Adsorption of Arsenate and Arsenite on to Reddish Brown Earth (RBE) in the Presence of Glyphosate

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Abstract - The use of Glyphosate (GPS) as a herbicide to control weeds in rice cultivation in many countries has become a controversial issue in the last few years. Arsenic is one of the most toxic elements found in contaminated water, and that can form complexes with glyphosate. Adsorption of arsenic species on to Reddish Brown Earth (RBE), which is the most productive and major rice-growing soil in Sri Lanka was examined when present glyphosate. Arsenic retention on RBE was examined as a function of pH under medium ionic strength (0.01M NaCl). All surface complexations were postulated by Fourier Transform Infrared (FTIR) Spectroscopy. It was shown that both arsenate and arsenite form bidentate complexes and also glyphosate and glyphosate- arsenite system form bidentate complexes, whereas, glyphosate- arsenate system forms monodentate complexes. As adsorption study showed that maximum arsenite adsorption of 60% at pH - 8.5 and arsenate adsorption of 94% at pH 3.5< pH< 8. Due to the presence of glyphosate, arsenite adsorption dropped to 54%. It indicates that the absence of glyphosate is favourable for the adsorption of arsenate. The FTIR showed a significant effect of glyphosate, on arsenite and arsenate adsorption. This study indicates that possible complexes were inner-sphere surface complexes of both arsenic species and glyphosate with –AlOH and –FeOH binding sites and outer sphere complexes between arsenite and glyphosate. This study shows that RBE can effectively be used to mitigate arsenate from the aqueous solutions than the arsenite and presence of glyphosate reduce the adsorption of both arsenic species, possibly due to adsorbing into GPS molecule.

Keywords - Glyphosate, Adsorption, FTIR, Arsenate, Arsenite, Reddish Brwn Earth, XRD

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1   INTRODUCTION

Reddish Brown Earth (RBE) is the most productive and major rice-growing soil in Sri Lanka (Wickramasinghe et al., 2000). It containing the high amount of fine sand, silt, and clay belong to the sandy clay loam textural. The RBE containing low salinity hence low electrical conductivity and that provide an idea of the amount of dissolved salt It is also a less contaminated soil type as indicated by total concentrations of trace elements such as Cu, Zn, Cd. X-ray diffraction studies indicated illite and kaolinite are major clay mineral and montmorillonite is the minor clay mineral in this soil (Sanjeevani et al., 2013).The presence of clay minerals and Fe/Al hydroxides or oxides affect to adsorption of many metals such as trace elements (Chang et al., 2012). Arsenic (As), one of most toxic contaminants found in water, is well known to have adverse effects, such as skin cancer, on human health.

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The consumption of arsenic contaminated water has led to human health crises in many countries such as Bangladesh, China, Taiwan and Argentina. Arsenic has two main inorganic species as arsenite (As^{3+}) and arsenate (As^{5+}). Mainly agricultural practices such as fertilizer applications, industrial discharges, volcanic activities, mining activities and rock weathering are caused by an addition of arsenic species into the environment. Adsorption of Arsenic is highly dependent on soil pH and Fe/Al oxide content (Chang et al., 2012). Arsenate is stable in the oxic environment as monovalent ($H_2AsO_4^-$) or divalent ($HAsO_4^{2-}$) anions. Arsenite is stable in a moderately reducing anoxic environment as uncharged (H_3AsO_3) and as ($H_3AsO_3^-$) anion. As(III) transform to As(V) in the oxic environment kinetically (Vithanage et al., 2006). In an oxide system with kaolinite or illite presence system, there is no any oxidation of arsenite and reduction of arsenate. But in montmorillonite presence system oxidation of arsenite can take place. In montmorillonite presence system transformation of arsenite to arsenate take place at the pH range 5 to 9 by <5% of total arsenite addition. Oxidation of arsenite at outside of that range 12% from total arsenite at pH 10.9 and 43% at pH 3.3 (Goldberg, 2002).

In the case of RBE, montmorillonite is a minor mineral therefore oxidation of arsenite to arsenate assumed as very low. In an solid-solution interface, surface complexation phenomena happen by assuming both 1-pk and 2-pk

models. 1-pk (surface >SOH, species >$SOH_2^{+1/2}$, >$SO^{-1/2}$), 2-pk (species >HOS, >$SOH^{+1/2}$, >SO^-) But 2-pk model is widely used and in the surface there are two steps can be happen as a hydroxalated process,

>SOH + H^+ ⟶ >SOH_2^+ and

>SOH ⟶ >SO^- + H^+
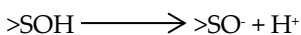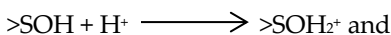
Arsenic adsorbed by this SO^- and complexations are formed with respect to an inner sphere and also outer sphere surface complexations between adsorbent surfaces and arsenic species (Vithanage et al., 2006).Adsorption of arsenic species with contaminated RBE was examined by a batch study as a function of the pH, both before and after adding of glyphosate [N – (phosphonomethyl) glycine] into the system. Glyphosate (GPS) is a post – emergent herbicide with broad spectrum and widely used in agriculture (Jonge et al., 2001). By microorganisms, it is converted into inactivated non-phytotoxic products in the soil and inactivated by binding with soil components. It has three amine groups, carboxylate and phosphonate groups. Glyphosate can form strongly coordination bonds with the transition metal ions and therefore it can be considered as a class of strongly chelating herbicide (Morillo et al., 1997). Sorption of GPS on the soil sorbents generally increase by increasing Fe^{+3}, Al^{+3} in to soil constituent. But in Na^+, Mg^{+2}, Ca^{+2} rich soil GPS sorption is generally low in the order Na^+ < Mg^{+2} < Ca^{+2} < Zn^{+2} < Mn^{+2} < Fe^{+3} < Al^{+3} (Jonge et al., 2001).

Glyphosate bind with soil through the phosphonate group. It is similar to the phosphate bind with soil. This binding mechanism does not appear to be related to cation exchange capacity of clay minerals but related with the valence of the cation in the clay minerals. That is one possibility of adsorption mechanism in addition to that, GPS formed bonds with clay through binding with a metal cation. Glyphosate adsorption strongly depends on cations which are associated with soil and also adsorption by soils, broken edges of clay minerals and oxides/ hydroxides pH in the system (Morillo et al., 2000). The adsorption of arsenic species into the soil components in presence of GPS happen by direct adsorption of the arsenic added through soil components – arsenic – GPS bonding. In addition to that only GPS adsorption takes place in the metal – GPS contaminated soil system.

2   MATERIAL AND METHODS

The soil sample was collected from a less contaminated location where not cultivated for about four years at 08 ˚ 06.713′N, 80 ˚28.353′E located in the dry zone of Sri Lanka. To obtain a composite sample there are three sub samples were collected from depth range 0 to 30 cm (Sanjeevani et al., 2013). The soil sample was passed through 63μm sieve and <63 μm portion was used to laboratory analysis after dried off the sample at 115° C. Initially, Soil solution was prepared in 2:1 ratio by dissolution of 1g of <63 μm fraction in 500 mL deionized water. The solution was stirred well rate at 12 rpm using magnetic stirrer for 20 minutes and 25 mL of soil suspension was filtered, dried and weighted. Repeat the same procedure to obtain behaves as a homogeneous. 2 g/L was identified as optimum RBE concentration that behave as a homogeneous system upon constant stirring; hence, this substrate concentration was used in all adsorption studies. All experiments were conducted with 2 g/L concentration of soil substrate under 0.01 M ionic strength. SEM study was conducted to obtain the surface characteristics of RBE without any chemical treatment. The sample was used to XRD analysis in order to determine the mineralogical composition. Arsenic species and GPS binding site were determined by using FTIR spectroscopy.

2.1 Adsorption isotherms

A series of a batch study were carried out to determine the adsorption isotherm of RBE due to absent and presence of GPS. 2 g/L of dried <63 μm sieved soil portion was added into the 500 mL of NaCl solution with ionic strength 0.01 M. The solution mixture was purged with nitrogen gas to minimize the CO_2 contamination within 10 min due to stirred well at 12 rpm within 20 min and allowed to equilibrate. After the six control test with spiking 1 μg/L, 10 μg/L and 100 μg/L arsenic species into the system, 10 μg/L arsenic concentration was selected as a suitable amount for the spike. Then the system was spiked with arsenite until total concentration becomes 10 μg/L. 25 mL swatches were transferred into polypropylene centrifuge tubes while changing the pH 3.5 to pH 10.0. The centrifuge tubes were purged with nitrogen properly and pH was measured before sealing the tube. Then the batch of samples was allowed to equilibrate for 24 hours under nitrogen purging condition. During experiment, the pH were measured several times and adjusted when required. During the retention period, suspensions were centrifuged twice. The supernatants were extracted filtered using membrane filter papers (0.45 μm). Remaining arsenite concentrations were measured using ICP-MS by assuming the total arsenic concentration is equal

to the total arsenite content. Absorption amounts of arsenite were calculated from the difference of initial and final concentrations of the arsenite. Above procedure was used to determine the adsorption of arsenate into RBE and also used to adsorption study of arsenate and arsenite into the RBE due to the presence of the GPS. In this case, 10 µg/L of GPS was used as the contaminant of soil.

2.2 Adsorption Data Modeling

The arsenate and arsenite data was modeled by assuming a single site Langmuir adsorption isotherm,

$$\tau = \frac{k[M]\tau_{max}}{(1+k[M])} \tag{01}$$

By assuming all adsorption sites have equal affinity for the adsorbate and also only monolayer adsorption, above equation modified as,

$$\tau = \frac{[As]_{initial}[As]_{final}}{[A][S]} \tag{02}$$

Where, τ is the amount of adsorbate adsorbed per unit surface area (mol m^{-2}), M is the equilibrium solution concentration (mol m^{-1}) of adsorbate, τ_{max} is the maximum adsorption density, and k is the equilibrium constant for the overall process. Where τ_{max} and k are adjustable parameters which estimated by non- linear least square fitting method, $[As]_{initial}$ and $[As]_{final}$ are initial and final arsenic concentrations (mol m^{-3}), [A] is the specific surface area (m² g^{-1}) and [S] is solid content (g L^{-1}) (Vithanage et al., 2006).

2.3 X-ray diffraction analysis (XRD)

The sieved sample was used to X-Ray Diffraction (XRD) analyses in order to determine the mineralogical composition. The analysis was done using D-5000 Diffractometer in which CuKα radiation was used at the wavelength of 1.54056 Å and 1.54439 Å. The comparison of the major peaks was carried out using the 2θ values and the d-spacing values with the standard data.

3 RESULT AND DISCUSSION

3.1 Mineralogical Composition

According to the XRD analysis of the clay fraction of the alfisol is shown in figure 1, kaolinite and quartz are major mineral constituents. The other clay minerals occur in small proportions are illite, K-feldspar, mica, and calcite. As shown in Figure 1, a small peak is present at 2θ 33. This possibly indicates the occurrence of goethite. The peak at 2θ

29 corresponds to the presence of alumina. Therefore it is expected that the surface properties of the soil sample is largely controlled by the presence of kaolinite and illite. Dominance of kaolinite reason for low cation exchange capacity of afisols (Sanjeevani et al., 2013).
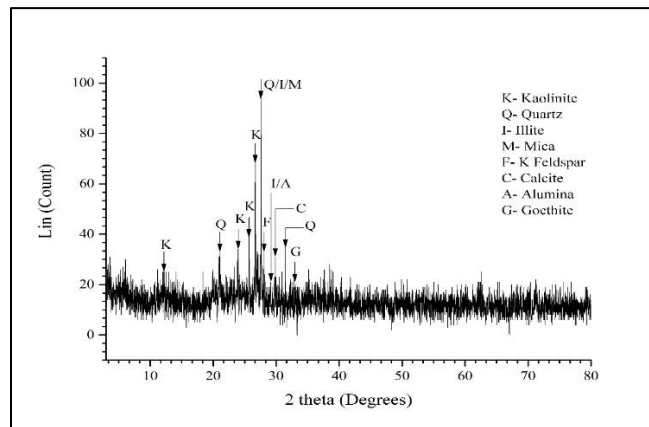

Fig. 1. X- ray diffractogram of the clay fraction of reddish brown earth.

3.2 Adsorption configuration

Kaolinite and illite are the dominant clay minerals in the system. Adsorption of arsenite, as represented in figure 2a showed 60% adsorption pH around 8.5 and show gradual increases of adsorption and after peak adsorption sudden decreases can be seen. Arsenite due to the presence of glyphosate (figure 2a) 54% maximum adsorption at around 8.5- 9 pH conditions. According to the results, adsorption of arsenite is high in glyphosate absent system than glyphosate present system. In this case, arsenite adsorbs into clay minerals which are kaolinite and illite, most dominant minerals in the sample and adsorb into Al and Fe oxides take place. In the sample, containing reactive surface sites >SiOH, >FeOH and >AlOH. But >FeOH and >AlOH are the effective site for adsorption. In the intrinsic acidic constants of >AlOH sites were comparable with amorphous aluminum oxide and >FeOH sites were similar to the amorphous iron oxide (Vithanage et al., 2006). According to the figure 2a, showed that total adsorption density increases with increasing pH. Around pH 9.5, maximal arsenite adsorption or desorption arsenite may take place. Therefore a decrease in adsorption capacity can be observed. Due to the presence of glyphosate similar behavior of arsenite was obtained in figure 4.8a but adsorption is less than glyphosate absent. Glyphosate adsorption behavior is similar to the inorganic phosphate adsorption and the binding mechanism does not relate to

cation exchange capacity of clay minerals, only depends on the valence of the cations in clay minerals (Jonge et al., 2001). Because of no relationship with cation exchange capacity, arsenite adsorption curve due to the presence of glyphosate almost similar to the glyphosate absent. So that both glyphosate and arsenite present system, show less adsorption capacity of arsenite with respect to the glyphosate absent system. Glyphosate can directly join with clay minerals through their phosphate group and it can form bonds through binding with metal cations (mirillo et al., 1999).

In arsenate system, 94% arsenate adsorption can be observed in figure 4.8b and it is taken place approximately constant behavior until pH 8, and also adsorb with similar sites to arsenite in the soil. According to the results arsenate adsorption is higher than arsenite adsorption because on arsenite adsorption depends on many factors and it more convoluted on specific chemical conditions of the soil.

Compare to the arsenite, arsenate binds strongly and extensively with most of the mineral constituent in soil (Fendrof et al., 2010). In glyphosate system, maximum arsenate adsorption shows 52% (pH 7.5) in figure 2b. Glyphosate binds with soil through the phosphonate group. It is similar to the inorganic phosphate bind with soil (Jonge et al., 2001). The binding behavior of inorganic phosphate and arsenate are similar to each other because their bond arrangement and sizes are approximately similar (Violante et al., 2008). The glyphosate may show similar behavior for arsenate. Therefore there is a competition between arsenate and glyphosate may occur due to adsorption. So arsenate in glyphosate presence system could be highly dependent each other. Because of the competition, the adsorption graph of glyphosate present system in figure 4.8b shows that irregular behavior. The experimental data was strongly correlated with arsenic adsorption of pure kaolinite, illite and amorphous iron and aluminum oxide as mentioned by Goldberg (2002). Whereas arsenite adsorption on iron oxide was different from the experimental data, it was contribute information about the mineralogical composition of the sample. According to Appendix IV, kaolinite show the identical results to the sample, therefore most prominent sorption sites were >AlOH which are provided by kaolinite.
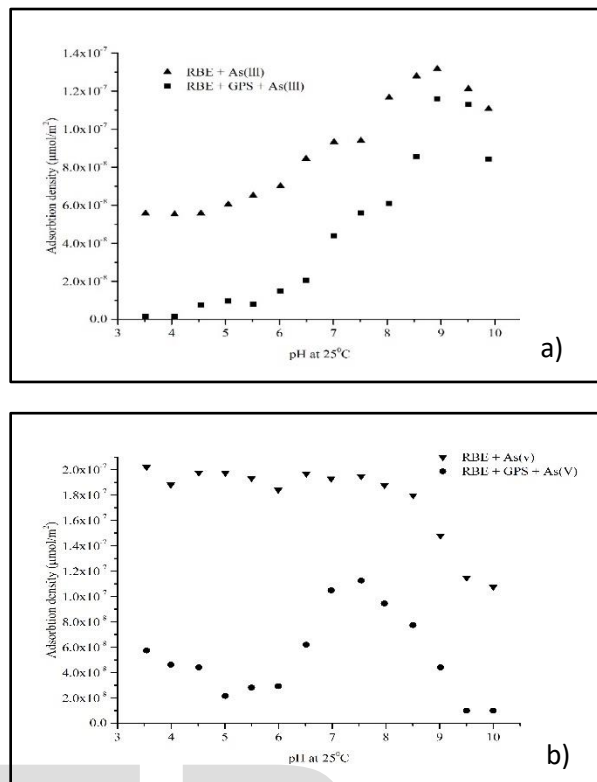

Fig. 2. Experimental results of adsorption due to present and absent of glyphosate of **a)** As(lll) and **b)** As(v) as a function of pH after 24 hrs retention time. Background ionic strength was 0.01 M NaCl. The pH of the system was varied from 4 to 10 using 0.1 M HCl or 0.1 M NaOH.

3.3 Fourier Transform Infrared Spectroscopy (FTIR) evidence for arsenic adsorption

Compared to the bare soil, in arsenate and arsenite system show less amount of -OH bonds than glyphosate present systems. This may be due to inner sphere surface complexation. The exchangeable –OH groups can be substituted by arsenic species and phosphonate groups in glyphosate. Therefore the addition of arsenic species and glyphosate caused the reduction of –OH bonds in the soil system. Formation of outer sphere complexes between arsenic species and glyphosate might affect on the reduction of adsorption due to presence of glyphosate. And also peaks are shifted from their original position which gives an idea about adsorption. In addition to overall differences, the system containing only glyphosate show the appearance of bands at 3670 cm^{-1}, 3650 cm^{-1} and 3692 cm^{-1} and also bands at 3656 cm^{-1} and 3630 cm^{-1} shifted to 3654 cm^{-1} and 3627 cm^{-1}. The shifts are ascribed to the variations in the interlayer environments of the –OH groups. Band at 3677 cm^{-1} become

very narrow due to adsorption of glyphosate into the soil. Bands at 3630 cm^{-1} indicate vibration of Al-Al-OH inner octahedral groups. Usually, clay minerals have inner octahedral exchangeable –OH groups by shifting to 3627 cm^{-1} give an idea about adsorption of glyphosate. Due to that, the –NH vibrations appeared in 3526 cm^{-1} in the spectrum. The arsenite containing system (figure 4a), does not show any difference from glyphosate adsorbed system (figure 3b), it is important to note that there is a similar significant effect of glyphosate on changes in soil functional group. But peak heights of 3620 cm^{-1} and 3642 cm^{-1} indicate that inner -AlOH bond reduction. Therefore amount of –OH bonds are reduced and peak at 3627 cm^{-1} become taller than glyphosate present system. So that ability to arsenite adsorption is higher than glyphosate adsorption and also peak at 3650 cm^{-1}(outer hydroxyls which are located at the surface and along broken edges) show similar kind of situation. In glyphosate, there can be –OH groups in the structure, that peaks appeared at 3627 cm^{-1} (in references 3625 cm^{-1}) (Jayasumana et al., 2014) (figure 3).

According to the observations, arsenite adsorption is higher than glyphosate. The peaks at 3677 cm^{-1} show inner surface hydroxyl vibration in soil. By adding arsenite, arsenate, only glyphosate and both arsenite and glyphosate, peaks at 3677 cm^{-1} become two peaks at 3670 cm^{-1} and 3677 cm^{-1} with narrow and smaller, that indicate bidentate surface complexation due to adsorption of that species. When both arsenate and glyphosate are present, the competition between arsenate and glyphosate may cause decreased adsorption, because phosphonate and arsenate have the similar molecular structure as phosphate (Sprankle et al., 1975) as shown in figure 5b the adsorption envelops also showed different patterns. Because of the competition, both glyphosate and arsenate adsorption becomes very less. This is indicated by the disappearance of peaks at 3627 cm^{-1}, 3650 cm^{-1} and 3670 cm^{-1}. In the system containing only arsenate or arsenite, the species bind with soil component most prominently by bidentate complexation. It is indicated by couple of peaks at 3642 cm^{-1}, 3650 cm^{-1} and 3670 cm^{-1}, 3677 cm^{-1}. But in glyphosate present systems, both monodentate and bidentate surface complexations are observed, which is resulted by the affect of the impediment of adsorbates structure (Vithanage et al., 2006).
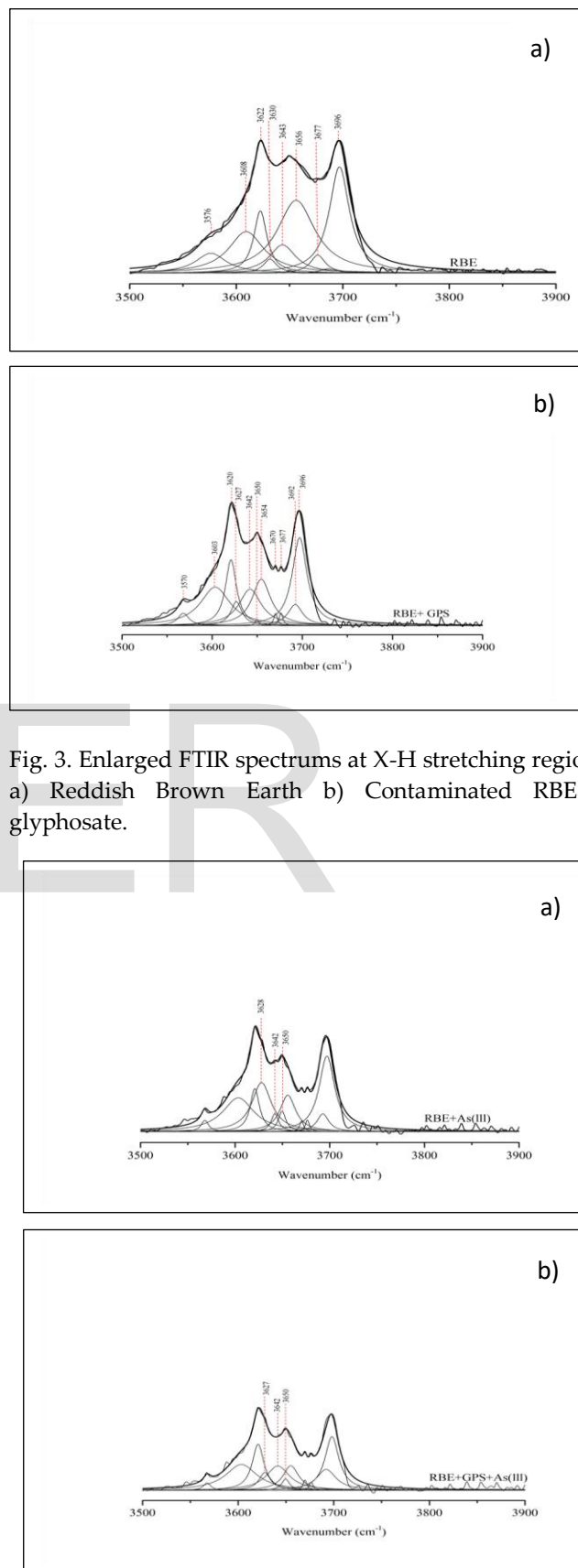

Fig. 3. Enlarged FTIR spectrums at X-H stretching region of a) Reddish Brown Earth b) Contaminated RBE by glyphosate.

Fig. 4. Enlarged FTIR spectrums at X-H stretching region of a) Contaminated Reddish Brown Earth by arsenite b) Contaminated RBE by glyphosate and arsenite.
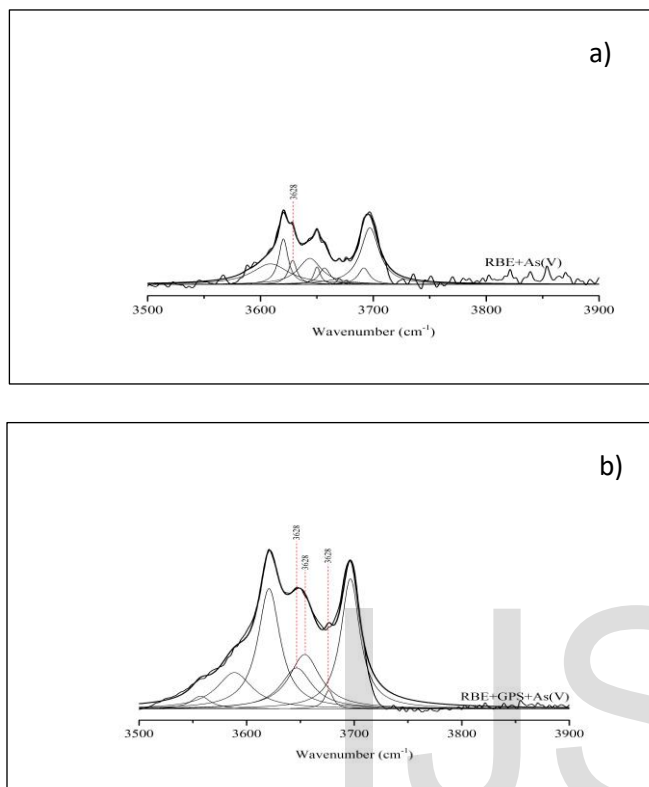

Fig. 5. Enlarged FTIR spectrums at X-H stretching region of a) Contaminated Reddish Brown Earth by arsenate b) Contaminated RBE by glyphosate and arsenate.

4 CONCLUSIONS

Natural reddish brown earth (RBE) (Alfisol) contained kaolinite, quartz as major mineral constituents; kaolinite and illite are the major clay minerals present in the sample. Feldspar, mica, calcite and montmorillonite occur in minute proportions. Natural RBE has contained mostly >AlOH sites but >FeOH can be present for surface complexation. The maximum arsenite adsorption was obtained at pH 8.5 irrespective of the presence of glyphosate. Maximum arsenate adsorption was obtained in the pH range 3.5 to 8. In glyphosate system, arsenate was sensitive to pH showing a maximum value at pH 7.5. A competitive adsorption occurs between arsenate and glyphosate for surface sites. These findings showed that arsenate was efficiently adsorbed on RBE surfaces than arsenite and presence of glyphosate resulted the reduction of the adsorption of both arsenic species. Arsenite form bidentate surface complexes and arsenate and glyphosate form both monodentate and bidentate complexes. Adsorption surfaces are provided by both outer tetrahedral surfaces –OH groups and inner octahedral –OH groups.

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