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Influence of Phosphate on Tungstate sorption on Hematite: A Macroscopic and Spectroscopic evaluation of the Mechanism

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Abstract

Environmental fate of tungstate (VI) oxyanion [i.e. mono tungstate and several polytungstate, generally expressed by W (VI)] is largely controlled by sorption on soil minerals, especially on iron oxide minerals. Molecular scale evaluation of W (VI) retention on iron oxides in the presence of competing oxyanions is scarce in the literature. Here we report surface interaction mechanisms of W (VI) on hematite in the presence of phosphorus (P) using macroscopic and *in situ* attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopic experiments. Batch sorption experiments were conducted using 2g L⁻¹ hematite and 100 μM W (VI) and P, in single ion system and in binary mixtures as a function of pH (4-11). *In situ* ATR-FTIR spectroscopic evaluation of P and W (VI) sorption on hematite was also carried out. The results from macroscopic experiments indicated that W (VI) sorption on hematite was not affected when W (VI) was added first. The influence of P on W (VI) sorption was noticed when W (VI) & P were added simultaneously or P was added first. The *in situ* ATR-FTIR spectroscopic data corroborated this finding. In addition, the spectroscopic data revealed that in the presence of P, surface complexation mode of W (VI) differed as noted from either the absence of W-O antisymmetric infrared (IR) band or the W-O-W stretching band. This study provides useful information on molecular level understanding of W (VI) surface complexation on hematite in the presence of competing ions such as P.

1. Introduction

Link of elevated tungstate (W (VI)) concentration in the tap water, ground water, and tree ring samples to the childhood leukemia cluster in NV highlighted the importance of tungsten (W) to be considered as an ‘emerging contaminant’ (EPA, 2017). Even though no conclusive results could be obtained from the Center of Disease Control’s (CDC) investigation to strengthen this link, the circumstantial evidence encouraged many researchers to perform a thorough investigation on W (VI) toxicity. Experiments on mice on chronic W (VI) exposure to a concentration of 15-200 mg L⁻¹ revealed that a 16 week W (VI) exposure can cause DNA damage and promote tumors (Kelly et al., 2013). Incubation with W powder for 3 months caused the death of 95% soil bacteria (Strigul, 2005).

Tungsten (W) is heavily used for domestic and industrial purposes (Koutsospyros et al., 2006). About 44,200 metric tons of W were mined in the world in 2001 (Shedd, 2001). This huge amount of W is generally used for tungsten-cemented carbide, metal wires, turbine blades, high temperature lubricants, incandescent lamp filaments, television sets, heat sinks, golf clubs, fishing weights, and hunting ammunitions (Koutsospyros et al., 2006). Toxicity of the lead (Pb) bullets triggered the use of W as a low caliber ammunition as well (Fisher et al., 2006; Thomas et al., 2009). In addition to the industrial and domestic uses, dissolution of W-bearing minerals was found to be another major source for the occurrence of W (VI) in the environment (Seiler et al., 2005).

Thus, the high provenance of W and its compounds in the environment and the suspected toxicity to human and ecological health has given rise to many fate studies (Koutsospyros et al., 2006). One possible fate of added W (VI) is sorption by soil minerals. Consequently, many studies evaluated the sorption mechanisms of W (VI) on various soil minerals (Gustafsson, 2003;

Xu et al., 2006, 2009; Lorenz, 2009; Lorenz et al., 2011; Kashiwabara et al., 2013; Davantes and Lefevre, 2015; Sun and Bostick, 2015; Hur and Reeder, 2016; Rakshit et al., 2017). In general, W (VI) displays a high affinity for iron-and aluminum hydr (oxide) minerals (Gustafsson, 2003; Xu et al., 2009; Hur and Reeder, 2016). To support the findings in macroscopic sorption isotherm and envelope, researchers determined molecular level information on surface retention mechanism using EXAFS and *in situ* ATR-FTIR spectroscopic tools as well (Davantes and Lefevre, 2015; Hur and Reeder, 2016; Davantes et al., 2017; Rakshit et al., 2017). These spectroscopic measurements are very sensitive and resulted in the detailed information about surface complexes at environmental range of W (VI) conc (Hur and Reeder, 2016; Davantes et al., 2017; Rakshit et al., 2017).

One of the disadvantages of studying the molecular mechanism of W (VI) interaction with mineral surfaces is that the currently available W (VI) solution speciation cannot always be linked to the probable surface complexation at a given solution property. This is because thermodynamic data were unavailable in the environmental range of W (VI) conc. (Rakshit et al., 2017). For example, the seminal papers, which determined W solution speciation, listed conc. range of W (VI) as 0.5-123 mM (Cruywagen and van der Merwe, 1987), 0.5 M (Shijun et al., 1998), 3 M (Smith and Patrick, 2000), and 2 mM (Hur and Reeder, 2016). Interestingly, W (VI) is known to polymerize at higher concentration even at unfavorable pH value (Hur and Reeder, 2016). Thus, extrapolating the solution speciation conducted at mM and M level to μM should be interpreted carefully.

Although important molecular level information about W (VI)-Fe/Al(hydr)oxide surface complex at an environmental range of conc. is currently available in the literature, no studies to the authors best of knowledge determined the nature of surface complexes in the presence of

competing anion such as phosphate (P) using surface sensitive spectroscopic probes. The likelihood of the coexistence of P and W (VI) in the environment is large. Thus, some macroscopic competitive sorption studies with W (VI) and P on Fe/Al(hydr)oxide/ clay minerals are already available in the literature (Gustafsson, 2003; Xu et al., 2009; Iwai and Hashimoto, 2017). These studies indicated that P has some influence in reducing W (VI) sorption on Fe/Al-(hydr)oxide minerals. However, due to the lack of molecular level information about probable surface complexes in the presence of P, the fit of surface complexation model (SCM) in the competitive system was not possible in some cases (Gustafsson, 2003). Thus, the molecular level spectroscopic studies on P and W (VI) competitive sorption on common iron oxide such as hematite are unavailable in the literature. Hence the main objective of this study is to probe surface interaction mechanism of W (VI) on hematite in the presence of P using macroscopic and *in situ* ATR-FTIR spectroscopic investigation under various solution properties.

2. Materials & Methods

2.1 Reagent and materials

Hematite was synthesized following a procedure described in our earlier study (Rakshit et al. 2017), which was mainly derived from the hematite synthesis procedures published by Sugimoto et al. (1993) and Elzinga and Kretzchmar (2013). In short, a 500 mL of 2 M FeCl₃ solution was mixed dropwise to a continuously stirred 500 mL 5.4 M NaOH solution within a period of 5 min. The gel-like precipitate was collected in a pyrex glass bottle, sealed, and heated in a drying oven at 101⁰C for 8 days. The solid was then cooled to room temperature, washed with Milli-Q water (18.2 MΩ cm) until the EC value was < 5 μS cm⁻¹. The suspension was then freeze-dried and stored in a dry place at room temperature. The mineral identity was confirmed

using X-ray diffraction (Rigaku, Woodlands, TX). The surface area of hematite produced by this procedure is in the range of $24 \text{ m}^2 \text{ g}^{-1}$ (Elzinga and Kretzchmar 2013). Sodium dihydrogen phosphate (NaH_2PO_4) and sodium tungstate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$) were purchased from Sigma Aldrich (St. Louis, MO).

2.2 Macroscopic Sorption Experiments

Three types of macroscopic batch sorption experiments were conducted to determine the competitive effect of P on W (VI) surface interaction on hematite. These experiments are termed ‘before’, ‘during’ and ‘after’ experiments. These batch sorption experiments were performed in an anaerobic chamber (Coy Laboratory Products, Grass Lake, MI) to avoid the interferences from carbonate during pH control (Leuz et al., 2006). For ‘before’, W (VI) stock was added to the hematite suspension (2 g L^{-1}) to make $100 \mu\text{M}$ concentration at $I = 0.01 \text{ M NaCl}$, and at a pH range of 4-11. The suspension was then equilibrated for 24h at a fixed temperature (298K). The pH was controlled using small additions of 0.1 M NaOH and HCl and the final pH value was recorded. The suspension was then centrifuged and decanted carefully to keep the solid in the centrifuge tube. The filtrate was collected to analyze the W (VI) in ICP-OES (iCAP 7400, Thermo Electron, West Palm Beach, FL). The remaining solid was washed with electrolyte solution (i.e. 0.01 M NaCl), centrifuged, and decanted to remove the interstitial sorbate. This wash solution was analyzed by ICP-OES to ensure that the sorbed fraction was not removed. A $100 \mu\text{M}$ P solution was then added to the solid at respective pH values and equilibrated for 24h at 298 K. The filtrate was then collected for analysis in ICP-OES for total W (VI) and P. Appropriate standards and quality control samples were run in ICP-OES to satisfy the standard quality control/ quality assurance protocol.

For ‘during’ experiments, 100 μ M of both W (VI) and P were added simultaneously, equilibrated for 24h at 298 K, I = 0.01 M NaCl, and with a pH range of 4-11. After that, the suspension was centrifuged, decanted, and the filtrate was analyzed for total W and P by ICP-OES. For ‘after’ experiments, the hematite suspension was equilibrated with 100 μ M P at pH range of 4-11. After 24h of equilibration at 298K, the content was centrifuged, decanted carefully to save the solid, and filtered. The filtrate was collected to analyze total P by ICP-OES. The solid was washed with 0.01 M NaCl solution to remove any interstitial P in the reaction mixture. The wash solution was collected and measured in ICP-OES to verify if any P was removed from the sorbed phase. A W (VI) stock solution was then added in the suspension of P sorbed hematite to attain an initial W (VI) concentration of 100 μ M at ionic strength of 0.01 M NaCl, and a pH range of 4-11, equilibrated at 298K for 24h, centrifuged, decanted, and filtered. The filtrate was analyzed for total W and P in ICP-OES. These three types of competitive sorption experiments portray a comprehensive view of the influence of P on sorption of W (VI) on hematite. All wet chemical experiments were performed in triplicates with a mean value and standard deviation plotted. Control experiments without the hematite in the reaction mixture were performed under the same conditions as the treatments above. Negligible change in W (VI) concentrations was noticed. Samples were not stored more than 48h before analyses in ICP-OES.

2.3 Spectroscopic Experiments

Evaluation of molecular level competitive reactions between W and P via *in situ* ATR-FTIR experiments were performed in Perkin Elmer Frontier Infrared spectrometer equipped with a liquid N₂-cooled mercury cadmium telluride (MCT-A) detector, a Balston-Parker air purger provided the optics compartment with H₂O- and CO₂-free air. The HATR flow cell was prepared

by evenly coating a 45° ZnSe ATR cell (Pike Technologies, Madison, WI) with a hematite suspension (approx. 2.5mg in 500µL suspension) and allowing it to dry overnight. The flow cell was sealed with a top plate, placed on the ATR sample platform of the IR spectrometer, connected to an Ar-purged reaction vessel containing 500 mL background electrolyte solution (0.01M NaCl) with pH maintained at an appropriate value using small volumes of 0.1M NaOH or HCl solution. A peristaltic pump (Watson Marlow 400, Falmouth, UK) circulated the solution from the reaction vessel to the flow cell at a rate of 2 mL min⁻¹. A magnetic stir bar at the bottom of the reaction vessel maintained constant mixing of the solution. This type of flow-cell set up has been used widely in the literature and in our previous studies (Elzinga and Sparks, 2007; Rakshit et al., 2013 a, b; Rakshit et al., 2017).

Each experiment began with a preliminary equilibration step, in which the background electrolyte solution was circulated through the HATR cell for approx. two hours and several background spectra were collected. After this pre-equilibration time, a final background spectrum was collected at an appropriate experimental pH. All other spectra were collected against a ratio of the final background spectrum so that only IR peaks resulting from the surface interactions between hematite and W (VI) or P were recorded. System pH was maintained at a specific value throughout the experiment. Competitive sorption experiments between W (VI) and P were initiated by introducing one analyte (either W or P) into the reaction vessel and monitoring interactions with hematite substrate via IR absorbance scans in the 1400- 700 cm⁻¹ range (Davantes and Le'fevre, 2015, 2017; Rakshit et al., 2017). Sorption was estimated to have reached equilibrium when no further increase in IR band intensity was observed. Final spectrum was collected and the process was repeated by incorporating the competing sorbate (P or W) in two 100µM concentration intervals. Higher than (1:1) ratio was used to understand the effect of

one sorbate on the other in case of excess concentrations. Background corrected raw spectra and difference spectra were presented.

To test the effects of pH in the competitive sorption, separate *in situ* ATR-FTIR experiment was conducted using 100 μM W (VI) and P. The experiment was started at a pH value of 8.01 and both W (VI) and P were introduced through injecting fresh stock solution in the reaction vessel simultaneously at a concentration of 100 μM each. When the sorption had reached equilibrium, the final spectrum was recorded and the pH was decreased to the next level. These steps were repeated until a pH value of 4.6. Since W (VI) is known to polymerize at acidic pH values, the reaction is started at alkaline pH values.

Results & Discussion

Effect of pH

a) Single Ion System: Tungstate (W (VI)) sorption envelope on hematite indicated almost 100% sorption until pH 7.7 and a gradual decrease of sorption to 50% at pH 10 (Figure 1 A.). Sorption envelope indicated negligible ionic strength dependence until pH 7.7, after that increasing ionic strength increased sorption. Lack of ionic strength dependence or increasing sorption with increasing ionic strength suggests inner-sphere mode of surface interactions (Hayes et al., 1988; McBride, 1997). For W (VI) sorption on goethite, Xu et al. (2006) reported 100% sorption until pH 5. After that the sorption decreased by 50% at pH 7 and to 80% at pH 10. Thus, the sorption envelope indicated much sharper decrease in case of goethite in other study. Interestingly, for W (VI) sorption on ferrihydrite (containing 1 mM Fe), Gustafsson, (2003) reported that approximately 100% of W (VI) sorbed until pH 7.5. After that a gradual decrease of sorption was noticed to a value of 40% at pH \sim 9.2. Detailed mechanistic interpretations of the

effects of pH on W (VI) sorption on hematite were published in our earlier study, in which *in situ* ATR-FTIR spectroscopy was used to probe the surface interaction mechanisms (Rakshit et al., 2017). The authors noted that at lower pH values, the IR bands due to the formation of inner-sphere type bond became more intense. A gradual shift of W-O stretching band to the higher wave number upon decrease of pH value corroborated this mechanistic finding as well.

b) Binary Mixtures with Phosphate: Three different systems were evaluated, in which W (VI) was added first, P was added first, and W (VI) and P were added simultaneously (Fig. 1B). These three sorption envelopes were plotted along with W (VI) single ion system at 0.01 M ionic strength to compare the sorption in the presence and absence of P. When W (VI) was added first, addition of P at (1:1) level did not show any effect on the sorption envelope. Only a minor reduction of sorption (2-4%) compared to W (VI) alone system was noticed at pH 10. Major differences in sorption were noted when W (VI) and P were added simultaneously or when P was added first. In both cases, sorption envelope indicated a reduction of about 30% W (VI) retention after pH value of 7. A similar difference was noticed at pH 4 for the ‘P added first’ system.

Gustafsson, (2003) reported no effect of 200 μM P on 50 μM W (VI) sorption on goethite until a pH value of 5.5. Almost 25% and 60% less sorption of W (VI) on goethite was noticed at pHs 6.5 and 7.5, respectively, in the presence of P. For the hematite used in our study, the sorption reduction at these pH values were lower ($\sim 30\%$ at pH 7). Lesser effects of P in our study could be due to the less amount of P (i.e. 100 μM) used in the competitive sorption experiments compared to that of Gustafsson, (2003). The chosen P concentration in our case was to mimic practical environmental range of concentration (Goldberg, 2010). Detailed interpretations of the mechanisms underlying these macroscopic competitive sorption

experiments were noted in the next section, in which *in situ* ATR-FTIR analyses of competitive sorption of P and W (VI) in binary mixtures were reported.

Analysis of *in situ* ATR-FTIR Spectra of W (VI) and P Binding on Hematite

a) Time Series Spectra: *In situ* ATR-FTIR spectra of competitive sorption of W (VI) and P on hematite were presented in Figures 2 A & B. The corresponding difference spectra were noted in Figures 2 A1 & B1. In Figure 2 A, the time series spectra indicated the competitive sorption system of W (VI) and P, in which W (VI) was added first and equilibrated before P addition. For clarity, only final equilibrated W (VI) spectrum was shown in Figure 2A. This spectrum illustrated IR bands associated with W-O symmetric (930 cm^{-1}) and antisymmetric (830 cm^{-1}) stretching due to strong inner-sphere type surface complexation of W (VI) with hematite surface as reported by earlier studies (Zorina and Syritso, 1972; Charton et al., 2002; Tomaszewicz et al., 2009; Kumar and Mohanta, 2011; Tribalis et al., 2014; Davantes and Lefevre, 2015; Rakshit et al., 2017). Subsequent time series spectra after $100\text{ }\mu\text{M}$ and $200\text{ }\mu\text{M}$ P additions were depicted to indicate the gradual growth of 1097 cm^{-1} IR band due to P surface complexation on hematite in the W +P mixed system (Figure 2A). The spectral subtraction of W (VI) only system from the mixed system resulted in the Difference spectra (2A1), which indicated that the addition of P did not cause any change of 930 cm^{-1} IR band (no negative peak at this position). Thus, the IR band representative of symmetric stretching modes of W-O bonds in WO_4 unit of W (VI) became unaffected in the presence of P. However, the IR band due to W-O antisymmetric stretching vibrations showed a negative intensity in the difference spectrum (Figure 2A1), suggesting a loss of antisymmetric W-O vibration in the presence of P. Therefore, the IR data showed evidences that W (VI)-hematite surface complexation mode most likely differed in the 'P added later' experimental system compared to the 'W (VI) only' system.

However, no release of W (VI) from hematite surface was noticed (Figure 2A1). This could be due to the fact that the surface interactions of W with hematite still occurred as evidenced by the existing W-O symmetric stretching band. Macroscopic sorption envelope data were consistent with the fact that addition of P did not induce any noticeable release of sorbed W (VI) in the pH range studied (pH = 4-10) (Figure 1B).

In situ ATR-FTIR spectra of W (VI) and P competitive sorption, in which P was added first, were presented in Figures 2 B and B1. Final equilibrated P spectrum was shown in Figure 2B and subsequent time series spectra after 100 and 200 μM W (VI) additions were plotted as well. The growth of W-O stretching band at $\sim 932\text{ cm}^{-1}$ was noticed with increasing time with concomitant decrease of IR band ($\sim 1100\text{ cm}^{-1}$) responsible for P surface complexation (Figure 2B). Difference spectrum clarified this observation (Figure 2B1). Strong W-O stretching band at 932 cm^{-1} in the difference spectrum is suggestive of the surface complexation of W (VI) in the presence of P when P was added first. A weak W-O antisymmetric stretching band can also be found at 831 cm^{-1} . Generally, earlier studies reported similar stronger symmetric stretching IR band in the $929\text{-}937\text{ cm}^{-1}$ range in the single ion system at similar pH values for W (VI) sorption on hematite (Rakshit et al., 2017). However, a much stronger antisymmetric stretching band around 831 cm^{-1} was reported in the single ion system compared to the current study with competitive system (i.e. W (VI) and P), thereby indicating the influence of P on the surface interactions of W (VI) with hematite (Figure 2B1).

Interestingly, W (VI) forced some desorption of P from the hematite surface in the system when P was added first. This is evidenced by a negative peak surrounding wave number from $1146\text{-}969\text{ cm}^{-1}$ in the *in situ* ATR-FTIR spectra (Figure 2 B1). Macroscopic sorption data of P, in which P was added-first, supported this observation (Figures 1B & Figure S1). In

contrast, no negative IR band due to P loss could be identified in the system when P was added later (Figure 1B1). In addition, the formation of weak antisymmetric W-O stretching band was absent in the difference spectrum of the *in situ* ATR-FTIR experiments, in which P was added later. These contrasting features of the IR data most likely indicate that the W (VI) sorption mechanism differed in the P first and in the P later systems compared to W (VI) only system.

b) pH Envelope: The *in situ* ATR-FTIR spectra of W (VI) surface complexation on hematite at different pH values was recorded in the presence of P when both W (VI) and P were added simultaneously (Figure 3A & B). Final equilibrated spectra of W (VI) & P were presented at pH range of 4.6-8.05. The initial pH was started at 8.05 because the probability of polytungstate surface species formation is higher at acidic pH (< 6) (Hur and Reeder, 2016; Rakshit et al., 2017). Lowering pH value from 8.05 to 4.6 increased the IR band intensities representing P sorption (~1041-1110 cm^{-1} range for all the pH values) and W (VI) sorption (W-O stretching band ~931-941 cm^{-1} range) on hematite (Figures 3 A & B). The enhancement of IR bands upon lowering pH is indicating increased sorption. The macroscopic data (Figure 1 B) are consistent with this observation. Shifts of both IR bands representing P sorption (~1041-1110 cm^{-1}) and W (VI) sorption (931-941 cm^{-1}) to the higher wave number upon decreasing pH value suggest increased degree of inner-sphere sorption, which is consistent with macroscopic pH envelope data (Figures 1 A).

In our earlier study, we found strong W-O-W stretching band at 875 cm^{-1} for the pH envelope of W (VI) sorption on hematite in the pH range of 6 to 4.6 (Rakshit et al., 2017). Other researchers indicated that the presence of this band represents the formation of polytungstate species (Tribalis et al., 2014). Inspection of the IR bands in the present study reveal similar IR bands at 875-877 cm^{-1} in the difference spectra of pH (4.6-8.05, 5.05-8.05, and 6.05-8.05).

However, the peak shapes are very different or weaker/ broader than the IR bands reported in the study of Rakshit et al. (2017) in single ion system. Thus, the presence of P most likely have affected the W-O-W stretching frequencies of these surface complexes, thereby indicating that the polytungstate surface species formation may have been somewhat affected.

Polyoxometalate Formation

The possibility of the formation of tungstophosphoric acid in the solution has been tested indirectly using *in situ* ATR-FTIR spectroscopy. Since we removed supernatant solute concentrations for P first and W first experiments, before adding either W or P in the reaction mixture, the formation of polyoxometalate or more specifically tungstophosphoric acid was not expected in those experiments. There was a possibility of polyoxometalate formation when binary mixtures of P and W (VI) were added simultaneously to the hematite suspension in the batch sorption experiments. *In situ* ATR-FTIR time series data of tungstophosphoric (TPA) acid was compared with that of simultaneous, P first and W first adsorption systems (Fig. S2 A, B) having similar solution properties. The IR bands responsible for P binding on hematite were significantly different in TPA compared to the P and W (VI) binary systems. In TPA, there is greater amount of W (VI) than P, which is evident by the intensities of the IR bands resulted from the sorption of TPA on hematite (i.e. greater intensity for the 932 cm^{-1} band than the 1082 cm^{-1} band). For the sorption experiments with P & W (VI) binary mixtures (1:1 and 2:1), different features were observed, i.e., intensity of the IR bands for P was always greater than W. In TPA the amount of W (VI) is always greater than P. Thus, we did not find any evidence of TPA formation in our experimental systems.

Conclusion

This study reports for the first time about detailed surface chemical interactions of tungstate with hematite in binary mixture with phosphate under environmentally relevant solution properties using *in situ* spectroscopic techniques (i.e. ATR-FTIR). The results indicate that W (VI) sorption on hematite was not affected when W (VI) was added first, however, some influence of P was noticed in the competitive sorption systems, in which either W (VI) & P were added simultaneously or P was added first. Time series spectra of *in situ* ATR-FTIR experiments corroborated these macroscopic observations. In addition, for the binary system, the spectroscopic data suggested that when P was present, surface complexation mode of W (VI) differed as noted from either the absence of W-O antisymmetric band or the W-O-W stretching band. Overall, for both W (VI) and P, increasing pH value decreased sorption as evident from both macroscopic and spectroscopic pH envelope data. This study will enhance the molecular level understanding of W (VI) surface complexation on iron oxides in the presence of competing ions such as P.

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FIGURE CAPTIONS

Fig. 1

A. W (VI) sorption on 2g L^{-1} hematite as a function of pH(4-10.65) at three ionic strength solutions ($I=0.01\text{M}$, 0.1M , and 0.5M NaCl). The initial W conc. = $100\mu\text{M}$.

B. The pH envelop for competitive sorption system: W 1st; W, P simultaneous; and P 1st. The pH envelope data from Fig1 A was replotted and marked as W alone for visual comparison with other competitive systems. The concentration of either W (VI) or P was $100\mu\text{M}$. The pH range 4 – 10. Ionic strength $I = 0.01\text{M NaCl}$.

Fig. 2

A. The *in situ* ATR-FTIR time series spectra of competitive sorption on hematite where W was added first. Initial W = $100\mu\text{M}$. ‘ $100\mu\text{M W Final}$ ’ indicates final equilibrated spectra with $100\mu\text{M W}$ sorbed on hematite deposit at 0.01M NaCl . ‘ $100\mu\text{M P} + \text{W Time 1}$ ’ represents the first IR spectra collected after addition of $100\mu\text{M P}$ in the reaction vessel. ‘ $100\mu\text{M W} + \text{P Final}$ ’ indicates the final equilibrated IR spectra of $100\mu\text{M W} + \text{P}$. ‘ $200\mu\text{M P} + 100\mu\text{M W}$ ’ indicates final equilibrated IR spectra after addition of $200\mu\text{M P}$ in the reaction vessel.

A1. Difference spectra obtained by subtracting raw spectra of final equilibrated $100\mu\text{M W}$ from final ($200\mu\text{M P} + 100\mu\text{M W}$) raw spectra. $I = 0.01\text{M NaCl}$

B. The *in situ* ATR-FTIR time series spectra of competitive sorption on hematite where P was added first. Initial P = 100 μ M. '100 μ M P Final' indicates final equilibrated spectra with 100 μ M P sorbed on hematite deposit in HATR cell at 0.01 M NaCl. '100 μ M P + W Time 1' represents the first IR spectra collected after addition of 100 μ M W in the reaction vessel. '100 μ M P + 200 μ M W' indicates final equilibrated IR spectra after addition of 200 μ M W in the reaction vessel.

B1. Difference spectra obtained by subtracting raw spectra of final equilibrated 100 μ M P from final (200 μ M W + 100 μ M P) raw spectra at I = 0.01M NaCl.

Fig. 3

A. The *in situ* ATR-FTIR spectra of 100 μ M W + 100 μ M P sorption (added simultaneously) on hematite at a function of pH values between 4.6 and 8.05 at ionic strength I=0.01M NaCl.

A1. Resultant difference spectra derived from subtracting each subsequent lower pH spectra from pH 8.05 spectra.

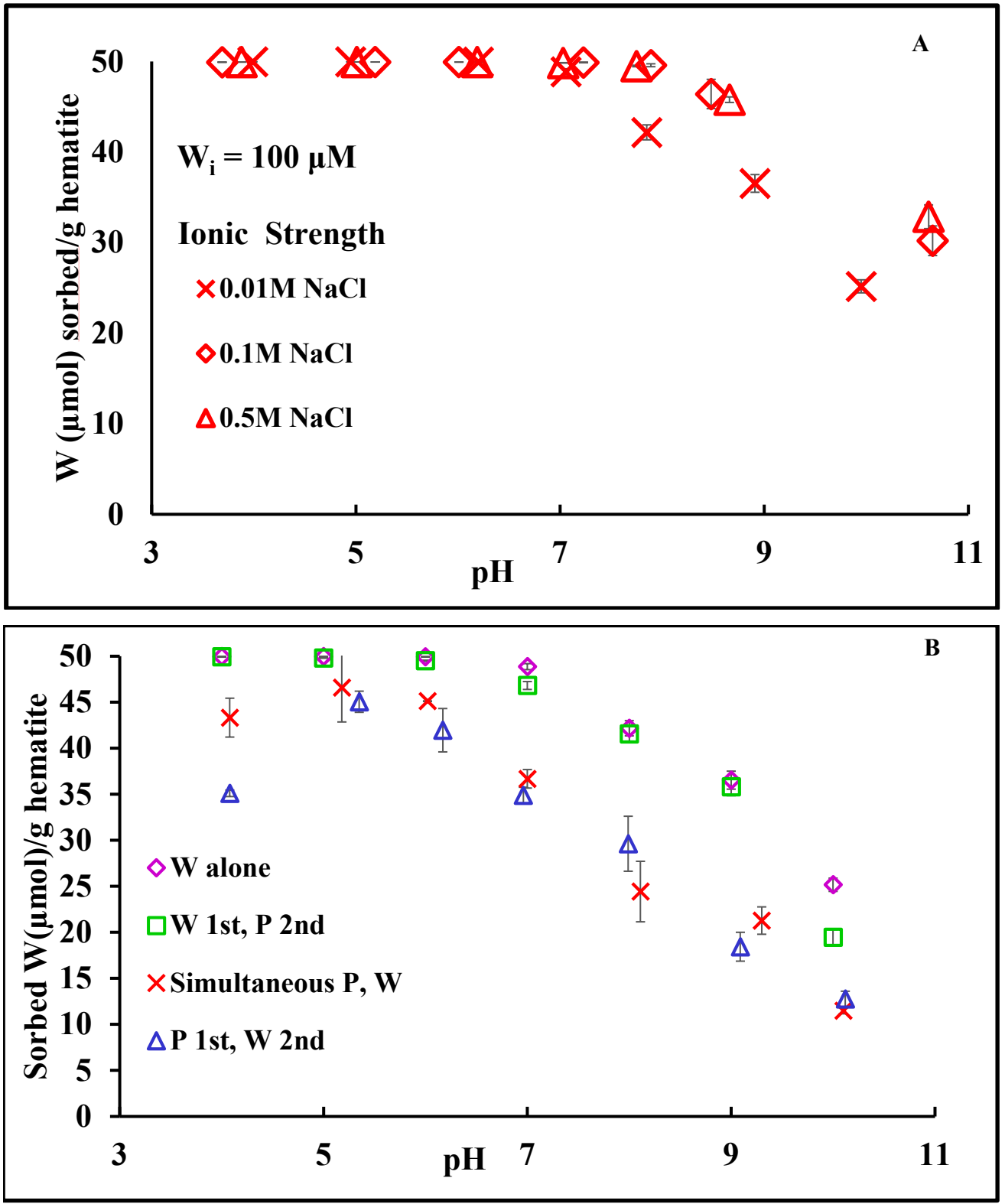


Fig. 1

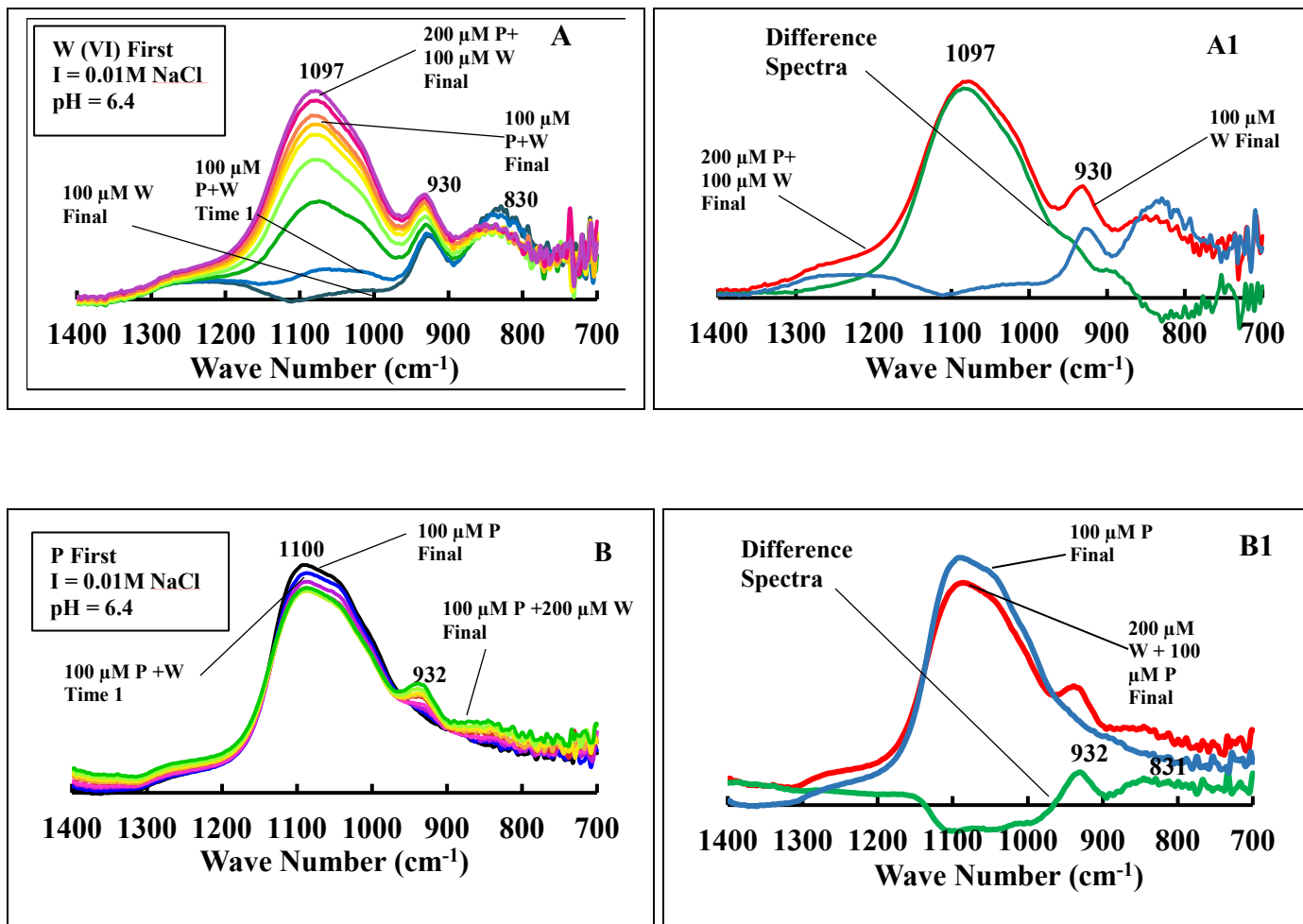


Fig.2

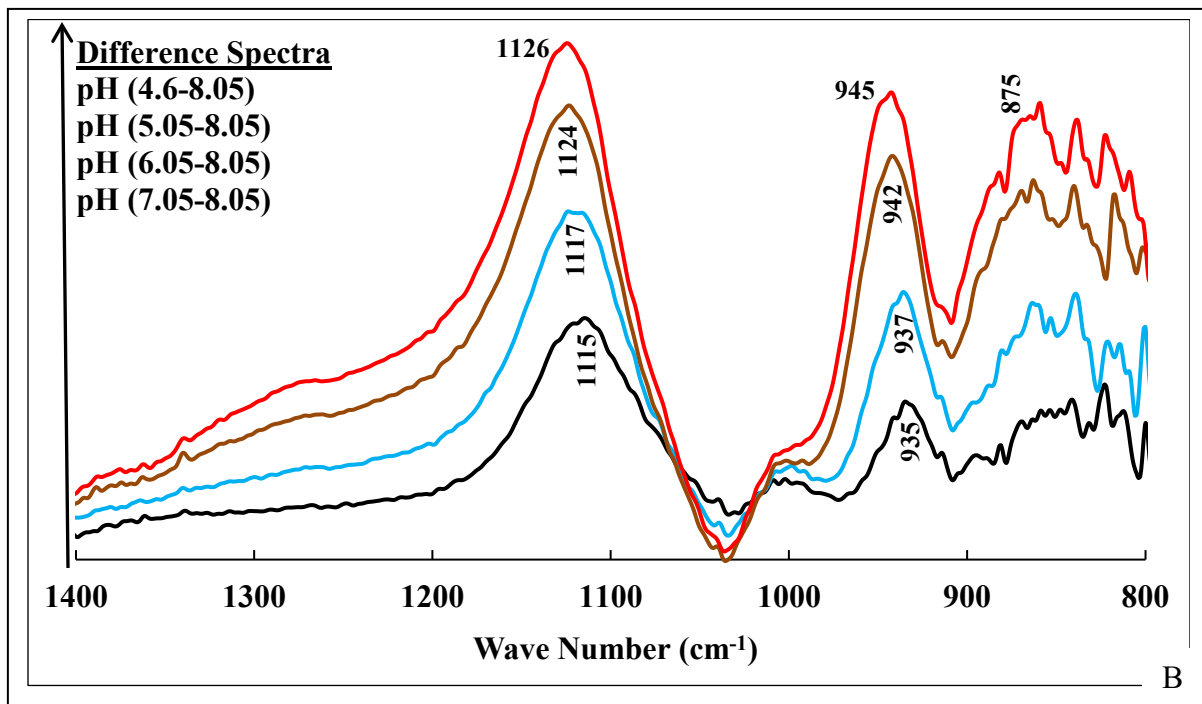
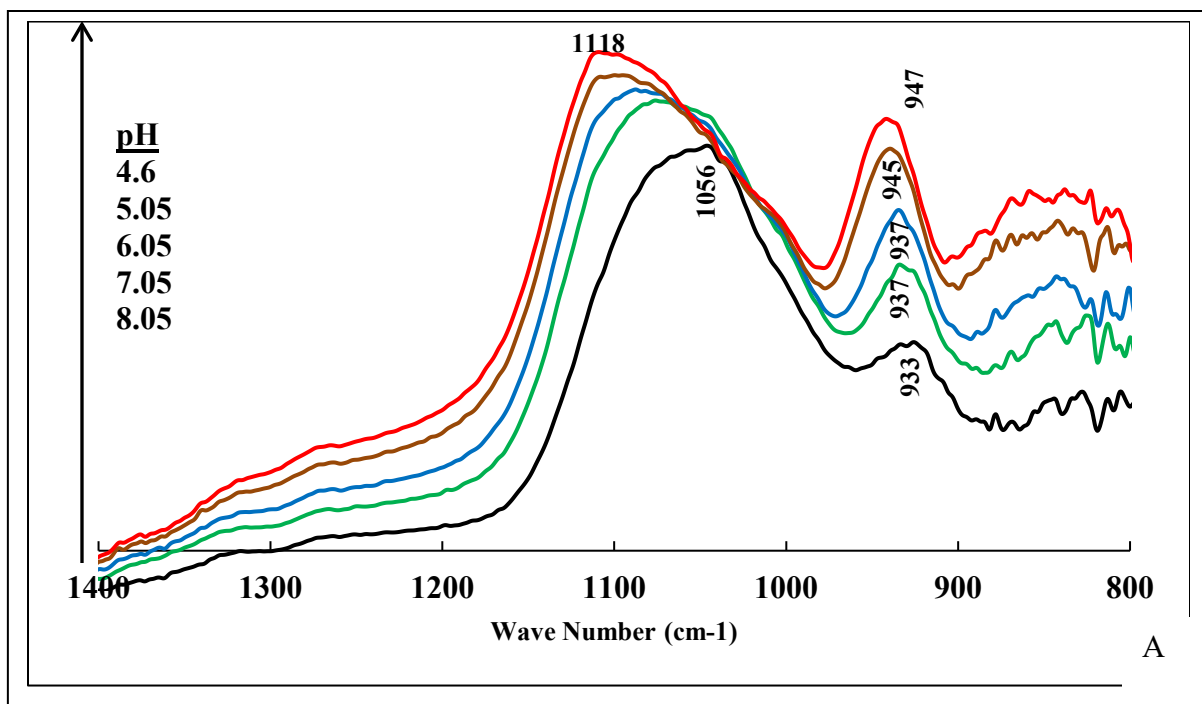


Fig. 3

SUPPORTING DOCUMENTS

Influence of Phosphate on Tungstate sorption on Hematite: A Macroscopic and Spectroscopic Evaluation on the Mechanism

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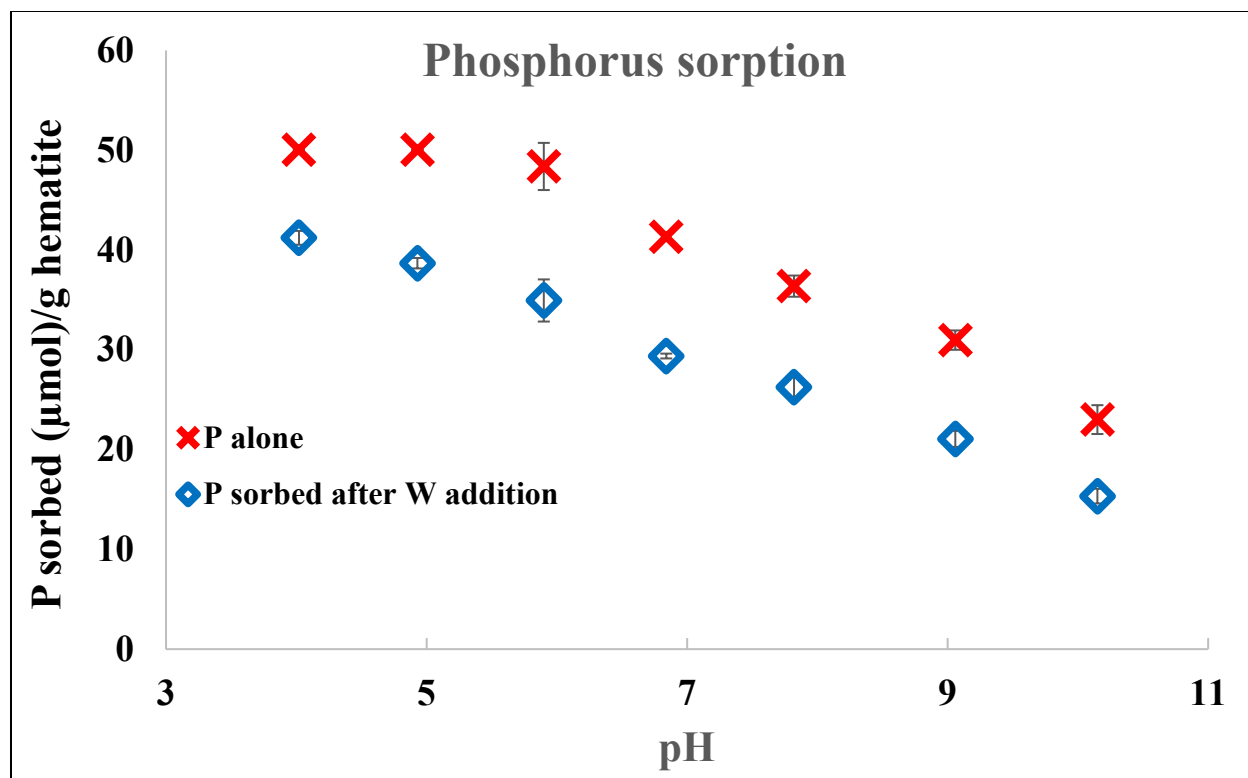


Figure S1. Sorption envelope of P alone (or P first) and P later at 0.01 M I (=NaCl).

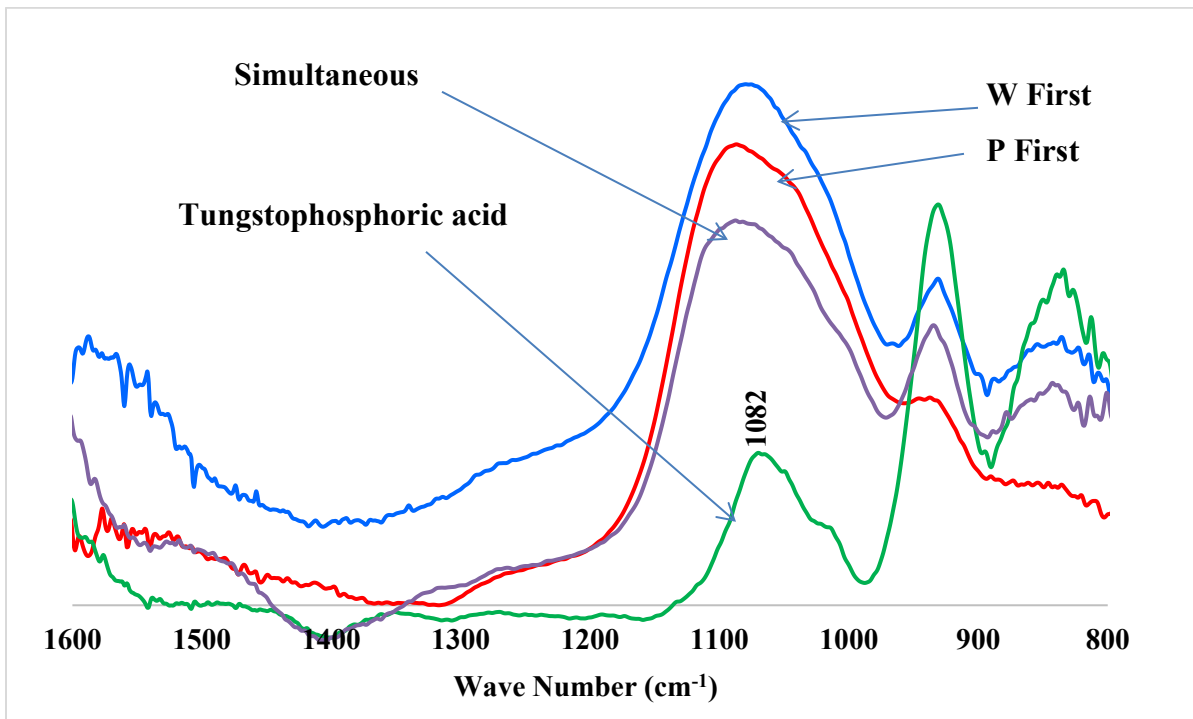
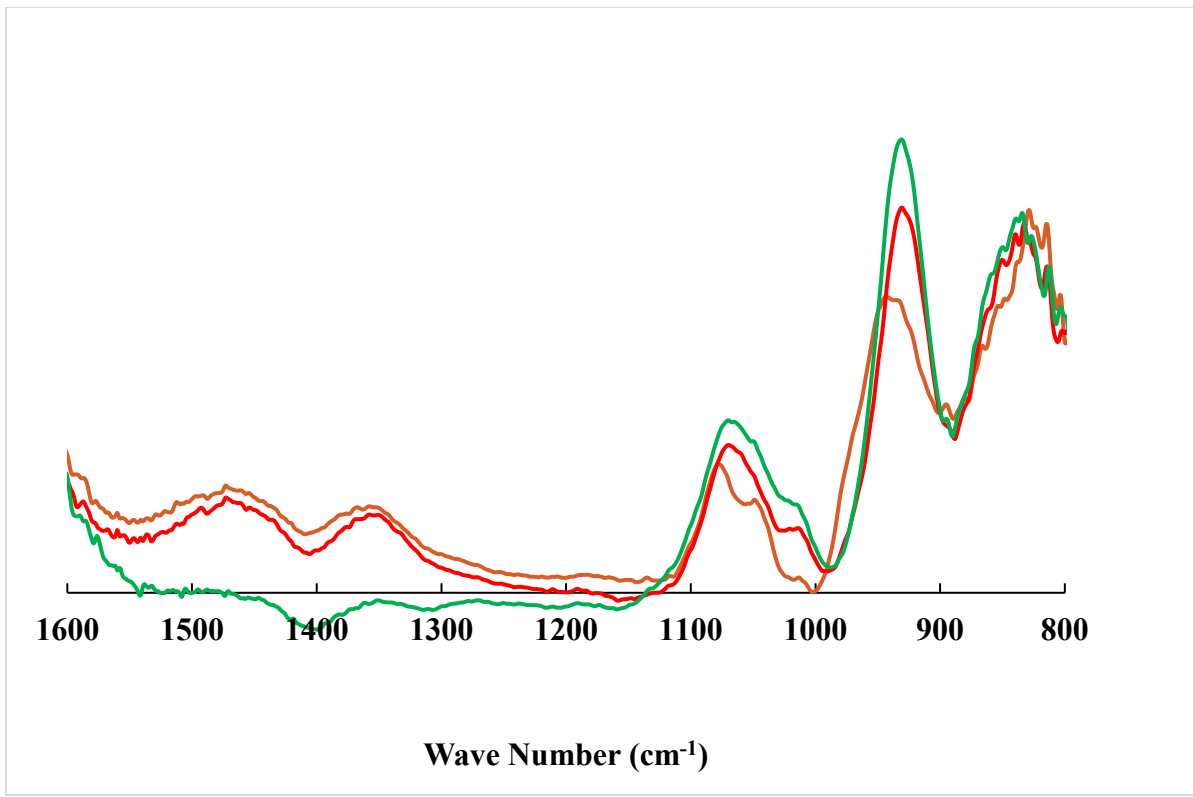


Fig. S2 A . Time series *in situ* ATR-FTIR spectra of tungstophosphoric acid adsorption on hematite at pH 6.4.

B. Normalized final time series scans (W 1st, P 2nd; P 1st, W 2nd; and Phosphotungstic Acid) All analyte concentrations = 100 μ M. All pH = 6.4, I = 0.01M NaCl.