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SHORT COMMUNICATION

Sorption Parameters of Carbendazim and Iprodione in the Presence of Copper Nanoparticles in Two Different Soils

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Abstract

Today, metal nanoparticles are being incorporated into soil through several routes, where they could alter the sorption behavior of other contaminants such as pesticides. Therefore, a short assay was carried out through sorption isotherms to evaluate the effect of copper nanoparticles (NCu) and copper sulfate (as the bulk form) at 50, 100, and 200 mg kg^{-1} on the sorption capacity of two commonly applied fungicides (carbendazim and iprodione) onto two agricultural soils, contrasting in organic matter content (2% and 14%) and texture (sandy and loamy) respectively. The isotherms were well described using the Freundlich model ($R^2 > 0.95$). Interestingly, at low organic matter, the pesticide sorption was notoriously increased in the presence of copper. However, NCu caused a minimal dose-dependent effect compared with their bulk form. Conversely, at high organic matter, the sorption was slightly altered by the presence of NCu. These findings constitute the first evidence that copper nanoparticles applied to agricultural soils can modify the sorption behavior of fungicides, which might increase their permanence in the environment. However, more detailed studies should be carried out in order to understand the interaction mechanisms between NCu/pesticides/soil and consequently their potential environmental risks.

Keywords Copper nanoparticles · Copper sulfate · Iprodione · Carbendazim · Freundlich isotherms

Highlights

- Sorption of fungicides in two soils in the presence of copper nanoparticles was studied.
- Copper nanoparticles increased the sorption of carbendazim and Iprodione
- Sorption capacity was remarkably increased in soil with low organic matter content.
- Sorption of pesticides was not dose-dependent in the presence of nanoparticles

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1 Introduction

The rapid population growth has been accompanied by increasing demands on agriculture worldwide, implying high costs to the environment. Currently, the application of pesticides in farming activities is indispensable for controlling various pest plants, which may lead to an increase in the productivity avoiding considerable economic losses. Among them, the fungicides are widely used for controlling several diseases caused by fungi. Carbendazim (methyl benzimidazol-2-ylcarbamate) is a systemic basic fungicide commonly used, and due to their characteristics, such as low water solubility and degradation rate, this compound can remain adsorbed to soil components for a long time through strong interactions with the colloids. (Berglöf et al. 2002). Iprodione (3-(3,5-dichlorophenyl)-N-isopropyl-2,4-dioxoimidazolidine-1-carboxamide) is an imidazole fungicide widely used as a contact pesticide against a wide-spectrum of fungal pathogens in plants (Morales et al. 2013). Iprodione is moderately persistent in soil, and its toxicity depends on the type of micro or macroorganisms (Strömqvist and Jarvis 2005; Morales et al. 2013; EFSA 2016). The environmental fate of both pesticides is mainly affected by sorption processes influenced by soil pH, organic matter, clay content, or the presence of humic acids. However, pH is mainly associated with effects on ionizable pesticides such as carbendazim (Violante et al. 2010; Morales et al. 2013; Palma et al. 2015; EFSA 2016).

In practice, a large amount of toxic agrochemical can co-exist in soil, and therefore, the pollution produced may be provoked due to a phenomenon of co-contamination. In this regard, agricultural soils may contain variable levels of metals such as copper, which can reach the soil as constituents of pesticides or by wastewaters irrigation and sewage sludge applications (Li et al. 2011; Suanon et al. 2016; Kirchmann et al. 2017). It has been demonstrated that a combined pollution of pesticides with metals in soil could lead to deleterious effects on microbial communities due to toxic synergistic effects (Dewey et al. 2012; Olaniran et al. 2013). Moreover, the presence of metals in soil may affect the behavior of pesticides, increasing or decreasing their sorption, and therefore their bioavailability (Leistra and Matser 2004; Li et al. 2011; Qian et al. 2011; Pei et al. 2014). In this sense, it has been reported that copper promotes the adsorption of carbendazim or iprodione (Leistra and Matser 2004) and causes antagonistic effects on atrazine sorption (Qian et al. 2011).

On the other hand, copper nanoparticles (NCu) have been extensively included in several products due to their recognized antimicrobial properties. In fact, a commercial nanopesticide based on $Cu(OH)_2$ nanosheets has been already used in agricultural activities due to their antifungal properties (Keller et al. 2017). The soil can be exposed to metal nanoparticles during their life cycle, through their application in bioremediation (Galdames et al. 2017; Wigger 2017; Giese et al. 2018), their release during the manufacture and utilization in agronomical applications (Wang et al. 2016; Duhan et al. 2017), or by disposal of wastes containing them such as solid wastes or sewage sludges (Fijalkowski et al. 2017; Funari et al. 2018). Considering this, it is expected that the co-existence of NCu with others chemical stressors of anthropogenic origin such as pesticides may occur in soil. Little information is available about the effects of a combined contamination between NCu and pesticides in soil as has been reported by Parada el al. (2019a), and how this could modify the sorption behavior of pesticides (Chen et al. 2016). Some studies have reported that alterations in the behavior of polycyclic aromatic hydrocarbons, phenols, or perfluorooctanesulfonate were caused by the presence of titanium nanoparticles (TiO_2-NPs), which increased or decreased their availability (Fang et al. 2015; Farkas et al. 2015; Qiang et al. 2016). On the other hand, although carbon-based or fullerene nanoparticles are very different from metal nanoparticles, increased toxic effects have been also observed in aquatic system when the herbicide diuron or the insecticide bifenthrin was combined with these nanoparticles (Brausch et al. 2010; Schwab et al. 2013). Moreover, a recent study demonstrated that NCu retarded the dissipation of atrazine in an agricultural soil (Parada et al. 2019b). The authors reported that this effect was caused mainly due to physicochemical alterations in soil more than microbial. However, knowledge gaps still exist about the effects of NCu on the adsorption behavior of pesticides in soil. Therefore, the potential benefits or risks of the co-occurrence of NCu and pesticides should be studied, even more when the hazards of nanoparticles in soil are still uncertain. This will allow us to know the level of protection before their application in soil.

According to the mentioned above, two commonly used fungicides (carbendazim and iprodione), which may be applied with copper in farming activities, were chosen to evaluate their sorption onto two typical agricultural soils in the presence of NCu at increasing concentrations. This work was only focused on the possible alterations in the fungicide sorption due to the presence of NCu. However, some hypothetic interaction mechanisms between fungicide-nanoparticles-soil were also discussed, which should be addressed in future studies.

2 Methodology

2.1 Materials

Carbendazim (CARB, 99% purity) and iprodione (IPR, 99% purity) were purchased from Chem Service (West Chester, USA) and selected because they are frequently used in agricultural activities and co-applied with copper. Copper nanoparticles (NCu) (40–60 nm particle size) were purchased from Sigma-Aldrich chemical company (St. Louis, MO, USA). The chemical structure of NCu was characterized by X-ray diffraction (XRD). As shown in Fig. 1, three characteristic peaks of copper were observed at $2\theta = 43°, 50°, 74°$ which correspond to (111), (200), (220) crystallographic planes of face-centered cubic (FCC) Cu crystals (JCPDS No.04-0784) (Suresh et al. 2014).

2.2 Soil Sampling

Two representative agricultural soils contrasting in organic matter content (OM) and texture were collected, and the main chemical properties of the soils are detailed in Table 1.

2.3 Batch Sorption Experiments

The batch sorption experiments were carried out in triplicate in 50-mL Teflon tubes containing 1.0 g of air-dried soil (≤ 2 mm) at its natural pH (~ 6.0 in water). The soil samples were equilibrated with 20 mL of 0.1 M KCl containing CARB or IPR at concentrations ranging from 0.1 to 1 mg L^{-1} and three concentrations of copper from NCu or $CuSO_4$ (2.5, 5.0, and 10 mg L^{-1} added at ion equivalent concentrations) on a reciprocal shaker for 24 h in the dark at 25 °C. These concentrations are comparable to doses of copper evaluated in previous studies performed in soil (Arias et al. 2006; Xu et al. 2015). Then,

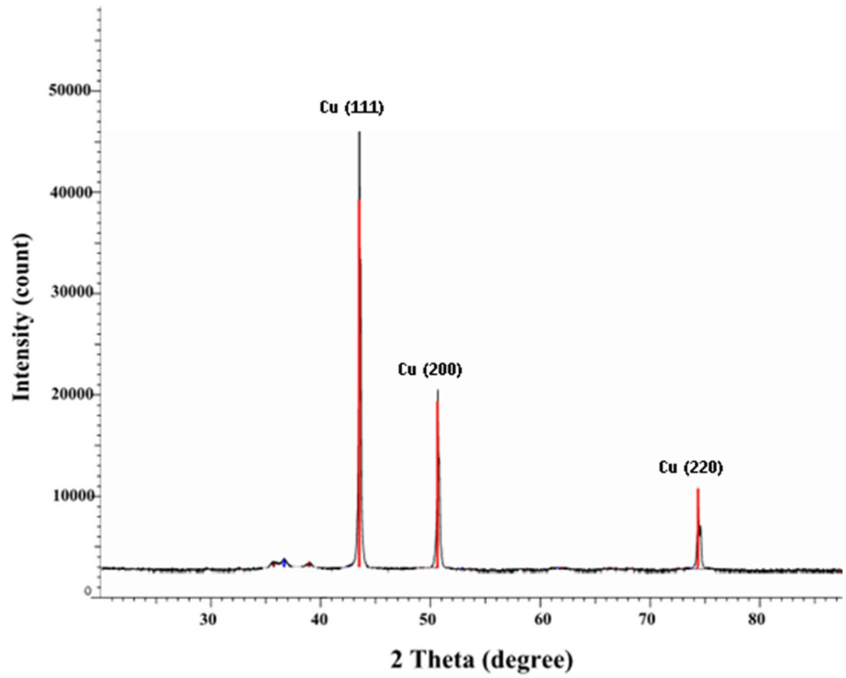

Fig. 1 XRD pattern of the copper nanoparticles

the samples were centrifuged (10 min at 10,000 rpm) and filtered (0.45-μm pore size) and the pesticide concentration was determined by HPLC using a Merck Hitachi L-2130 pump equipped with a Rheodyne 7725 injector with a 20-μL loop and a Merck Hitachi L-2455 diode array detector. The separation was achieved using a C18 column (Purospher Star C18, 4.6 × 100 mm). For IPR, Eluent A was phosphoric acid (0.1%) and eluent B was methanol (80/20). The flow rate was set at 1.0 mL min^{-1} in an isocratic mode. The column temperature was maintained at 30 °C. The detector was set at 220 nm for the data acquisition. For CARB, the mobile phase comprised was methanol/water/acetic acid 30/65/5 vol/vol/vol. The flow rate was set at 0.7 mL min^{-1} in an isocratic mode. The column temperature was maintained at 35 °C. The detector was set at 280 nm for the data acquisition. Instrument calibrations and quantification were performed against pure CARB and IPR reference standards (0.1–10 mg L^{-1}).

2.4 Data Analysis of Adsorption

The mass of CARB and IPR that was assumed to be adsorbed to the soil after the equilibration was calculated (Eq. (1)) and described using the empirical Freundlich isotherm model (Eq. (2)) which works well for heterogeneous adsorbents (Sposito 1980):

$$Q_s = \frac{(C_i - C_e)\,V_s}{W_s} \tag{1}$$

$$Q_s = K_f \times C_e^{1/n} \tag{2}$$

where Q_s is the mass of CARB or IPR adsorbed by the soil (mg Kg^{-1}), C_i is the initial concentration of CARB or IPR and C_e is the solution concentration after their equilibration (mg L^{-1}), V_s is the volume of solution (L), and W_s is the mass of the soil (Kg). K_F is the Freundlich distribution coefficient (mg^{1-n} L^n Kg^{-1}), and $1/n$ is an exponential empirical parameter that accounts for non-linearity in adsorption behavior. The Freundlich adsorption parameters (i.e., K_F and $1/n$) were determined by non-linear regression based on equilibrium batch results using the software Origin 7.5 (OriginLab Corporation, Northampton, MA 01060). Linear regression parameters were also derived using Origin 7.5 with the model intercept forced through zero. The Freundlich model was assumed because it is suitable to represent non-ideal sorption on heterogeneous surfaces, as well as, sorption on surfaces with non-uniform energy of distribution (Yan et al. 2008).

3 Results and Discussion

The capacity of some soils to sorb pesticides and metals has been studied to evaluate their bioavailability and therefore their environmental fate (Violante et al. 2010; Wu et al. 2011). However, little information exists about the effects of their co-existence on sorption parameters, and even more when the metals are present as nanoparticles. As shown in Fig. 2, both copper forms (NCu and $CuSO_4$) increased the sorption level of CARB and IPR in Renaico soil. However, an interesting differential effect was observed due to NCu. In detail, the sorption level of both pesticides (CARB in a lesser extent) was increased due to NCu. Nevertheless, no considerable alterations were observed as the NCu concentration was increased (Fig. 2a and c). These effects were contrasting to the

Table 1 Some chemical and physical properties of studied soils

Soil Series	Classification (USDA)	Particle size distribution %			pH	OM (%)	CEC[1]	Sum of bases[1]	Al^{1}_{ext}	N[2]	P[2]	K[2]	Fe[2]	Cu[2]
		Clay	Silt	Sand										
Freire	Typic Placudands	27.4	43.8	28.8	6.0	14.0	12.4	12.4	1055	19	8.0	86	61.6	1.96
Renaico	Fluventic Haploxeralfs	6.3	26.2	66.5	5.9	3.0	2.65	2.6	570	28	6.0	115	31.6	2.09

[1] $cmol + kg^{-1}$
[2] $mg\ kg^{-1}$

observed with $CuSO_4$ (Fig. 2b and d), where a clear dose-dependency was found for the sorption of both pesticides. This highlight that the presence of NCu at the lowest concentration produced a similar effect to the produced with the highest concentration on the IPR and CARB sorption in a soil of low OM content, which can be supported by the low variation in the estimated Freundlich coefficients (Table 2) between the different NCu concentrations (K_F for IPR 60.6–71.8; K_F for CARB 55–70) compared with their bulk form (K_F for IPR 75.5–79.5; K_F for CARB 83.3–228). The sorption intensity values ($1/n$) estimated were not remarkably modified, which was indicative of a weak binding capacity between IPR and CARB with Renaico soil ($1/n$ near to the unit) in the presence of NCu or $CuSO_4$.

A contrasting effect to Renaico soil was observed in Freire soil, where only slight changes were observed in the sorption

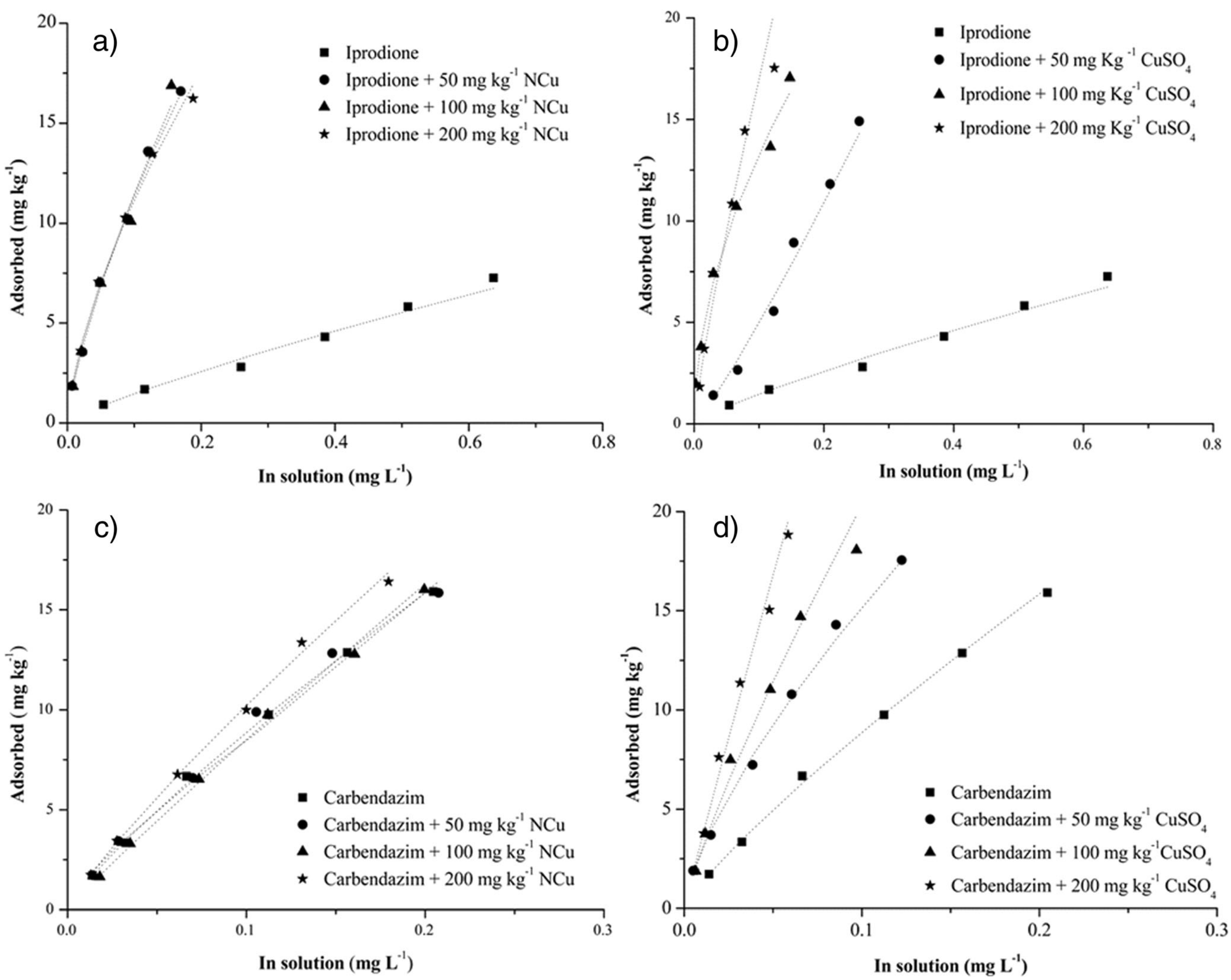

Fig. 2 Carbendazim and iprodione sorption under different concentrations of copper nanoparticles (NCu) and copper sulfate ($CuSO_4$) in Renaico soil series

Table 2 Parameters of Freundlich model K_F (mg^{1-n} L^n Kg^{-1}), $1/n$ and R^2 for the sorption of iprodione and carbendazim in the presence of copper nanoparticles and copper sulfate in Renaico soil series

Treatment	Carbendazim			Iprodione		
	K_F	$1/n$	R^2	K_F	$1/n$	R^2
Control	58.1 (2.0)	0.81 (0.02)	0.99	10.9 (0.5)	0.94 (0.06)	0.99
NCu 50 mg kg^{-1}	55.2 (3.7)	0.78 (0.04)	0.96	60.6 (4.3)	0.72 (0.03)	0.99
NCu 100 mg kg^{-1}	67.9 (3.3)	0.90 (0.02)	0.99	71.8 (9.2)	0.80 (0.06)	0.98
NCu 200 mg kg^{-1}	70.2 (4.7)	0.84 (0.03)	0.99	67.7 (2.9)	0.73 (0.03)	0.99
$CuSO_4$ 50 mg kg^{-1}	83.3 (6.7)	0.73 (0.03)	0.99	75.5 (4.0)	0.98 (0.09)	0.98
$CuSO_4$ 100 mg kg^{-1}	102.5 (12.9)	0.73 (0.05)	0.99	77.4 (13.6)	0.69 (0.07)	0.97
$CuSO_4$ 200 mg kg^{-1}	228.0 (37.2)	0.88 (0.05)	0.99	79.5 (11.1)	0.73 (0.04)	0.98

Values in parentheses represent standard errors

capacity due to NCu and $CuSO_4$ (Fig. 3). However, a more noticeable increase in the CARB sorption was supported by higher Freundlich coefficients estimated (K_F for NCu 41–51; K_F for $CuSO_4$ 47.6–56) compared with IPR (K_F for NCu 38.2–38.7; K_F for $CuSO_4$ 37–40.9) (Table 3).

It has been demonstrated that copper can modify the sorption level of some pesticides in soil including CARB (Li et al. 2011; Liu et al. 2013; Wu et al. 2014). However, its effects at nanoscale have been scarcely demonstrated. In this regard, Parada et al. (2019b) reported that zero-valent NCu (40–

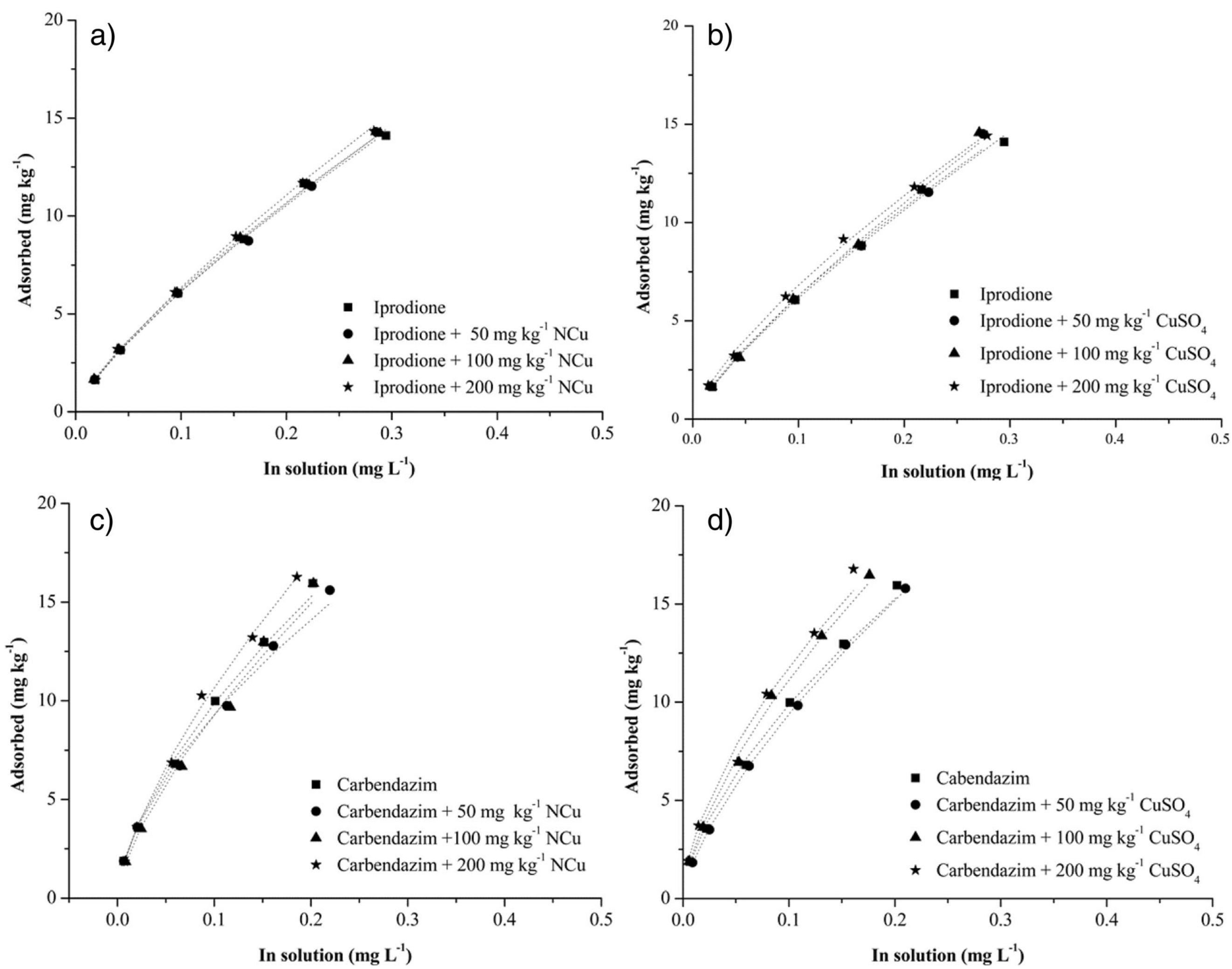

Fig. 3 Carbendazim and iprodione adsorption under different concentrations of copper nanoparticles (NCu) and copper sulfate ($CuSO_4$) in Freire soil series

Table 3 Parameters of Freundlich model K_F (mg^{1-n} L^n Kg^{-1}), $1/n$ and R^2 for the sorption of iprodione and carbendazim in the presence of copper nanoparticles and copper sulfate in Freire soil series

Treatment	Carbendazim			Iprodione		
	K_F	$1/n$	R^2	K_F	$1/n$	R^2
Control	46.5 (1.4)	0.67 (0.02)	0.99	36.8 (1.4)	0.77 (0.02)	0.99
NCu 50 mg kg^{-1}	41.5 (2.0)	0.65 (0.03)	0.96	38.7 (1.5)	0.80 (0.02)	0.99
NCu 100 mg kg^{-1}	52.8 (4.8)	0.76 (0.05)	0.99	36.9 (0.1)	0.77 (0.00)	0.99
NCu 200 mg kg^{-1}	51.0 (2.8)	0.68 (0.03)	0.99	38.2 (0.6)	0.77 (0.01)	0.99
$CuSO_4$ 50 mg kg^{-1}	47.6 (1.1)	0.70 (0.01)	0.99	40.9 (2.4)	0.82 (0.04)	0.99
$CuSO_4$ 100 mg kg^{-1}	53.3 (2.7)	0.68 (0.02)	0.99	42.9 (1.8)	0.84 (0.03)	0.99
$CuSO_4$ 200 mg kg^{-1}	56.0 (5.2)	0.67 (0.04)	0.99	37.0 (1.1)	0.73 (0.02)	0.99

Values in parentheses represent standard errors

60 nm) increased the sorption level of the herbicide atrazine (ATZ) and retarded its dissipation, more than $CuSO_4$. Interestingly, contrary to our results, the authors found a noticeable dose-dependent effect of NCu on the ATZ sorption in a soil of high OM content, which demonstrates that NCu can alter the sorption of the pesticides. However, besides the influence of the soil type, this effect may be specific depending on the chemical composition of each pesticide.

Due to physicochemical characteristics of Renaico soil series, we expected that the presence of NCu would cause less pronounced changes in the sorption capacity of the pesticides than in Freire soil series. Nevertheless, the sorption capacities of IPR and CARB in Renaico soil series were more increased in the presence of NCu and $CuSO_4$. Apparently, the low OM and clay content of Renaico soil would not have been a restriction for IPR and CARB sorption. Moreover, this indicated that non-competitive binding occurred between pesticides and copper (NCu or $CuSO_4$) and that probably a complexation between copper-soil-pesticide could have occurred, although with a low intensity as evidenced by the $1/n$ values obtained (Table 2). In this regard, Lalah et al. (2009) reported that copper caused retention of DDT in a sandy soil with low OM. On the other hand, it has been reported that the silt fraction in soil could be partially reactive, and therefore interact with metals and pesticides due to the accumulation of soil organic carbon in this fraction (Rodríguez-Rubio et al. 2003; Mandzhieva et al. 2014; Matus et al. 2016). As above mentioned, no remarkable changes in the sorption capacity of both pesticides were observed in Freire soil series. This could be also explained by the high OM that allows a higher availability of active sites for the sorption. In this sense, it has been reported that copper presents a high affinity by OM and forms complexes with Al or Fe in soils (McBride 1982; Keizer and Bruggenwert 1991; Silveira and Alleoni 2003).

It has been reported that copper can form complexes with biocides such as penconazole, glyphosate, iprodione, ofloxacin, and sulfatiazole (Undabeytia et al. 1996; Arias et al. 2006; Pei et al. 2014; Wu et al. 2014). Then, given that some pesticides and copper can form complexes, it is reasonable to suppose that NCu could be creating the same bridges between CARB or IPR and the soil in the same way that their bulk form. Therefore, new indirect active sites for the sorption of CARB, IPR, or copper could have been formed. Then, direct and indirect sorption will represent the total sorption (evidenced by an increase in the K_F values). This possible indirect sorption would be coincident with the $1/n$ values that are close to the unit, suggesting a cooperative sorption process (heterogeneous sorption) (Li et al. 2011). Similar to our results, Li et al. (2011) reported that the sorption of CARB increased in the presence of cadmium ions in soil. The same sorption behavior was revealed for IPR in the presence of copper, which could be related to the capacity of copper to form complexes with IPR, as well as to increase its sorption (Arias et al. 2006; Leistra and Matser 2004). However, the different responses in the pesticide sorption level with NCu compared with the bulk form could be related to their higher reactivity and affinity for OM, as reported by Julich and Gäth (2014).

4 Conclusions

The sorption behavior of both pesticides evaluated in this study was considerably different in the two tested soils. We demonstrated that copper nanoparticles increase considerably the sorption capacity of carbendazim and iprodione in soil under a scenario of low organic matter content, more than high organic matter. On the other hand, compared with their bulk form, the effect of copper nanoparticles on the pesticide sorption was not dose-dependent in the soil of low organic matter content, which could be related with the recognized higher reactivity of the nanoparticles. However, studies of advanced test methods are required to identify the possible interaction mechanisms between nanoparticles/soil/pesticides. In fact, this is the first report about the effect of copper nanoparticles on the sorption of two widely used fungicides, and although our work was not focused on interaction mechanisms between nanoparticles/soil/pesticide, the results shed new lights about the effects of copper nanoparticles on the pesticide sorption in soil.

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