

## Zinc adsorption on goethite as affected by glyphosate

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### Abstract

Cosorption of metals with herbicides on minerals affects their mobility and their environmental effect. Batch experiments were conducted to evaluate the interaction between Zn and glyphosate [*N*-(phosphonomethyl)glycine (GPS; H<sub>3</sub>L)] with regard to the effect of GPS on Zn adsorption on goethite. The herbicide GPS markedly affected Zn adsorption on goethite when they coexisted in a goethite suspension. When solution pH was not intentionally adjusted, addition of GPS decreased Zn adsorption on goethite, since the equilibrium solution pH was significantly decreased in the presence of GPS and correspondingly the negative surface charges of goethite decreased. Zinc adsorption on goethite in the presence and absence of GPS at different pH of the equilibrium solution was studied in order to know if pH was the only variable for Zn adsorption with coexisting GPS. At lower pH (pH < 5), the presence of GPS increased the adsorption of Zn, because Zn adsorbed on the sites of goethite via GPS bridge. However, at higher pH (pH > 5), the presence of GPS decreased the adsorption of Zn on goethite, because GPS reacted with solution Zn to form water-soluble complexes that had lower affinity to the goethite surface in comparison with Zn itself. Zeta potential of goethite significantly decreased after adsorption of GPS, suggesting a chemical bond occurred between GPS and the mineral. FTIRs also show that GPS adsorbs on goethite by coordinating through carboxylate group.

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### 1. Introduction

Glyphosate (*N*-[phosphonomethyl]glycine, GPS) is a non-selective, postemergence herbicide that is widely used in agronomic and vegetable crops, and in orchards. GPS has three functional groups (–NH, –COOH, and –H<sub>2</sub>PO<sub>3</sub>), which can form strong coordination bonds with metal ions to give bidentate and tridentate complexes [1–6]. The complexation of GPS with metal cations might affect their distribution and bioavailability in soils [7–11].

In recent years, there were interests in the studies of interaction between Cu, Cd, and GPS [3,8,12–15]. Morillo et al. [16–18] studied the cosorption of GPS and Cu<sup>2+</sup> on three soils with different characteristics and minerals. The adsorption of Cu decreased in general with increasing solution GPS concentration, on the other hand, the presence of Cu in the solution

enhanced GPS adsorption on soils. But Cu decreased GPS adsorption onto montmorillonite. Maqueda et al. [12] studied cosorption of GPS and Cu<sup>2+</sup> on goethite, and found that in the presence of Cu, the adsorption of GPS on goethite increased about 9%, and Cu adsorption on goethite also increased in the presence of GPS.

In some cases, GPS has been used in phytoextraction of heavy metals as a chemical complexation agent. Application of GPS enhanced Pb accumulation in crops [19]. GPS application at high doses can significantly influence metal uptake by Indian mustard [20].

Iron oxides are relatively abundant in soils and sediments, and therefore it is essential to understand their roles in sorption of metal and organic chemical. Some of the most commonly found iron oxides are ferrihydrite, hematite, and goethite. The chemical nature and high specific surface area of iron oxides as discrete particles and coatings on other minerals make these oxides efficient sinks for many contaminants including both cations and anions. Adsorption of metals to oxides in soils and sediments is important because it affects their mobility

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and bioavailability. Wang et al. [21] studied cosorption and adsorption of Zn and GPS in soils, and found Zn and GPS affected their adsorption on the soil surface by each other. However, the interaction between Zn and GPS adsorption on Fe oxides are not well understood. In this study, we examined Zn adsorption on goethite in the presence and absence of GPS.

## 2. Materials and methods

### 2.1. Mineral and chemicals

The goethite used in this study was synthesized based on the method described by Nowack and Sigg [22] using reagent-grade  $\text{Fe}(\text{NO}_3)_3$ . Excess salts were removed by electro dialysis until the electrical conductivity of the washing solution was nearly equal to that of deionized water. GPS, as a nonresidual herbicide [12], was purchased from Sigma Co. All other chemicals were of analytical grade. Deionized water was used for all experiments.

### 2.2. Zn adsorption as affected by GPS

Zn adsorption on goethite with and without GPS were performed by adding 0.1 g goethite in 15 ml of  $0.01 \text{ mol L}^{-1} \text{ NaNO}_3$  solution in a centrifuge tube. And then, 5 ml of  $0.01 \text{ mol L}^{-1} \text{ NaNO}_3$  solution with different concentrations ( $0\text{--}5 \text{ mmol L}^{-1}$ ) of  $\text{Zn}(\text{NO}_3)_2$  was added in each tube to build a series of Zn. Five milliliters of  $0.01 \text{ mol L}^{-1} \text{ NaNO}_3$  solution containing 0, 1.25, 2.5 or  $5 \text{ mmol L}^{-1}$  GPS were respectively added in each of the Zn series. The final solution volume was 25 ml. The suspension Zn concentrations in each Zn series were 0, 0.01, 0.02, 0.1, 0.2, 0.5, and  $1.0 \text{ mmol L}^{-1}$ , and the GPS concentrations were 0, 0.2, 0.4 and  $1.0 \text{ mmol L}^{-1}$ , respectively, for different Zn series. The centrifuge tubes were continuously shaken for 2 h at  $25^\circ\text{C}$ , centrifuged at  $9000 \times g$  for 10 min, and then filtered through a  $0.45 \mu\text{m}$  membrane filter. The Zn concentration in the supernatant was determined by atomic absorption spectrometer (Hitachi 180-80). The amount of Zn adsorbed was calculated from the difference between its solution concentrations before and after equilibrium. All solution pH values after equilibrium were measured by a pH meter. All experiments were performed in duplicate.

### 2.3. Effect of pH on Zn adsorption on the goethite in the presence and absence of GPS

The effect of pH on Zn adsorption on goethite was conducted in  $0.1 \text{ mmol L}^{-1}$  Zn solution with pH ranging from 3 to 10, which was adjusted by adding different volumes of  $0.01 \text{ mol L}^{-1}$  NaOH or  $0.01 \text{ mol L}^{-1}$   $\text{HNO}_3$ . Four GPS concentrations of 0, 0.25, 0.5, and  $1.0 \text{ mmol L}^{-1}$  were used. Other experimental conditions and measurements were the same as described in Section 2.2.

### 2.4. Measurement of zeta potential of goethite

Zeta potential measurements were conducted using a JS94H microelectrophoresis instrument (Powereach instruments, Shanghai, China). Goethite sample was prepared in  $0.01 \text{ mol L}^{-1} \text{ NaNO}_3$  solution (electrolyte) and the aqueous suspension was equilibrated at different pH values for 24 h. The equilibrated slurry was injected into the microelectrophoresis cell using disposable syringes. A minimum of ten readings was taken and the mean value was reported. Prior to each measurement, the electrophoresis cell was thoroughly washed and rinsed with deionized water followed by rinsing with the sample solution to be measured.

### 2.5. FTIRs of goethite after equilibrated with GPS and Zn

Infrared spectra (IR) were recorded after GPS and  $\text{Zn}^{2+}$  were adsorbed on goethite alone or together using a Perkin–Elmer 2000 FTIR spectrometer fitted with a deuterated triglycine sulfate (DTGS) detector covering the frequency range  $500\text{--}4000 \text{ cm}^{-1}$ . The sample cell was purged with nitrogen gas throughout data collection to exclude carbon dioxide and water vapor. Ten milligrams of the dried samples was dispersed in 200 mg of spectroscopic grade KBr to record the spectra.

## 3. Results and discussion

### 3.1. Adsorption of Zn on goethite in the presence and absence of GPS

The adsorption of Zn (initial Zn concentration from 0 to  $85.36 \text{ mg L}^{-1}$ ) on goethite with and without GPS were shown in Table 1. When the initial Zn concentration was  $1.71 \text{ mg L}^{-1}$

Table 1  
Adsorption of Zn on goethite in the presence and absence of glyphosate (GPS)

Initial Zn concentration	Solution Zn concentration after equilibrium ( $\text{mg L}^{-1}$ )			
	0 mM GPS	0.2 mM GPS	0.4 mM GPS	1.0 mM GPS
0.00	$0.00 \pm 0.00$	$0.00 \pm 0.00$	$0.00 \pm 0.00$	$0.00 \pm 0.00$
0.85	$0.00 \pm 0.00$	$0.00 \pm 0.00$	$0.31 \pm 0.09$	$0.68 \pm 0.00$
1.71	$0.01 \pm 0.00$	$0.04 \pm 0.01$	$0.57 \pm 0.22$	$1.34 \pm 0.02$
8.54	$2.65 \pm 0.25$	$2.87 \pm 0.05$	$4.57 \pm 0.00$	$6.53 \pm 0.12$
17.07	$8.33 \pm 0.02$	$8.96 \pm 0.05$	$10.9 \pm 0.23$	$13.2 \pm 0.00$
42.68	$23.8 \pm 0.78$	$24.7 \pm 0.07$	$26.4 \pm 0.46$	$30.6 \pm 0.28$
85.36	$53.1 \pm 0.53$	$55.6 \pm 1.38$	$57.4 \pm 0.67$	$61.5 \pm 0.60$

Table 2  
Equilibrium solution pH as affected by initial Zn and GPS concentrations

Initial Zn concentration (mmol L <sup>-1</sup> )	Initial GPS concentration (mmol L <sup>-1</sup> )			
	0	0.20	0.40	1.00
0	6.92 ± 0.05	6.43 ± 0.01	5.36 ± 0.01	3.60 ± 0.01
0.01	6.80 ± 0.03	6.36 ± 0.04	5.30 ± 0.04	3.59 ± 0.00
0.02	6.79 ± 0.01	6.27 ± 0.03	5.28 ± 0.01	3.62 ± 0.04
0.10	6.36 ± 0.09	5.93 ± 0.01	5.17 ± 0.01	3.61 ± 0.01
0.20	6.21 ± 0.01	5.77 ± 0.05	5.04 ± 0.03	3.60 ± 0.02
0.50	6.03 ± 0.01	5.60 ± 0.00	5.00 ± 0.00	3.58 ± 0.00
1.00	5.91 ± 0.01	5.42 ± 0.01	4.78 ± 0.05	3.65 ± 0.01

in the equilibrium solution, almost all of Zn was adsorbed on goethite, and only 0.01 mg L<sup>-1</sup> Zn was left in the equilibrated solution. The quantity of Zn adsorption on goethite increased with the increasing Zn concentration in the equilibrium solution. Zinc adsorption to goethite is an endothermic chemical type of reaction resulting in the formation of inner-sphere complexes revealed by X-ray absorption spectroscopy [23].

When GPS was presented in the solution, Zn concentration in the equilibrium solution increased. It also means that the quantity of Zn adsorption on goethite significantly decreased. The reduction of Zn adsorption was directly related to the solution GPS concentration. The higher the solution GPS concentration, the less the Zn adsorbed on goethite. For a previous study, Wang et al. [21] found that the presence of GPS decreased the adsorption of Zn on two soils with different characteristics.

The herbicide GPS is an acid with several functional groups [12,14,15]. In general, the effect of organic acids on heavy metal adsorption may include three different mechanisms: enhanced sorption by forming ternary surface complexes involving surface groups of goethite, reduced ion sorption due to competition between the surface ligands and the dissolved organic ligands for dissolved metal, or change of solution pH to affect adsorption [8]. Among them, equilibrium solution pH is one of the most important factors responsible for decreased Zn adsorption in the presence of GPS. There was a significant decrease in the equilibrium solution pH when GPS existed, as shown in Table 2. For 0.01 mmol L<sup>-1</sup> Zn treatment, GPS decreased the pH of equilibrium solution from 6.80 to 6.36, 5.30, 3.59 in 0.2, 0.4, and 1.0 mmol L<sup>-1</sup> GPS, respectively. The more GPS added initially, the lower pH in equilibrium solution, and the less Zn adsorbed on goethite. Morrilo et al. [18] and Zhou et al. [8] studied the effect of GPS on the adsorption of Cd and Cu on soils, respectively. They also concluded that the presence of GPS decreased the equilibrium solution pH and decreased adsorption of heavy metals on the soil surface.

Zinc adsorption on goethite in the presence and absence of GPS at different equilibrium solution pH was studied in order to find out if pH was the only variable for Zn adsorption with coexisting GPS. Fig. 1 shows the effect of pH on Zn adsorption at four levels of GPS on the goethite. It indicated that Zn adsorption on goethite increased with the increasing equilibrium solution pH. When the solution pH reached 6.5, Zn adsorption on goethite reached the maximum. When the equilibrium solution pH was below 5, the presence of GPS increased Zn adsorption

on goethite; while the solution pH was above 5, GPS decreased Zn adsorption on the goethite in comparison with Zn adsorption in the absence of GPS at a same pH. It suggests that the formation of Zn–GPS complexes affected Zn adsorption on goethite. Previous studies reported that the concentrations of free Cu<sup>2+</sup> or Cd<sup>2+</sup> in equilibrium solution were drastically reduced in the presence of GPS [8,13,16]. At higher pH, Zn can be precipitated, but GPS can strongly complex with Zn to inhibit precipitation of Zn such as Zn(OH)<sub>2</sub> and etc., so the presence of GPS increased Zn concentration in solution. Meanwhile, goethite has higher negative charge, with little adsorption capacity of GPS [21]. All GPS species in solution have negative charges as HL<sup>2-</sup> and L<sup>3-</sup>, which have strong chelating capacity with Zn to form complexes. Possible Zn–GPS species include: ZnHL, ZnL<sup>-</sup>, ZnL<sub>2</sub><sup>4-</sup>, and Zn(OH)L<sup>2-</sup> as shown in Fig. 2. Speciation calculation by the computer program WinSGW [21] shows that: the prevailing species in solution with the pH range 2.0–4.0 are Zn<sup>2+</sup>, and H<sub>3</sub>L or H<sub>2</sub>L<sup>-</sup>, with little coordination; with 4.0 < pH < 8.0, the predominating Zn and GPS species are ZnHL, ZnL<sup>-</sup>, and H<sub>2</sub>L<sup>-</sup> or HL<sup>2-</sup>; and with pH greater than 8, the predominating Zn and GPS species are ZnL<sup>-</sup>, ZnL<sub>2</sub><sup>4-</sup>, and H<sub>2</sub>L<sup>-</sup>, HL<sup>2-</sup>, respectively. When the solution pH is above 5, the complexes of Zn and GPS have high negative charge and have lower affinity to the goethite surface than Zn<sup>2+</sup> itself, while the goethite surface has much

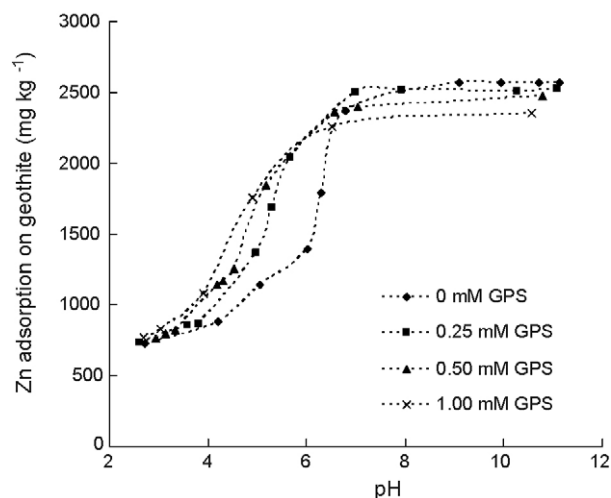


Fig. 1. Adsorption of Zn on the goethite in the presence and absence of GPS as affected by solution pH.

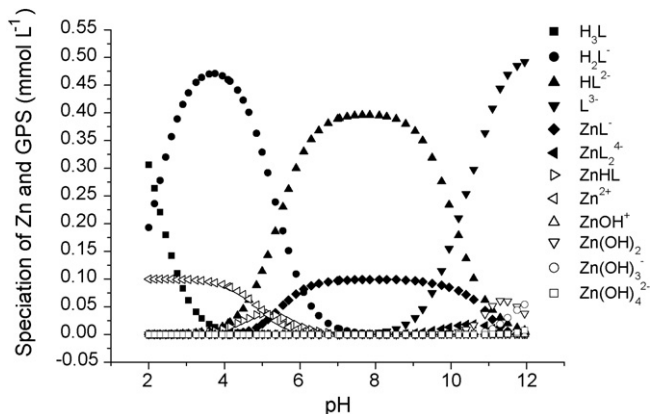


Fig. 2. Zn and glyphosate (GPS) species of  $0.1 \text{ mmol L}^{-1}$  Zn solution in the presence of  $0.5 \text{ mmol L}^{-1}$  GPS, calculated by the computer program WinSGW.

more negative charge at high pH. Similar results were reported by Morriolo et al. [18] and Zhou et al. [8].

Similar to the reaction of Zn and GPS on goethite, the complexation of Cu with GPS was studied using anodic stripping voltammetry by Morillo et al. [24]. The complexes of Cu(II) and GPS presented a labile behavior and GPS showed a low but noticeable degree of heterogeneity, probably due to complexation of Cu(II) by more than one GPS species. It resulted in Cu adsorption on montmorillonite drastically decreased in the presence of GPS due to the decrease of free Cu(II) ion concentration by the formation of Cu–GPS complexes; surface loading of GPS on montmorillonite, obstructing interlamellar Cu adsorption, and reduced the competitiveness of Cu with protons for interlamellar positions. Wang et al [13] studied Cd adsorption behaviors on montmorillonite in the presence of GPS by a  $\text{Cd}^{2+}$  ion selective electrode. When the equilibrium solution pH was below 6.7, GPS had little effect on Cd adsorption; but when the equilibrium solution pH was above 6.7, GPS significantly decreased Cd adsorption quantity in montmorillonite. Therefore, pH strongly affected metal behavior on soil and mineral systems.

### 3.2. Zeta potential of goethite after adsorption of GPS

Fig. 3 shows the zeta potential of goethite surface equilibrated with  $0.1 \text{ mmol L}^{-1}$  Zn in the presence and absence of GPS. The zeta potential of goethite decreased with the increasing solution pH. Goethite, adsorbed by Zn, possessed positive surface charges when pH was below 5.5. The presence of GPS significantly increased the negative surface charges of goethite. In other words, goethite has higher adsorption capacity of  $\text{Zn}^{2+}$  in the presence of GPS, which adsorbed on goethite surface by chelating with Fe. Ramstedt et al. [14] studied cosorption of Cd and GPS on manganite, and also found that the presence of GPS increased Cd adsorption at  $\text{pH} < \text{pH}_{\text{iep}}$ . There are several possible explanations for these behaviors: increased electrostatic attraction for the surface due to a reduced positive surface charge caused by adsorbed GPS and the formation of a ternary surface complex and the formation of Cd containing precipitate. At  $\text{pH} > \text{pH}_{\text{iep}}$ , Cd adsorption on manganite decreased, because

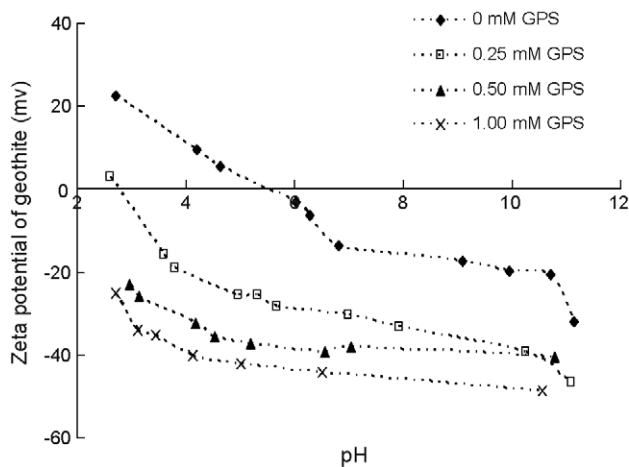


Fig. 3. Effect of GPS on zeta potential of the goethite adsorbed by Zn.

of the decreased affinity of the negatively charged surface of mineral for Cd–GPS species and the competing formation of Cd–GPS complexes in solution.

At pH below 5.5, the predominating GPS species are  $\text{H}_3\text{L}$  and  $\text{H}_2\text{L}^-$ ; while solution pH was above 5.5 the predominating GPS species are  $\text{H}_2\text{L}^-$ ,  $\text{HL}^{2-}$ ,  $\text{L}^{3-}$ , which have strong coordination with metals. The complexes of Zn and GPS contain high negative charges ( $\text{ZnL}^-$ ,  $\text{ZnL}_2^{4-}$ ), which exhibited low affinity to the goethite surface, therefore, the presence of GPS decreased adsorption of Zn on goethite.

### 3.3. FTIR studies

The IR spectra of the Zn(II)–GPS goethite system presented herein (Fig. 4) covering the frequency range of  $500\text{--}4000 \text{ cm}^{-1}$ . The bands at  $795$  and  $887 \text{ cm}^{-1}$  of the spectrum are characteristic of goethite and arise due to  $\gamma$ - and  $\delta$ -OH bending modes of in- and out-of-plane bending modes [25]. The intense band at

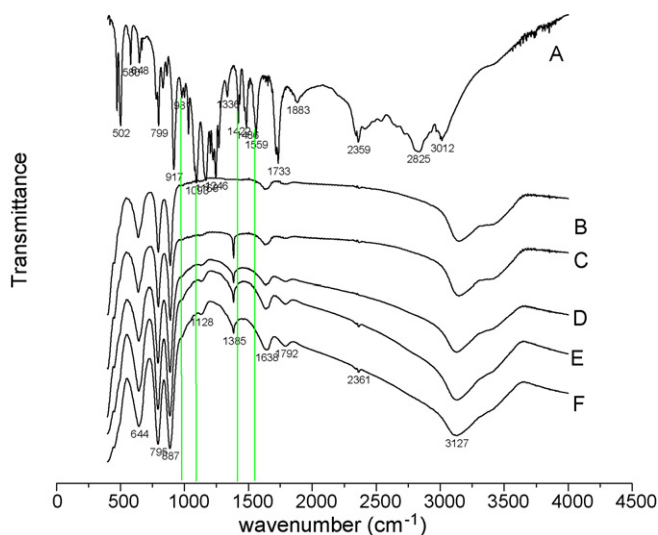


Fig. 4. FTIR spectra of the goethite after equilibrated with  $0.4 \text{ mmol L}^{-1}$  Zn and different concentrations of Zn in solution (A: GPS; B: goethite; C: GPS + goethite; D: GPS + goethite +  $0.02 \text{ mM Zn}$ ; E: GPS + goethite +  $0.2 \text{ mM Zn}$ ; F: GPS + goethite +  $1 \text{ mM Zn}$ ).

3127  $\text{cm}^{-1}$  is possibly due to the bulk  $-\text{OH}$  stretching. The symmetric stretching of  $\text{Fe}-\text{O}$  is indicated by a band at 644  $\text{cm}^{-1}$  [25]. GPS has its characteristic absorption bands in the frequency range 900–1700  $\text{cm}^{-1}$ . Thus, the IR spectra represent structures in the ternary system viewed from the perspective of the GPS ligand. Absorption bands associated with the different donor groups of GPS are located at distinctly different positions within this frequency range. Strong carboxylate bands are detected between 1300 and 1700  $\text{cm}^{-1}$ , while the region 950–1200  $\text{cm}^{-1}$  is dominated by strong bands originating from the phosphonate group (Fig. 4). This rough assignment is in agreement with the vast literature on IR spectroscopy of carboxylates and phosphonate [26]. The peak at 1638 and 1385  $\text{cm}^{-1}$  are assigned to the carboxylates of the asymmetric and symmetric  $-\text{C}=\text{O}$  stretches, and the peak at 1128  $\text{cm}^{-1}$  is assigned to phosphonate. Protonation/deprotonation and complexation at the reactive donor sites of GPS can hence be studied. According to Sheals et al. [26], the uncomplexed  $\text{L}^{3-}$  display two strong bands at 1559 and 1422  $\text{cm}^{-1}$  for the asymmetric and symmetric  $\text{C}=\text{O}$  stretches. These results indicated that there is a direct interaction between GPS and Fe at goethite surface, and the interaction occurs through the carboxylate group, because the split between the asymmetric and symmetric vibration increases, in comparison with free  $\text{L}^{3-}$ , suggesting the coordination by the carboxylate group. The uncomplexed  $\text{L}^{3-}$  also display two strong bands at 981 and 1093  $\text{cm}^{-1}$  assigning to  $\text{P}-\text{O}$  stretching motions of the phosphonate moiety [26]. This result showed that there is coordination between Zn and GPS through the phosphonate, for the asymmetric  $\text{P}-\text{O}$  stretch experience and upward shift to 1128  $\text{cm}^{-1}$ . Our finding is consistent with the previous studies [6,14,26,27]. According to the IR spectroscopic studies we can conclude that GPS adsorbed on goethite by coordination through the carboxylate group, and Zn adsorbed on goethite through GPS as a bridge to coordinate with the phosphonate of GPS.

#### 4. Conclusions

The presence of GPS affected the adsorption of Zn on the goethite through altering solution pH and formation of complexes with Zn. GPS increased Zn adsorption on goethite at low pH values ( $<4.5$ ), while decreasing the adsorption at high pH. The former decreases the movement of Zn from soil to underground water, which minimizes the potential risk to water quality. But in alkaline soil, application of GPS increases metal mobility resulting in increasing metal bioavailability. In addition to that, Zn adsorption takes place on sites where GPS is previously adsorbed and GPS acts as a bridge between the goethite and Zn when goethite possesses positive charged surface.

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