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Competitive adsorption/desorption of dimethoate pesticide and phosphorus fertilizer in texturally different soils

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Abstract

This study aims to comprehend the competitive and non-competitive adsorption/desorption of phosphorus fertilizer and dimethoate insecticide in clay soil and clay loam soil. Characterization of the examined soils was the first step in the process, which was followed by agrochemical non-competitive adsorption, competitive adsorption, and desorption from the soil samples. Dimethoate was more absorbed than phosphorus, according to non-competitive experiments. The addition of phosphorus considerably reduced the dimethoate's adsorption capacity on the soils under test. The adsorption rates of dimethoate and phosphorus decreased to 7.21–7.82% and 9.59–9.02%, respectively, in the presence of both phosphorus and dimethoate in the clay and clay loam soils. Compared with adsorption, the desorption of the tested agrochemical into $CaCl_2$ *resulted in low values. These results highlight the environmental and public health importance of competition among agrochemicals.*

Keywords: Adsorption; desorption; dimethoate; phosphorus; soils

Introduction

Complex phenomena that are impacted by numerous mechanisms determine how agrochemicals behavior and end up in the environment (Abdel-Raheem *et al.,* 2023a, b; El-Aswad *et al.*, 2024a, b; Abd Ul-Malik *et al.*, 2024; Ibrahim *et al.*, 2024). The adsorption/desorption process is one crucial one (Fouad *et al.*, 2024a). Therefore, precise estimations of the environmental load of agrochemicals and the successful application of remediation techniques depend on a basic understanding of adsorption/desorption mechanisms (Sebaiy *et al.*, 2024; Ogbeh *et al.*, 2025). The concentration of each agrochemical in the solution as well as the sorbent's relative sorption affinity determine how much the sorption behavior is impacted by multiple solute interactions (Ayenew and Getu, 2025). Adsorption isotherms offer useful data for analyzing how agrochemicals interact with soil, forecasting their bioavailability, and determining their final environmental destiny (Davari *et al.*, 2015; Drar *et al.*, 2023; Fouad *et al.*, 2024b, c; Fouad *et al.*, 2025).

There are many publications concerning the adsorption behavior of individual agrochemicals on clays, clay minerals and soils (Bao *et al.*, 2013). Nevertheless, the competitive sorption of agrochemicals has only been covered in a small number of publications (Helios-Rybicka and Wójcik, 2012). Consequently, additional study is required to comprehend the competitive adsorption of agrochemicals in various soil types (Jalali and Moradi, 2013). In actual soil settings, different

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contaminants are frequently found in combinations (Bao *et al.,* 2013; Fouad and Abdel-Raheem, 2024). The destiny and movement of fertilizers and pesticides in soil, as well as their availability to plants, can be significantly influenced by competitive adsorption and desorption (Jalali and Moharrami, 2007; Bao *et al.*, 2013; Wang *et al.*, 2020; Abd-Eldaim *et al.*, 2023; Fouad *et al.*, 2024d, e). According to studies, coexisting chemicals may have an impact on pesticide adsorption on soil because they vie for the same adsorption sites (Jin *et al.*, 2013; Wang *et al.*, 2020). When there are insufficient adsorption sites in the soil and two or more pesticides are present, competitive adsorption occurs at the water-solid interface (Pateiro-Moure *et al.*, 2010; Wang *et al.*, 2020). Consequently, competitive sorption, as opposed to phase partitioning, is a feature of surface adsorption in diluted systems (Pateiro-Moure *et al.,* 2010).Furthermore, overlap in the range of sites that the solutes can occupy also leads to competitive adsorption (Pateiro-Moure *et al.*, 2010). Competitive adsorption may be crucial to the fate and movement of pollutants in soil because of the variety and complexity of organic molecules found in the natural environment (Sipos, 2009).

The spread of pesticides and fertilizers is a common practice in agriculture to combat pests and improve soil properties, thus increasing plant growth (Conde-Cid *et al.,* 2019). Organic and inorganic fertilizers can be introduced into the soil during pesticide application (Agbenin and Olojo, 2004). The ability of soils to selectively retain metals is essential for their availability and movement within the soil profile, which can contaminate groundwater (Agbenin and Olojo, 2004). In a copper–calcium system, copper was sorbed selectively. A system containing copper and cadmium decreased zinc adsorption, especially at $pH < 6.5$. Similarly, for pH values between 5 and 6, copper sorption decreased when zinc and cadmium were present. Harter (1992) found that the presence of nickel did not reduce copper adsorption, most likely due to the fact that copper retention processes are more complex than those of nickel. Copper is selectively sorbed from the calcium solution, while cobalt and nickel vie for sorption sites in soil.

Dimethoate is contact and systemic organic thiophosphate compound that is effective against a broad range of insects, such as mites, aphids, leafhoppers, beetles and weevils, when it is applied to a wide range of crops. American Cyanamid introduced and patented it in the 1950s (Ahmad, *et al.,* 2022). Dimethoate is acetylcholinesterase inhibitor that disables cholinesterase, and exposure to dimethoate occurs via inhalation, ingestion or/and contact (Qin *et al.*, 2025). Mostly used as foliar sprays, dimethoate is made as emulsifiable concentrates or wettable powders. It degrades somewhat quickly and is easily absorbed and disseminated throughout plant tissues. Due to its high solubility in water and low adsorption in soil, dimethoate is comparatively nonpersistent yet extremely mobile in the environment (Van Scoy *et al.,* 2016).

Since dimethoate and phosphorus can be introduced into the soil together through the application of inorganic fertilizer, organic manure, or pesticides, information on their adsorption from solutions in which both are present must be added to the individual adsorption/desorption characteristics summarized above in order to properly evaluate the environmental threat posed by dimethoate and phosphorus, or their availability. It is commonly known that the addition of a second adsorbate reduces adsorption. Therefore, the objective of this work is to study the noncompetitive adsorption/desorption and competitive adsorption/desorption of dimethoate pesticide and phosphorus fertilizers in clay and clay loam soils, which, to best of our knowledge, represents original research not previously performed.

Materials and Methods

Soils

The soils used were clay and clay loam agricultural soils sampled at 0–25 cm depth from Alexandria Governorate, North Egypt. Samples were collected from the upper layers (0–25 cm) of soil profiles from different locations. This soil has not been treated with dimethoate and phosphorus. The soil was allowed to air dry before being extensively homogenized and sieved at a particle size of less than 2 mm to exclude the coarser fraction (El-Aswad *et al.,* 2023). The soil properties were determined according to conventional methods (Table 1).

Table 1: Physicochemical characteristics of the studied soils

Sample ID	A1	A2
Texture class	**Clay soil**	**Clay loam soil**
Coordinates (N/E)	31.2642900/30.0050364	31.1006/5804
EC (dS m^{-1})	2.06	1.32
pH	8.22	8.25
OM (%)	1.26	3.31
$CaCO_3$ (%)	15.47	7.87

Agrochemical

The optimum value of λ_{max} is shown in Figure 1B and Figure 2B. The concentration of the agrochemical was determined using the k value, which was found to be the slope of the standard curve.

Adsorption tests

According to the OECD, the competitive and noncompetitive adsorption of dimethoate and phosphorus at room temperature was assessed in a batch equilibrium system. To determine the proper soil-solution ratio (1:10), 2 g of soil samples were weighed into 75mL glass bottles for dimethoate and/or phosphorus and corrected with 10 mL $CaCl_2$ (0.01 M) (Fouad *et al.,* 2024f). The agrochemical was added in amounts equal to 1, 10, 20, 30, 40, 50 µg g^{-1} dry weight soil. For 24 hours, the samples were shaken at 23±2°C and 175 revolutions per minute. The materials were then

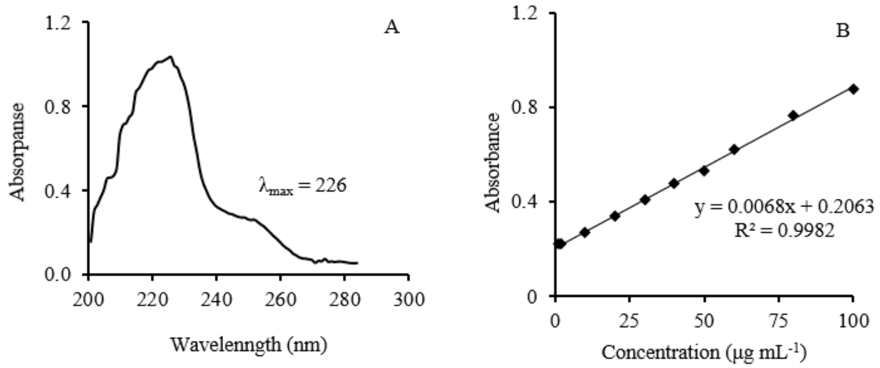

Figure 1: Spectral-density curve (A) and calibration-density curve (B) of dimethoate

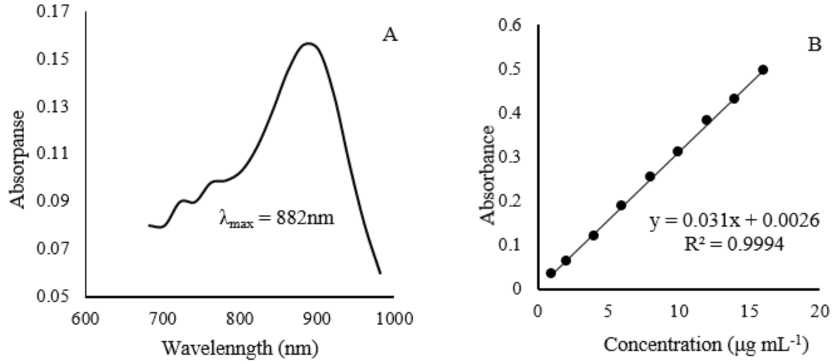

Figure 2: Spectral-density curve (A) and calibration-density curve (B) of phosphorus

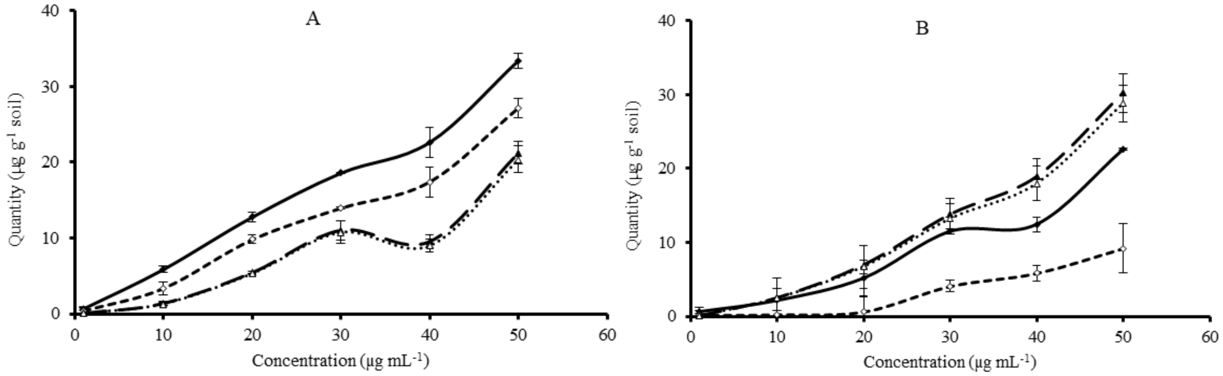

Figure 3: Non-competitive (A) and competitive (B) adsorption/desorption isotherms of dimethoate and phosphorus in clay soil

centrifuged for 10 minutes at 4000 rpm. Then, using a UV-Vis spectrophotometer, the amounts of phosphorus and dimethoate in the supernatant were measured. Each of the aforementioned dimethoate and phosphorus concentrations was gathered and combined to create a combination of dimethoate + phosphorus for the purpose of binary mixture adsorption. After that, the samples were combined with soil and put through tests of competitive adsorption. The agrochemical concentration differential between the original and final equilibrium solutions was used to compute the quantity of dimethoate and phosphorus retained by the adsorbent.

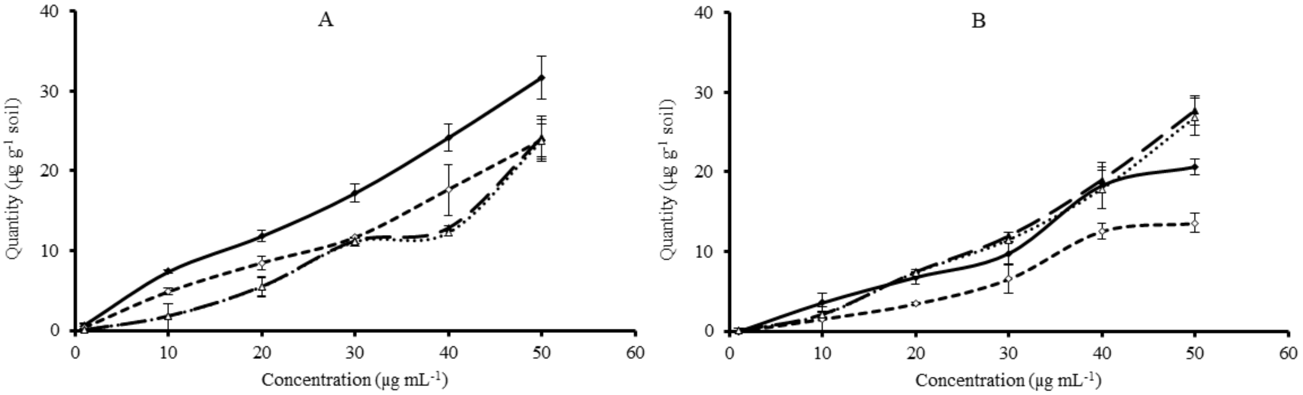

Figure 4: Non-competitive (A) and competitive (B) adsorption/desorption isotherms of dimethoate and phosphorus in clay loam soil

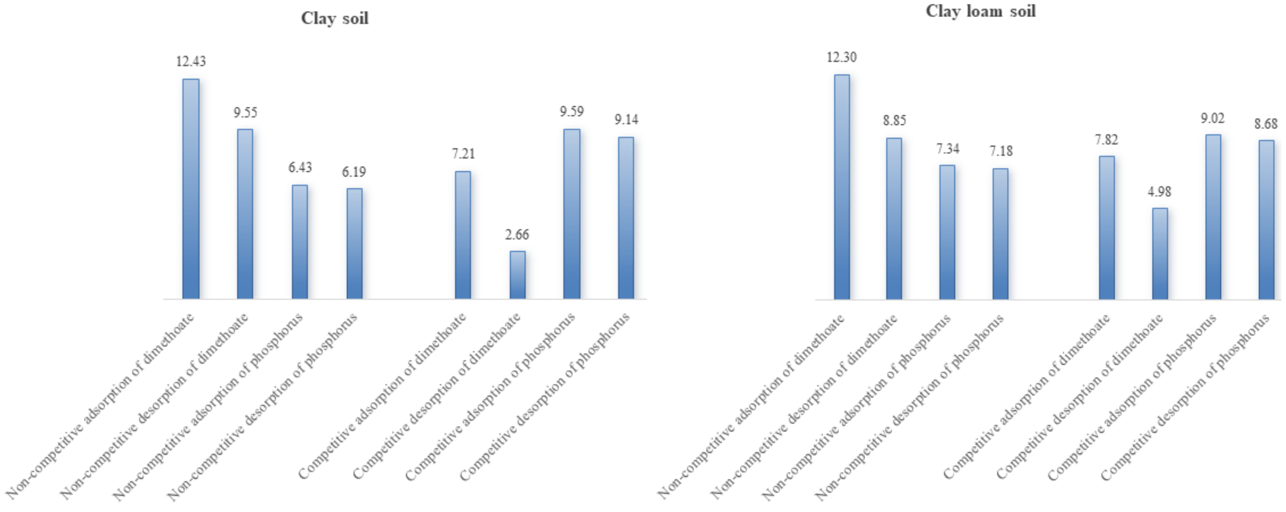

Figure 5: Percentages of non-competitive and competitive adsorption–desorption in the tested soils

Results and Discussion

Figure 3A shows the isotherms of the adsorption/desorption of dimethoate and phosphorus alone into the clay soil. Notably, the adsorption and desorption isotherms were greater for dimethoate than for phosphorus in the clay soil, and there were no significant differences in the adsorption and desorption isotherms for phosphorus. The adsorption and/or desorption isotherms of dimethoate in presence of phosphorus at concentrations of 1, 10, 20, 30, 40, and 50 μg mL^{-1} in clay soil are shown in Figure 3B. When phosphorus was added, dimethoate's adsorption ability on clay soil dramatically dropped. Adsorption and desorption isotherms were greater for each of the two agrochemicals as the added concentration increased, with the highest adsorption and desorption values corresponding to the highest agrochemical doses added. As shown in Figure 4, in comparison to the single system, the combined system's dimethoate and phosphorus adsorption capability on the clay soil was noticeably lower. This demonstrates that the adsorption of phosphorus and dimethoate on the soil has a competitive interaction. This resulted from the two agrochemicals competing for the same soil adsorption site (Wang *et al.,* 2020). In line with our findings, Fouad *et al.,* (2024f) found that in a coexisting system, imidacloprid and KNO_3 adsorption on soils decreased. Furthermore, in clay soil, dimethoate's influence on phosphorus adsorption was significantly weaker than that of coexisting phosphorus. This might be explained by the fact that phosphorus has a higher potential to adsorb on soil than dimethoate. Stronger competition for binding to the soil's adsorption site resulted from phosphorus's higher adsorption affinity.

Adsorption-desorption isotherms of dimethoate and phosphorus in clay loam soil were obtained when dimethoate and phosphorus were present in a single system, as shown in Figure 4A. In the clay loam soil, more dimethoate was adsorbed than phosphorus was. To create various starting concentrations of the mixture, varying amounts of dimethoate and phosphorus solutions were combined, all maintaining a consistent soil-to-liquid ratio (1:10). Figure (4B) displays the competitive adsorption isotherms of phosphorus and dimethoate from binary combinations. When phosphorus was added, dimethoate's adsorption ability on clay loam soil dramatically dropped. The adsorptive and/or desorption of dimethoate decreases with increasing phosphorus concentration. Consistent with our results, the adsorption of chlortetracycline, oxytetracycline and tetracycline (Conde-Cid *et al.,* 2019), propiconazole and difenoconazole (Wang *et al.,* 2020) into the soil decreased in the combined system. Additionally, the adsorption of dimethoate and phosphorus was relatively similar in the tested soils when the agrochemicals were added at low doses. However, at a certain concentration, the differences became evident, with phosphorus being the least adsorbed in noncompetitive adsorption and dimethoate being the least adsorbed in competitive adsorption. Polar compounds generally have a higher competitive power than nonpolar or low-polarity compounds (Bao *et al.,* 2013).

As illustrated in Figure 5, the combined system's dimethoate and phosphorus adsorption capacity on the two soils was noticeably less than that of the single system. The adsorption isotherms of dimethoate and phosphorus in the combined system decreased to 7.21% and 2.66% and 7.82% and 4.98% into clay and clay loam soils, respectively. The desorption of phosphorus was much easier than that of dimethoate in the tested soils, which may be due to the chemical composition. The desorption rates of dimethoate and phosphorus into $CaCl_2$ were low: approximately 9.55, 8.85, 6.19, and 7.18% and 2.66, 4.98, 9.14, and 8.68% for noncompetitive and competitive clays in clay and clay loam soils, respectively. Desorption tests were conducted by substituting any other agrochemical for $CaCl_2$ in order to evaluate the capacity of agrochemicals to displace one another. These results suggest that the adsorption of phosphorus and dimethoate on the soil has a competitive connection, and that competitive adsorption becomes more pronounced as the cosolute concentration rises (Wang *et al.,* 2020). This resulted from the two agrochemicals competing for the same soil adsorption site (Xing *et al.,* 1996; Wang *et al.,* 2020). Put another way, through competitive adsorption, the presence of agrochemicals reduces the adsorption capacity of other agrochemicals on soil.

Conclusions

The fate and movement of pollutants in the environment are significantly influenced by the agrochemicals' adsorption in soils. In this research, the adsorption and/or desorption of dimethoate and phosphorus alone and in combination were investigated into clay soil and clay loam soil. The adsorption capacity of dimethoate was much greater than that of phosphorus on same tested soil in the individual systems. The agrochemical's competitive adsorption trials demonstrate its capacity to displace one another from its adsorption sites: the concentration of the adsorbed dimethoate pesticide dropped as the phosphorus fertilizer competitor's applied concentration rose. These results should be taken into account when pesticides and fertilizers are added to the soil together.

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