	0.031	0.19	0.846
Zn*Ni	-0.321	-2.01	0.048

viously revealed the combined pollution characteristics of Cd adsorption onto the surficial sediments by resolution IV of the 2^{10-5} fractional factorial design method. When compared with resolution IV, the total contri-bution to cadmium adsorption of the second-order interaction effect decreased from 61.48% to 12.92%. This indicates that resolution V overestimates the second-order interaction effect of cadmium adsorption onto the sediments [21]. The single factor of Cd plays a critical role in inhibition of the absorption of Cd. The sum of the contribution of synergism and antagonism was 49.84% and 50.16%, respectively, revealing that the synergism and antagonism of Cd absorption reached a balanced state in the combined pollution system. The main effects of heavy metals had a greater influence than that of the pesticides. All of the heavy metals except Cd inhibit the absorption of Cd.

Establishing the Multiple Linear Regression Model

The statistical module of the Minitab software was used to establish an adsorption model of multiple linear regression between the main effects of the adsorption capacity of Cd on the sediment with 10 types of pollutant factors and the second-order interaction effects.

Table 8. Best subset regression of AT-MRAM.

Vars	R-Sq	R-Sq (ad)	Mallows Cp	S	Dimethoate	Metalaxyl	Atrazine	Malathion	Prometryn	Ni	Cu*Cd	Cu*Pb	Cu*Ni	Cd*Pb	Cd*Zn	Cd*Ni	Pb*Zn	Pb*Ni	Dimethoate *Metalaxyl	Dimethoate *Atrazine	Dimethoate *Malathion	Dimethoate *Prometryn	Dimethoate* Cu	Dimethoate* Cd	Dimethoate* Pb	Dimethoate* Zn	Dimethoate* Ni
1	78.6	77.4	16.6	1.8551	X																						
2	79.3	77.9	14.7	1.8345	X												X										
3	79.9	78.4	12.9	1.8145	X					X							X										
4	80.5	78.8	11.5	1.7961	X					X				X			X										
5	80.9	79.1	10.6	1.7816	X					X				X		X	X										
6	81.4	79.4	10.0	1.7688	X					X		X		X		X	X										
7	81.8	79.7	9.6	1.7577	X					X		X		X	X	X	X										
8	82.2	80.0	9.3	1.7466	X					X		X		X	X	X	X		X								
9	82.5	80.1	9.5	1.7391	X			X		X		X		X	X	X	X		X								
10	82.8	80.3	9.7	1.7322	X			X		X		X		X	X	X	X		X								
11	83.0	80.4	10.1	1.7267	X		X	X		X		X		X	X	X	X		X								
12	83.2	80.4	11.0	1.7248	X		X	X		X		X		X	X	X	X		X								
13	83.4	80.4	12.2	1.7260	X		X	X		X		X		X	X	X	X		X								
14	83.4	80.3	13.7	1.7303	X		X	X		X		X		X	X	X	X		X								
15	83.5	80.2	15.3	1.7348	X		X	X		X	X	X		X	X	X	X		X								
16	83.6	80.1	16.9	1.7399	X		X	X	X	X	X	X		X	X	X	X		X								
17	83.6	80.0	18.7	1.7461	X	X	X	X	X	X	X	X		X	X	X	X		X								
18	83.6	79.8	20.5	1.7527	X	X	X	X	X	X	X	X		X	X	X	X		X		X						
19	83.7	79.6	22.3	1.7599	X	X	X	X	X	X	X	X		X	X	X	X		X		X		X				
20	83.7	79.5	24.2	1.7672	X	X	X	X	X	X	X	X	X	X	X	X	X		X		X		X				
21	83.7	79.3	26.1	1.7753	X	X	X	X	X	X	X	X	X	X	X	X	X		X		X	X	X				
22	83.7	79.1	28.0	1.7836	X	X	X	X	X	X	X	X	X	X	X	X	X		X		X	X	X			X	
23	83.7	78.9	30.0	1.7923	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X		X	X	X			X	

Initially, all 10 pollutant factors and their second-order interaction terms were set as independent variables as follows:

$$Y_{(Cd)}=9.57-\Gamma_{Dimethoate}(0.353)X_{Dimethoate}-\Gamma_{Metalaxyl}(0.078)X_{Metalaxyl}+\Gamma_{Atrazine}(0.199)X_{Atrazine}+\Gamma_{Malathion}(0.216)X_{Malathion}-\Gamma_{Prometryn}(0.095)X_{Prometryn}-\Gamma_{Cu}(1.22)X_{Cu}+\Gamma_{Cd}(2.91)X-\Gamma_{Pb}(0.918)X_{Pb}-\Gamma_{Zn}(0.706)X_{Zn}-\Gamma_{Ni}(0.306)X_{Ni}-\Gamma_{Dimethoate*Metalaxyl}(0.242)X_{Dimethoate}X_{Metalaxyl}+\Gamma_{Dimethoate*Atrazine}(0.141)X_{Dimethoate}X_{Atrazine}+\Gamma_{Dimethoate*Malathion}(0.072)X_{Dimethoate}X_{Malathion}+\Gamma_{Dimethoate*Prometryn}(0.044)X_{Dimethoate}X_{Prometryn}+\Gamma_{Dimethoate*Cu}(0.063)X_{Dimethoate}X_{Cu}-\Gamma_{Dimethoate*Cd}(0.170)X_{Dimethoate}X_{Cd}+\Gamma_{Dimethoate*Pb}(0.104)X_{Dimethoate}X_{Pb}-\Gamma_{Dimethoate*Zn}(0.043)X_{Dimethoate}X_{Zn}+\Gamma_{Dimethoate*Ni}(0.211)X_{Dimethoate}X_{Ni}-\Gamma_{Metalaxyl*Atrazine}(0.068)X_{Metalaxyl}X_{Atrazine}-\Gamma_{Metalaxyl*Malathion}(0.238)X_{Metalaxyl}X_{Malathion}+\Gamma_{Metalaxyl*Prometryn}(0.055)X_{Metalaxyl}X_{Prometryn}+\Gamma_{Metalaxyl*Cu}(0.121)X_{Metalaxyl}X_{Cu}-\Gamma_{Metalaxyl*Cd}(0.110)X_{Metalaxyl}X_{Cd}+\Gamma_{Metalaxyl*Pb}(0.064)X_{Metalaxyl}X_{Pb}-\Gamma_{Metalaxyl*Zn}(0.207)X_{Metalaxyl}X_{Zn}+\Gamma_{Metalaxyl*Ni}(0.087)X_{Metalaxyl}X_{Ni}-\Gamma_{Atrazine*Malathion}(0.149)X_{Atrazine}X_{Malathion}+\Gamma_{Atrazine*Prometryn}(0.207)X_{Atrazine}X_{Prometryn}-\Gamma_{Atrazine*Cu}(0.043)X_{Atrazine}X_{Cu}+\Gamma_{Atrazine*Cd}(0.255)X_{Atrazine}X_{Cd}-\Gamma_{Atrazine*Pb}(0.064)X_{Atrazine}X_{Pb}-\Gamma_{Atrazine*Zn}(0.273)X_{Atrazine}X_{Zn}-\Gamma_{Atrazine*Ni}(0.155)X_{Atrazine}X_{Ni}-\Gamma_{Malathion*Prometryn}(0.159)X_{Malathion}X_{Prometryn}+\Gamma_{Malathion*Cu}(0.168)X_{Malathion}X_{Cu}+\Gamma_{Malathion*Cd}(0.041)X_{Malathion}X_{Cd}+\Gamma_{Malathion*Pb}(0.081)X_{Malathion}X_{Pb}-\Gamma_{Malathion*Zn}(0.146)X_{Malathion}X_{Zn}-\Gamma_{Malathion*Ni}(0.099)X_{Malathion}X_{Ni}+\Gamma_{Prometryn*Cu}(0.167)X_{Prometryn}X_{Cu}+\Gamma_{Prometryn*Cd}(0.184)X_{Prometryn}X_{Cd}+\Gamma_{Prometryn*Pb}(0.066)X_{Prometryn}X_{Pb}+\Gamma_{Prometryn*Zn}(0.239)X_{Prometryn}X_{Zn}-\Gamma_{Prometryn*Ni}(0.183)X_{Prometryn}X_{Ni}-\Gamma_{Cu*Cd}(0.103)X_{Cu}X_{Cd}-\Gamma_{Cu*Pb}(0.256)X_{Cu}X_{Pb}+\Gamma_{Cu*Zn}(0.585)X_{Cu}X_{Zn}-\Gamma_{Cu*Ni}(0.061)X_{Cu}X_{Ni}-\Gamma_{Cd*Pb}(0.294)X_{Cd}X_{Pb}-\Gamma_{Cd*Zn}(0.244)X_{Cd}X_{Zn}-\Gamma_{Cd*Ni}(0.269)X_{Cd}X_{Ni}+\Gamma_{Pb*Zn}(0.313)X_{Pb}X_{Zn}+\Gamma_{Pb*Zn}(0.031)X_{Pb}X_{Ni}-\Gamma_{Zn*Ni}(0.321)X_{Zn}X_{Ni} \quad (1)$$

…where $Y_{(Cd)}$ is the adsorption capacity (mg/g) of Cd on the sediment; the independent variable, X_i, is the pollutant concentration level (mol/L); X_iX_j is the interaction of the two variables, X_i and X_j – which indicates that one of the independent variables on the dependent variable of the intensity depends on the concentration level of the other independent variables. The coefficient before each independent variable is expressed by Γ_i. The results of the test of goodness of fitting to model (1) are shown in Table 6. The multiple correlation coefficients square (R^2) value in Table 6 is 87.91%, which indicates that independent variables of model (1) can be used to explain the Cd adsorbed on the sediment, demonstrating that the fitting effect of model (1) is better. The forecast R^2 obtained from repeat experiments was much lower than the correlation coefficients square (R^2), indicating that the model exhibits an overfitting phenomenon and some independent variables should not be introduced. As shown in Table 7, the results of the T test for AT-MRAM was >0.05, confirming that the main effects and second-order interaction effects of the 10 types of factors that we studied in this paper had no significant impact on the adsorption of Cd onto the sediment. As a result, we established a new multiple linear regression model using the best subset regression modeling method to characterize the composite contamination condition of Cd and other pollutants adequately.

Establishing the Best Subset Regression Model

Best subsets regression is a method that can select an independent variable subset and identify the best-fitting regression models with user-specified predictors. The model was selected according to two standards, the maximum R^2 and Mallows' Cp, which estimates the mean square error to obtain as low a value as possible. In this study, the best subset regression model of Cd was established, and the output equation of each model was set to 2 to select the best subset combination.

As shown in Table 8, we should choose the eighth as the best subset regression model because its Mallows' Cp value is lowest and its adjusted R^2 was more than 80%. The best subset regression model was as follows:

$$Y_{(Cd)}=9.57-\Gamma_{Dimethoate}(0.353)X_{Dimethoate}-\Gamma_{Cu}(1.22)X_{Cu}+\Gamma_{Cd}(2.91)X_{Cd}-\Gamma_{Pb}(0.918)X_{Pb}-\Gamma_{Zn}(0.706)X_{Zn}-\Gamma_{Ni}(0.306)X_{Ni}-\Gamma_{Cu*Pb}(0.256)X_{Pb}X_{Pb}-\Gamma_{Cd*Pb}(0.294)X_{Cd}X_{Pb}-\Gamma_{Cd*Zn}(0.244)X_{Cd}X_{Zn}-\Gamma_{Cd*Ni}(0.269)X_{Cd}X_{Ni}+\Gamma_{Pb*Zn}(0.313)X_{Pb}X_{Zn}-\Gamma_{Dimethoate*Metalaxyl}(0.242)X_{Dimethoate}X_{Metalaxyl}-\Gamma_{Zn*Ni}(0.321)X_{Zn}X_{Ni}+\Gamma_{Cu*Zn}(0.585)X_{Cu}X_{Zn} \quad (2)$$

Conclusions

The following conclusions can be drawn based on the results of our study:

1. In this study we used a resolution V 2^{10-3} fractional factorial experiment to filter out the significant main effects and the second-order interactive effects and characterize the combined degree of Cd pollution according to estimated effects. The adjusted R^2 of the best subset regression model is more than 80%; thus, the model can be used to predict the adsorption capacity of Cd.
2. Compared with the resolution IV 2^{10-5} fractional factorial design method, the freedom of the resolution V 2^{10-3} fractional factorial design method increases from 21 to 45. The total contribution to cadmium adsorption of the second-order interaction effect decreases from 61.48% to 12.92%. This indicates that resolution IV overestimates the second-order interaction effect on cadmium adsorption on the sediments.

3. This method can also be used to study the main effects and second-order interactions of other pollutants.

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