

## Research Article

# Geochemical Association of Ni<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, Ag<sup>+</sup>, Cu<sup>2+</sup>, and Co<sup>2+</sup> Ions in Natural Pyrite

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The natures of competitive adsorption of six metal ions on the natural pyrite surface have been studied with an objective to provide strong foundations towards mode of association/occurrence of trace elements on pyritic surface. Some parameters, for instance, adsorption edge, mechanism, correlation coefficient, monolayer coverage, pH, and thermodynamic parameters, have been considered here. The significant results are the order of increasing trend of adsorption edges which has been found to be  $Pb^{2+} < Cu^{2+} < Ni^{2+} < Zn^{2+} < Co^{2+} < Ag^+$ . Nonuniformity in variation of adsorption edge of a particular metal ion in presence of a second metal ion in solution is evident from the study. However, in case of  $Ag^{2+}$  and  $Co^{2+}$  ions two adsorption edges are observed. These variations have been explained based on the formation of hydroxo complexes which are pH dependent. The competitive monolayer coverage of each metal ion as a function of pH has shown variation in the extent of adsorption. Computed higher correlation coefficient in a binary system indicates retardation in adsorption of metal ion in presence of a second metal ions on pyrite surface showed exothermic processes due to the spontaneous nature at low temperature. Our study has strongly revealed promising adsorbent characteristics of natural pyrite with considerable geochemical and environmental implications.

#### 1. Introduction

Water discharged by industrial activities and from mines is often contaminated by a variety of harmful substances including metal ions [1–5] which have a deleterious effect on the water environment. To remove the harmful metal ions from polluted water, it is quite essential to precisely understand the method of purification of water. Much effort is being expended in the development of several processes for production of clean water. Application of activated carbon for the removal of metal ions from aqueous phase by adsorption is largely known [1–5], but competitive adsorption of metal ions on natural pyrite surface is limited. To study the adsorption characteristics, it is prerequisite to know the nature of association of various metal ions on the sulphide minerals. Association of inorganic elements in the coal organic matter and their extent of incorporation have been reported [6–12]. In regard to minerals, calcite, dolomite, siderite, and so forth are the carbonate minerals while pyrite and/or marcasite is the well-known sulphide minerals [13]. According to Miller and Given [14], jarosite and goethite are often encountered as natural weathering processes of pyrite. However, in addition to pyrite some sulphide minerals with varying quantities such as chalcopyrite (CuFeS<sub>2</sub>), sphalerite (ZnS) [15], galena (PbS) [16], millerite (NiS), and linnaeite (CoNi)<sub>3</sub>S<sub>4</sub> [8] are also occurring in natural systems and are also associated with pyrite.

Finkelman [8] reported a good number of elements associated with sulphide: Sb, As, Bi, Cd, Co, Cu, Ga, Ge, In, Pb, Hg, Mo, Re, Se, Te, Sn, and Zn. Of these As, Cd, Hg, and Pb are of particular environmental concern [17]. Swaine [18]

reported that the elements Cu, Ni, Pb, and Zn are all sulphide related. According to Spears and Martinez-Tarazona [19], Pb, Cu, Ni, Cd, Zn, and possibly Mn are associated with pyrite.

Both pyrite and marcasite are disulphide, that is, FeS<sub>2</sub>. Pyrite [19] can be described as a distorted NaCl-type structure having S-S bond length of 217 pm while marcasite structure is a variant of the rutile (TiO<sub>2</sub>) structure with S-S bond distance of 221 pm [20]. Both pyrite and marcasite exert considerable control over the elements present, including many elements of environmental interest [21]. Pyrite contains a disulphide unit  $(S_2^{2-})$  and the electron density around the disulphide unit is quite high [22]. Since concentration of gold on sulphide mineral surface occurs through adsorption as well as reduction processes, these suggest that sulphide minerals have some unusual surface properties [23]. This is consistent with the fact that metals, namely, Na, K, Ca, Mg, Al, Ni, Cu, Ag, Pb, Zn, Cd, and As have been reported to occur at the surfaces of pyrite [24]. In our earlier study, we have found that Co, Ni, Cu, and Zn are significant mineral bound elements in Assam coal [11]. Moreover, Pb and Ag [21] and also Hg have high affinity for pyrite. According to Abraitis et al. [25],  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ , and similar divalent cations can undergo substitution for  $Fe^{2+}$  in six-fold coordination in pyrite structure because of their favourable size and charge characteristics. Such substitution can lead to the electrical properties of pyrite (that acts as semiconductor) resulting in defects in crystal structure with charged entities [25, 26]. Another interesting observation on pyrite oxidation is that pyrite containing no impurity is least reactive, and pyrite with As is more reactive than those with Ni and Co [27]. It is quite likely that minor trace metal deposition on the pyrite surface may be possible from ore deposits as nanoparticles. Recently, adsorption of Cd on surface of pyrite has been reported [28]. Formation of secondary sulphide of Cu and Ag in the pore water as replacement reaction at the pyrite surface is also known [29]. Further decomposition of pyrite in the environment releases heavy metals such as As, Co, Pb, Ni, and Zn into neighbouring waterways [29]. More recently Tauson et al. reported an interesting work on gold distribution in a large number of pyrite samples and found that gold is uniformly distributed in pyrite and is chemically bound in majority of cases [30]. Since pyrite occurs at different environment and is also formed by various processes [31-34] competitive adsorption of metal ions on pyrite surface deserves an in-depth study. Considering all these, six metal ions, namely, Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Ag<sup>2+</sup>, and Pb<sup>2+</sup> are considered here for the adsorption of these metal (in the form of metal ions) at the surface of natural pyrite.

The objective of present investigation is to study the interaction between pyrite and dissolved metal ions  $(Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Ag^{2+}, and Pb^{2+})$  in aqueous medium. The questions that serve to focus are (a) what is the nature of individual adsorption of the metal ions on the pyrite surface and their adsorption edges, (b) what is adsorption behavior of a particular metal ion in presence of second metal ion, (c) what is the influence of the second metal ion on the adsorption edge of the first metal ion, (d) what is the probable mechanism of adsorption process, (e) how does



FIGURE 1: XRD spectra of acid washed pyrite samples.

adsorption isotherm vary in the process of adsorption of different metal ions, (f) what is the influence of pH on the fraction surface coverage of a particular metal ion in presence of any second metal ion, (g) what are the thermodynamic parameters that control the adsorption process, and finally (h) whether purification of metal ion from a multimetal ionic system is possible or not?

#### 2. Experimental

2.1. Pyrite Sample. A rock sample containing natural pyrite was collected from the Barapani Area ( $25^{\circ}36'-25^{\circ}42'$ N and  $91^{\circ}55'$ E) of East Khasi Hills, Meghalaya, India, where sulphide mineralization is extensive. The golden yellow layer of pyrite was carefully removed from the rock. The pyrite sample was crushed, physically fractionized to <150  $\mu$ m, and kept in 1 M HCl for one day. The solid materials were filtered, washed thoroughly with double distilled water followed by methanol to dry, and stored in air tight polypropylene bottle. The acid washed sample contains less than 9% impurity.

The sample thus prepared was subjected to X-ray diffraction analysis in a JDX-11, P3A, and JEOL X-ray diffractometer using Fe filtered Cu- $K_{\infty}$  radiation and presented in Figure 1.

2.2. Adsorption of Individual Metal Ion. In this study six metal ions, namely,  $Co^{2+}$ ,  $Ni^{2+}$ ,  $Cu^{2+}$ ,  $Zn^{2+}$ ,  $Ag^{2+}$ , and  $Pb^{2+}$  have been chosen. Analytical grade  $NO_3^{-}$  salts of Co, Ni, Cu, Zn, Ag, and Pb were used. A stock solution of 1000 ppm was prepared for each metal ion in double distilled water. 150 mL of solution for each of the elements with concentration of 150 ppm (prepared from the stock solution) was equilibrated for half an hour with 0.1 g powdered acid washed dry pyrite sample. The ionic strength was adjusted to 0.1 M using NaNO<sub>3</sub> solution with occasional shaking. The initial pH of the solution was adjusted to 4.0 using 0.01 M

 $HNO_3$ . An aliquot of 10 mL from the mother solution at the initial pH was removed after 30 min and then immediately flittered. The filtrate and the washing were stored in air tight polypropylene container. The process was repeated up to pH 10.0 by decreasing pH using 0.01 M NaOH solution.

2.3. Adsorption in Binary Systems. For competitive adsorption, metal ions of equal concentrations (75 mL of 150 ppm) of two different metal ions were taken and treated with 0.1 g acid washed dry pyrite sample. The experimental conditions and procedure are the same as for individual metal ion adsorption. All the experiments were conducted under isothermal condition at 28°C.

2.4. Determination of Metal. For metal analysis of the aliquots,  $100 \,\mu\text{L}$  concentrated HNO<sub>3</sub> and one drop of 5% K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> solution were added to each aliquot following Baruah [22]. The concentration of metal in each aliquot was measured using Perkin Elmer (Model 2380) atomic absorption spectrophotometer (AAS) equipped with mercury-hydride system. Blank runs were simultaneously carried out to understand the accuracy and precision.

#### 3. Adsorption Isotherm

Assuming the adsorption process to be chemisorptions, in this investigation, the Langmuir adsorption equation [35] has been used to model the experimentally obtained adsorption data which is based on the assumption that, the solid surface contains equivalent number of adsorption sites which can hold adsorption species and cannot proceed beyond monolayer coverage [36]. The Langmuir equation can be written as follows:

$$\frac{\Gamma}{\Gamma_{\alpha}} = \frac{K_{aj}}{1 + K_{aj}},\tag{1}$$

where  $\Gamma$  is adsorption density in mole Kg<sup>-1</sup> and  $r_{\infty}$  in correspondence to a saturated coordination site type on monolayer coverage,  $a_j$  is the activity of the *j*th species at the solid-solution interface, and K is a constant which signifies quantifying the affinity of the adsorbate for the adsorbent or adsorption coefficient. Further, the ratio of the fraction of the molecules which collide with empty adsorbent surface and adsorbed there and the rate of desorption of molecules from a saturated surface can be related to K. Equation (1) can be rearranged to

$$\frac{1}{\Gamma} = \left(\frac{1}{\Gamma_{\alpha} K_{aj}}\right) + \frac{1}{\Gamma_{\alpha}}.$$
(2)

Equation (2) describes a straight line when  $\Gamma^{-1}$  is plotted against  $a_j^{-1}$ . In aqueous solution, where the concentration of the concerned species is very low, the activity  $(a_j)$  of the ions can be replaced by their concentration  $(C_j)$  in the bulk solution at a particular pH and temperature. Therefore, (2) takes the form

$$\frac{1}{\Gamma} = \left(\frac{1}{\Gamma_{\alpha} K C_j}\right) + \frac{1}{\Gamma_{\alpha}}.$$
(3)

The values of  $r_{\infty}$  and K were evaluated graphically by plotting  $\Gamma^{-1}$  against  $C_j^{-1}$ . Use of  $C_j$  in (3) instead of  $a_j$  in the adsorption isotherm equation (2) does not alter the usefulness of the later equation in aqueous system.

#### 4. Results and Discussion

4.1. pH Dependant of Adsorption. In aqueous phase, the individual pH dependence for adsorption of Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Ag<sup>2+</sup>, and Pb<sup>2+</sup> ions on pyrite surface in the pH range 4-10 has been calculated and their distribution patterns against pH at a temperature of 28°C have been shown in Figures 2 to 7, respectively. For every solution, there is a critical pH range or adsorption edge at which the adsorption increases drastically and this abnormal pH dependence of metal ion adsorption has been found in this investigation as well. The adsorption edges for the metal ions have been found to be pH 6.8 for Ni<sup>2+</sup>, 7.5 for Zn<sup>2+</sup>, 5.5 for Pb<sup>2+</sup>, 8.9 for Ag<sup>+</sup>, 5.8 for  $Cu^{2+}$ , and 8.6 for  $Co^{2+}$  ions. The adsorption edge for sulphide has revealed that the critical pH range varies with the nature of metal ions. It is understood that the adsorption edge is more likely to be a function of the nature of the metal ion rather than the nature of adsorbent in adsorption processes. The studied metal ions evidenced increasing trend of adsorption edges in the order of  $Pb^{2+}$  <  $Cu^{2+}$  <  $Ni^{2+}$  <  $Zn^{2+}$  <  $Co^{2+}$  <  $Ag^+$ . It is apparent from Figures 2 to 7 that, for each metal ion, there is a critical pH range at which maximum adsorption of the metal ion occurs on the pyrite surface. Graphically these pH values have been calculated accordingly: 9.3 for Ni<sup>2+</sup>, 8.0 for Zn<sup>2+</sup>, 7.0 for Pb<sup>2+</sup>, 10.0 for  $Ag^+$ , 7.0 for  $Cu^{2+}$ , and 9.7 for  $Co^{2+}$  ions (Figures 2 to 7).

The adsorption edge of a particular metal ion may or may not vary if a second metal ion is present in a solution. Table 1 shows the adsorption edges of the metal ions under study in presence of a second metal ion. This reveals that, for Ni<sup>2+</sup> ion, the adsorption edge will decrease if the Cu<sup>2+</sup> ion is present in the solution whereas, in presence of each of the metal ions, the value increases and the increasing order is  $Cu^{2+} < none < Zn^{2+} = Co^{2+} < Pb^{2+} < Ag^+$ . In case of  $Zn^{2+}$ ion, the adsorption edge of it decreases when each of the Ni<sup>2+</sup>,  $Pb^{2+}$ ,  $Co^{2+}$ ,  $Cu^{2+}$ , or  $Ag^+$  ion is present in the solution. The increasing order is  $Co^{2+} = Ag^+ < Cu^{2+} < Ni^{2+} = Pb^{2+} < none$ . For the adsorption of  $Pb^{2+}$  ion, the presence of second metal ion increases the adsorption edge for the adsorption of it. The Increasing order is none  $\langle Zn^{2+} \langle Ag^+ = Co^{2+} \langle Ni^{2+} \langle Cu^{2+} \rangle$ . However, the magnitude of increase in adsorption of Pb<sup>2+</sup> ion in presence of any second metal ion is almost equal. A noteworthy feature of Ag<sup>+</sup> ion adsorption edge in presence of a second metal ion is that two adsorption edges are observed. The first adsorption edge in presence of a second metal ion is always lower than that of individual  $\mathrm{Ag}^{+}$  ion adsorption edge and the order is  $Cu^{2+} < Ni^{2+} < Zn^{2+}$  Pb<sup>2+</sup> = Co<sup>2+</sup> < none. The second adsorption edge of Ag<sup>+</sup> ion adsorption in the presence of Ni<sup>2+</sup> or Zn<sup>2+</sup> increases while that decreases in presence of  $Pb^{2+}$ ,  $Cu^{2+}$ , or  $Co^{2+}$  ion. The increasing order is  $\hat{Pb}^{2+} < Cu^{2+}$ = Co<sup>2+</sup> < none < Ni<sup>2+</sup> < Zn<sup>2+</sup>. For Cu<sup>2+</sup> ion, presence of Ni<sup>2+</sup> ion has no impact on shifting the adsorption edge whereas it



FIGURE 2: Percent adsorption versus pH for  $Ni^{2+}$  adsorbed on pyrite: in presence of (a) none; (b)  $Zn^{2+}$ ; (c)  $Pb^{2+}$ ; (d)  $Ag^+$ ; (e)  $Cu^{2+}$ , and (f)  $Co^{2+}$  ions.

is marginal in the presence of other second metal ions. The increasing order is  $Pb^{2+} = Ag^+ = Co^{2+} < Zn^{2+} < Ni^{2+} =$  none. Like  $Ag^+$  ion adsorption, in case of  $Co^{2+}$  ion, two adsorption edges are evident from Table 1 with a second metal ion,  $Pb^{2+}$ ,  $Ag^+$ , or  $Cu^{2+}$ . In the presence of all second metal ions, the first adsorption edge is lower than single  $Co^{2+}$  ion adsorption edge. The increasing order of first adsorption edge is  $Cu^2 < Ag^+ < Pb^{2+} < Zn^{2+} < Ni^{2+} <$  none.

An understanding of the pH dependence of adsorption of metal ions can be correlated with the behavior of the metal ions in aqueous solution. Due to hydration, a metal ion forms an aqua complex when a salt is dissolved in water [37]:

$$M^{n+} + mH_2O = [M(H_2O)_m]^{n+}$$
(4)

The formation of the aqua complex is pH dependent and the coordinated aqua molecules may vary with the nature of



FIGURE 3: Percent adsorption versus pH for  $Zn^{2+}$  adsorbed on pyrite: in presence of (a) none; (b)  $Zn^{2+}$ ; (c)  $Pb^{2+}$ ; (d)  $Ag^+$ ; (e)  $Cu^{2+}$ , and (f)  $Co^{2+}$  ions.

the metal ion. The reaction of an aqua complex in aqueous solution is the loss of a proton to give hydroxo aqua complex [37, 38]:

$$\left[M(H_2O)_m\right]^{n+} = \left[M(OH)(H_2O)_{m-1}\right]^{(n-1)+} + H^+$$
(5)

The first hydrolysis constant  $pK_1$  of an aqua metal ion is dependent on the ionic charge and radius of the metal ion

[37]. The  $pK_1$  values of the aqua metal ions, studied here at 25°C follow, the order:

$$Pb^{2+}(7.8) < Cu^{2+}(8.0) < Zn^{2+}(8.96) < Co^{2+}(9.85)$$
  
 $< Ni^{2+}(9.86) < Ag^{+}(11.1)$  (6)



FIGURE 4: Percent adsorption versus pH for  $Pb^{2+}$  adsorbed on pyrite: in presence of (a) none; (b)  $Ni^{2+}$ ; (c)  $Zn^{2+}$ ; (d)  $Ag^+$ ; (e)  $Cu^{2+}$ , and (f)  $Co^{2+}$  ions.

It is well known that hydrolysis of aqua metal ions proceeds with increase in pH and at a particular pH, there will be a considerable change of free metals ions in the solution. In the present study, the pH at which notable changes (Figure 8) of free metal ions (in absence of pyrite) are observed as follows:

$$Pb^{2+}(6.0) < Cu^{2+}(6.2) < Zn^{2+}(7.1) < Co^{2+}(8.0)$$
  
= Ni<sup>2+</sup>(8.0) < Ag<sup>+</sup>(8.2) (7)

It is interesting to note that the pH, at which these metal ions underwent extensive hydrolysis, follows an exactly



FIGURE 5: Percent adsorption versus pH for  $Ag^+$  adsorbed on pyrite: in presence of (a) none; (b)  $Ni^{2+}$ ; (c)  $Zn^{2+}$ ; (d)  $Pb^{2+}$ ; (e)  $Cu^{2+}$ , and (f)  $Co^{2+}$  ions.

similar order with those of their corresponding  $pK_1$  values [39].

Comparison of the pH stability range of various hydroxyl species of a particular metal ion and its adsorption edge may give a good indication of the type of species that are adsorbed in the vicinity of the adsorption edge. Variation of solution pH changes the nature of hydroxyl species formation [38]. For instance, at very low pH, Ni<sup>2+</sup> ion exists as such but, on increasing the pH, this free Ni<sup>2+</sup> ion changes to [Ni(OH)]<sup>+</sup>, [Ni<sub>2</sub>(OH)]<sup>3+</sup>, and [Ni<sub>4</sub>(OH)<sub>4</sub>]<sup>4+</sup> ions below pH 7 while after neutral pH, these species transform to Ni(OH)<sub>2</sub> and ultimately form [Ni(OH)<sub>6</sub>]<sup>4-</sup> in strongly alkaline medium



FIGURE 6: Percent adsorption versus pH for  $Cu^{2+}$  adsorbed on pyrite: in presence of (a) none; (b)  $Ni^{2+}$ ; (c)  $Zn^{2+}$ ; (d)  $Pb^{2+}$ ; (e)  $Ag^+$ , and (f)  $Co^{2+}$  ions.



FIGURE 7: Percent adsorption versus pH for  $Co^{2+}$  adsorbed on pyrite: in presence of (a) none; (b)  $Ni^{2+}$ ; (c)  $Zn^{2+}$ ; (d)  $Pb^{2+}$ ; (e)  $Ag^+$ , and (f)  $Cu^{2+}$  ions.

[38]. Similarly,  $Pb^{2+}$  ion changes to  $[Pb(OH)]^+$ ,  $[Pb_2(OH)]^{3+}$ ,  $[Pb_3(OH)_4]^{2+}$ ,  $[Pb_4(OH)_4]^{4+}$ , and  $[Pb_6(OH)_8]^{4+}$  up to pH 7 beyond which  $Pb(OH)_2$  is formed which finally transforms to plumbites with the progress of pH [39]. Observation of an

adsorption edge of pH 6.8 for Ni<sup>2+</sup> and pH 5.5 for Pb<sup>2+</sup> ions indicates the adsorption of  $[Ni_4(OH)_4]^{4+}$  and  $[Pb_3(OH)_4]^{2+}$  as well as  $[Pb_4(OH)_4]^{4+}$  ions, respectively, on the pyrite surface. Therefore, it can be strongly recommended that metal

TABLE 1: Adsorption edge  $(pH_{50})$  of metal ions in absence and presence of a second metal ion and their correlation coefficients in presence of a second metal ion.

| Metal ion        | In presence of   | PH <sub>50</sub> | Correlation coefficient |
|------------------|------------------|------------------|-------------------------|
|                  | None             | 6.8              | _                       |
|                  | Zn <sup>2+</sup> | 7.1              | 0.959                   |
| Ni <sup>2+</sup> | Pb <sup>2+</sup> | 7.6              | 0.969                   |
| 111              | $Ag^+$           | 8.5              | 0.964                   |
|                  | Cu <sup>2+</sup> | 6.7              | 0.962                   |
|                  | Co <sup>2+</sup> | 7.1              | 0.960                   |
|                  | None             | 7.5              | _                       |
|                  | Ni <sup>2+</sup> | 6.9              | 0.903                   |
| $7n^{2+}$        | Pb <sup>2+</sup> | 6.9              | 0.919                   |
| ZII              | $Ag^+$           | 6.6              | 0.889                   |
|                  | Cu <sup>2+</sup> | 6.8              | 0.921                   |
|                  | Co <sup>2+</sup> | 6.6              | 0.904                   |
|                  | None             | 5.5              | _                       |
|                  | Ni <sup>2+</sup> | 6.5              | 0.499                   |
| $Db^{2+}$        | Zn <sup>2+</sup> | 6.3              | 0.901                   |
| ru               | $Ag^+$           | 6.4              | 0.797                   |
|                  | Cu <sup>2+</sup> | 6.6              | 0.774                   |
|                  | Co <sup>2+</sup> | 6.4              | 0.853                   |
|                  | None             | 8.9              | —                       |
|                  | Ni <sup>2+</sup> | 5.2, 9.1         | 0.941                   |
| $A \alpha^+$     | Zn <sup>2+</sup> | 5.9, 9.5         | 0.969                   |
| 118              | Pb <sup>2+</sup> | 6.6, 8.3         | 0.861                   |
|                  | Cu <sup>2+</sup> | 5.1, 8.6         | 0.946                   |
|                  | Co <sup>2+</sup> | 6.6, 8.6         | 0.889                   |
|                  | None             | 5.8              | —                       |
|                  | Ni <sup>2+</sup> | 5.8              | 0.868                   |
| $Cu^{2+}$        | Zn <sup>2+</sup> | 5.7              | 0.838                   |
| Cu               | Pb <sup>2+</sup> | 5.6              | 0.802                   |
|                  | $Ag^+$           | 5.6              | 0.809                   |
|                  | Co <sup>2+</sup> | 5.6              | 0.800                   |
|                  | None             | 8.6              | —                       |
|                  | Ni <sup>2+</sup> | 7.9              | 0.940                   |
| $Co^{2+}$        | Zn <sup>2+</sup> | 7.2              | 0.942                   |
| 0                | Pb <sup>2+</sup> | 6.6, 8.6         | 0.939                   |
|                  | $Ag^+$           | 6.4, 8.6         | 0.971                   |
|                  | Cu <sup>2+</sup> | 5.5, 7.8         | 0.960                   |

ions in the form of hydroxyl species have played a role in the functioning of adsorbate; however, the nature of hydroxyl species may differ depending on the pH of the medium. It is evident that the hydroxyl species mechanism would be worthwhile in understanding the adsorption process.

4.2. Chemistry of Adsorption. Although various models have been known for the adsorption processes, the model of adsorbed hydrolysed species would be appropriate to explain the adsorption mechanism. The correlation between  $pK_1$  and adsorption edge as mentioned has led us to understand that

the hydroxyl species play a dominant role for adsorption processes. Moreover, Kornicker and Morse [40] reported that the tendency of metal ions undergoing hydrolysis has appeared to be an important factor in the adsorption processes with respect to pyrite. The mechanism of adsorption on the pyrite surface  $(\cdots S)$  can be outlined as follows:

$$\cdots S + [M(OH)_m]^{(n-m)+} \longrightarrow \cdots S - [M(OH)_m]^{(n-m)+}$$
(8)

Thus it is quite reasonable to believe that the hydroxyl species act as adsorbate on the adsorbent surface and the extent of adsorption is primarily governed by the degree of hydrolysis of the aqua complex. This is because the sulphur atom of the pyrite surface has two lone pairs of electrons constituting high electron density which can function as potentially strong nucleophilic site and can coordinate with electron deficient species.

While studying adsorption processes, a clear understanding of the nature of the adsorbing species present in solution and the site of coordination on the adsorbent surface would be vital in explaining the adsorption mechanism. It has been reported that surface complexion is due to the interaction between the adsorbent functional groups and metal ions. For oxides and oxyhydroxides, it is well known that the interaction of adsorbate with these minerals occurs between oxygen donor ligands and the metal ions [41]. Therefore, it can be expected that the surface of pyrite acts as coordination sites. Sulphur is softer than oxygen [42] and hence the interaction will be stronger between sulphur coordination site of pyrite and the adsorbing metal ionic species. When pyrite is treated with a metal salt solution, in aqueous medium, the surface Fe<sup>2+</sup> ions which act as electrophilic sites on exposer to water can bind strongly with water molecules resulting in aqua complexes on the pyrite surfaces. These coordinated water molecules may release protons depending upon the pH of the medium making the pyrite surface negatively charged as well as developing oxygen donor sites:

$$\cdots S + mH_2O$$
  

$$\longrightarrow \cdots S - (H_2O)_m \longrightarrow \cdots S - [(OH) (H_2O)_{m-1}]^- + H^+$$
  

$$\longrightarrow \cdots S - [(OH)_2 (H_2O)_{m-2}]^- + H^+, \text{ and so forth.}$$
(9)

Thus the surface of pyrite has enormous hydroxyl groups. This is supported by the fact that the surfaces of  $As_2S_3$  or  $Sb_2S_3$  have excess of hydroxyl groups at pH greater than 3.5 [41] The negative charge developed on the pyrite surface is compensated by diffused counter ion layer of positively charged H<sup>+</sup> ions [41]. Electrophoretic studies of pyrite have shown that pyrite has an isoelectric point (the pH at which the net charge is zero, i.e., pH<sub>pzc</sub>) between pH 6.2 and 6.9 [30, 43]. Renders and Seward [41] reported that at pH less than isoelectric point (i.e., pH less than 2.5 to 3.5) the surfaces of  $As_2S_3$  and  $Sb_2S_3$  start to become positively charged.

From the above discussion, it can be concluded that the development of charge as well as the nature of coordination sites on the pyrite surface is pH dependent. Above the isoelectric point, the pyrite surface has an excess of negative

charge while, below it, the surface starts to develop positive charge. Therefore, the formation of oxygen donor sites on the pyrite surface can be expected above the isoelectric point. It also seems likely that the presence of a second metal ion may shift the isoelectric point.

Hydrolysis of aqua complex depends upon its  $pK_1$  value. A lower  $pK_1$  value indicates the higher degree of hydrolysis of the aqua metal ion. Its hydrolysis proceeds with decrease in pH and on neutralizing the protons; the hydrolysed species ultimately gets precipitated on the adsorbent surface thereby decreasing the concentration of the free metal ion to negligibly small amount even at very low pH.

4.3. Extent of Adsorption. The extent of hydrolysis of an aqua metal ion is also influenced by the presence of a second aqua metal ion due to common ion effect; the common ion is being the proton. In a mixture of two metal salt solutions, the aqua metal ion having lower pK1 value will tend to suppress the degree of hydrolysis of the second aqua metal ion having higher  $pK_1$  value. For instance, the  $pK_1$  value for  $Ni^{2+}$  ion is 9.86 while that of  $Zn^{2+}$  ion is 8.96 revealing that aqua  $Zn^{2+}$ ion will be hydrolysed at a lower pH to that of aqua Ni<sup>2+</sup> ion. Once aqua  $Zn^{2+}$  ions get hydrolysis, it  $(Zn^{2+})$  will suppress the hydrolysis of aqua  $Ni^{2+}$  ions because of the release of  $Ni^{2+}$  of proton and its involvement in common ion effect. This means that hydrolysed Zn<sup>2+</sup> species will preferentially be adsorbed on the pyrite surface and, therefore, the presence of Ni<sup>2+</sup> ion shifts the adsorption edge of  $Zn^{2+}$  ion to a lower pH. This principle is in concordance with our experimental results. If this principle is true, the adsorption edge of Ni<sup>2+</sup> ion should increase to a higher pH. Our experimental results strongly support it because the adsorption edge of Ni<sup>2+</sup> ion is 6.8 which increases to 7.1 in presence of  $Zn^{2+}$  ion.

A question is why the adsorption edge of a particular metal ion in presence of another metal ion is observed at a higher pH. The surface of pyrite has excess of hydroxyl groups at pH greater than 4 due to surface induced hydrolysis. This reveals that the negatively charged surface of the adsorbent can be compensated by a diffused counter ion layer made up of positively charged species which may be either free metal ion or proton. Therefore, there is a strong likelihood that, in aqueous solution, the concentration of H<sup>+</sup> in this diffused layer may be greater than that of the bulk solution because of its exceedingly high ionic mobility and the lower concentration of free metal ions on the near surface environment; the movement of the latter is being a diffusion control process. This diffused counter ion layer made up of positively charged species would have an adverse effect on adsorption, prohibiting accumulation of metal ion species of pyrite surface. While performing the experiment at a particular pH and standing for some time, there appeared relative decrease of pH (which was subsequently adjusted by adding NaOH solution). This suggests an increase in the extent of hydrolysis of the aqua complex releasing proton. This could be the reason for the observed increase in the adsorption edge as well as the pH of maximum adsorption at a higher pH in a binary system (Table 1).

Another interesting observation is that the presence of any second metal ion increases the adsorption edge of  $Pb^{2+}$ ion to a higher pH. The pK<sub>1</sub> value of Pb<sup>2+</sup> ion is the lowest among the studied metal ions; therefore, its hydrolysis is quite rapid at the beginning pH (pH 4). The hydrolysed species undergo polymerization thereby slowing down the adsorption process causing a shift of adsorption edge (to a higher pH) in presence of any second metal ion.

The adsorption edge for the adsorption of Ag<sup>+</sup> ion on pyrite surface is the highest which is in accordance with the highest pK1 value among the investigated metal ions. Due to the highest  $pK_1$  value, aqua  $Ag^+$  ion will be hydrolysed at quite high pH. But the contrasting result is that two adsorption edges are observed when Ag<sup>+</sup> ion is contaminated with a second metal ion, (a) at a lower pH than the individual Ag<sup>+</sup> ion adsorption edge and (b) in the vicinity of the individual adsorption edge. This unusual behavior of Ag<sup>+</sup> ion adsorption demands the need of some other type of mechanisms that might be operating in the system for the observance of first adsorption edge. Since the pK<sub>1</sub> value of any second metal ion is lower than that of Ag<sup>+</sup> ion, it is revealed that the second metal ion will hydrolyse at a lower pH and will be adsorbed on the pyrite surface as hydrolysed species. However, at lower pH, the greater amounts of Ag<sup>+</sup> ion will remain as aqua metal ion which is susceptible to adsorb on the pyrite surface already covered by the hydrolysed species of the second metal ion, through physiosorption for electroneutrality requirements. It is also equally important to consider the affinity of these metal ions towards the pyrite surface. With Ag<sup>+</sup> ion being a soft acid [33], it will preferentially react with sulphur donor sites (of pyrite) due to soft-soft interaction. Once all the active sites on the adsorbent surface are covered by Ag<sup>+</sup> ions and other hydrolysed species of the second metal ion, the observance of the second adsorption edge at higher pH will not be through physiosorption rather than chemisorptions of the hydrolysed Ag<sup>+</sup> ions. Another factor that might have relevance in this context is the affinity of the adsorption sites. The adsorption sites which have higher affinity for a particular adsorbate may not be the same for other adsorbate species. It is quit justified to believe that those adsorption sites which have affinity for Ag<sup>+</sup> ion could have adsorbed at relatively lower pH resulting in the observance of the first adsorption edge. Similar type of mechanism might have been operating in the absorbance of Co<sup>2+</sup> ion where two adsorption edges are observed in binary systems.

As the experiment is performed with nitrate salts, therefore, a question arises whether nitrate ion has any influence on deactivating the pyrite surface. It has already been mentioned that there is abundance of hydroxyl groups on the pyrite surface even at pH 4. Once the hydroxyl group is present on the pyrite surface, due to electrostatic repulsion, it will possibly drive away the nitrate ions from the vicinity of the pyrite surface. It is also equally important to consider the fact that at low pH adsorbate in the form of positively charged hydroxyl species is adsorbed on the pyrite surface and, therefore, nitrate ion cannot enter the coordination sphere



FIGURE 8: Percent adsorption versus pH in absence of pyrite: (a)  $Ni^{2+}$ ; (b)  $Zn^{2+}$ ; (c)  $Pb^{2+}$ ; (d)  $Ag^{+}$ ; (e)  $Cu^{2+}$ , and (f)  $Co^{2+}$  ions.

of the hydroxyl species due to saturation of the coordination sites. As a result, there will be a negligible impact of the nitrate ions in both leaching of trace elements and oxidation of pyrite surface. 4.4. Monolayer Coverage. The constants ( $\Gamma_{\alpha}$  and K) derived from (3) are given in Table 2. The values of  $\Gamma_{\alpha}$  are given in mole Kg<sup>-1</sup> because in this unit  $\Gamma_{\alpha}$  is not dependent on the true surface area of the adsorbent.

| Mataliana        | p                 | H 4            | pl                | H 5            | p]                | H 6            | pl                | H 7            | pl                | H 8            | р                 | H 9            | р                 | H 10           |
|------------------|-------------------|----------------|-------------------|----------------|-------------------|----------------|-------------------|----------------|-------------------|----------------|-------------------|----------------|-------------------|----------------|
| Ivietal lolis    | $\Gamma_{\infty}$ | $K\times 10^5$ |
| Ni <sup>2+</sup> | 0.0384            | 0.2141         | 0.0384            | 0.2429         | 0.0388            | 0.0355         | 0.0390            | 0.8325         | 0.0391            | 3.4894         | 0.0399            | 715.8965       | 0.0400            | 2213.7522      |
| $Zn^{2+}$        | 0.0365            | 0.0445         | 0.0370            | 0.0555         | 0.0372            | 0.0627         | 0.0372            | 1.0392         | ND                | ND             | ND                | ND             | ND                | ND             |
| Pb <sup>2+</sup> | 0.0395            | 5.0620         | 0.0397            | 5.8835         | 0.0396            | 21.8618        | ND                | ND             | ND                | ND             | ND                | ND             | ND                | ND             |
| $Ag^+$           | 0.0387            | 0.4928         | 0.0390            | 0.5511         | 0.0386            | 3.1112         | 0.0394            | 1.4277         | 0.0390            | 1.5385         | ND                | ND             | ND                | ND             |
| Cu <sup>2+</sup> | 0.0386            | 0.2230         | 0.0386            | 0.3803         | 0.0394            | 46.5077        | ND                | ND             | ND                | ND             | ND                | ND             | ND                | ND             |
| Co <sup>2+</sup> | 0.0383            | 0.2168         | 0.0383            | 0.2023         | 0.0384            | 0.2606         | 0.0388            | 0.8589         | 0.0384            | 4.3945         | ND                | ND             | ND                | ND             |

ND: not determinable.

The monolayer coverage  $(\Gamma_{\alpha})$  for each of the metal ions in presence of a second metal ion as a function pH shows some interesting results (Table 2). The monolayer coverage for Ni<sup>2+</sup> ion adsorption on pyrite surface increases marginally with the increase in pH. This reveals that the presence of the second metal ion has no profound influence on the adsorption behavior of Ni<sup>2+</sup> ion. In case of Zn<sup>2+</sup> ion, the monolayer coverage is the lowest amongst the other metal ions studied here. An interesting feature of the Zn<sup>2+</sup> ion adsorption is that the  $\Gamma_{\alpha}$  value increases from pH 4 to 5, beyond this it is quite constant signifying pH independence of adsorption on the pyrite surface. Contrary to Zn<sup>2+</sup> ion adsorption, the adsorption of Pb<sup>2+</sup> ion is the highest among all the metal ions considered here. Negligible variation of  $\Gamma_{\alpha}$  further suggests the pH independence of Pb<sup>2+</sup> ion adsorption on pyrite surface in presence of second metal ion. However a significant observation is notified while studying the adsorption isotherm of Ag<sup>+</sup> ion in presence of any second metal ion; that is, the monolayer coverage initially increases from pH 4 to 5, then declines from pH 5 to 6, again increases to pH 7, and finally decreases. The zigzag pattern for Ag<sup>+</sup> ion adsorption reveals that the adsorption behavior of this metal ion in presence of second metal ion is highly influenced by pH. In presence of second metal ion, the monolayer coverage of Cu<sup>2+</sup> ion on pyrite surface is almost the same between pH 4 and 5 while, above pH 5, it increases to a considerable extent. The extent of adsorption for Co<sup>2+</sup> ion varies slightly in the initial pH (pH 4 to 6). However, the monolayer coverage increases from pH 6 to 8 and finally decreases.

The monolayer coverage of a particular metal ion on pyrite surface indicates the complete saturation of coordination sites. It has been reported that surface complexion is due to the coordination of adsorbate species with the adsorbent donor sites. The pyrite surface has both oxygen (in aqueous phase) and sulphur coordination sites that could bind metal ion leading to adsorption. The highest monolayer coverage of Pb<sup>2+</sup> ion on pyrite surface can be accounted for the fact that this ion has a strong affinity for both oxygen and sulphur donor ligands. On the contrary, the lowest coverage of Zn<sup>2+</sup> ion on pyrite surface is due to its preferential binding with oxygen donor ligands at pH 4. However, with the increase in pH from 4 to 7, a continuous increase of monolayer coverage can be attributed to increase the affinity of Zn<sup>2+</sup> ion towards oxygen and sulphur donor ligands. This is strongly supported by the fact that in qualitative analysis,  $Zn^{2+}$  ion is not precipitated as ZnS in acidic medium while, at neutral to basic medium, it could be precipitated.

The question why there is a zigzag trend in the monolayer coverage is observed specially with the adsorbate,  $Ag^+$  ion. The pyrite sample does have heterogeneous surface sites [25] with specific adsorption affinities and these sites could be activated to different strength on varying the pH. This resulted in the change of surface charge, the nature of the coordination site, and the activity of the coordination site as well as the nature of the adsorbent. When chemisorptions occur on a nonuniform surface, the adsorbed species first cover sites having higher adsorption coefficient (K). It is also not unlikely that Ag<sup>+</sup> ion can form silver sulphide due to soft-soft interaction on pyrite surface forming a secondary layer which can behave as an adsorbing surface. However the activity of this secondary surface may be different with respect to solution pH. This is strongly supported by the fact that, while studying distribution of silver in pore water, it has been reported that silver forms silver sulphide on the pyrite surface [23]. It is also justified to consider the process of physical adsorption involving dipole-dipole interaction between the monolayer species and the adsorbate. This could be the reason for the abnormal trend observed with respect to Ag<sup>+</sup> ion adsorption (Table 2).

The increase or decrease of monolayer coverage can be correlated with the affinity of the adsorbate towards pyrite surface or adsorption coefficient (K). From Table 2, it is quite evident that when the affinity of the adsorbate (nature of which is highly pH dependent) decreases, there is decrease in the monolayer coverage. However, an unusual behavior is observed with the adsorbate,  $Ag^+$  ion at pH 6. At this pH, although the affinity of the adsorbate increases, the monolayer covers are the lowest. Silver ion being the monovalent metal ion studied here shows some unusual behavior as is evident from the observance of two adsorption edges. The first adsorption edge is observed in the pH range 5.1-6.6 in presence of any second metal ion. This reveals a decrease in monolayer coverage around pH 6. However, it can be expected that the monolayer coverage will be dominant in the vicinity of the second adsorption edge because the pK<sub>1</sub> value (11.1) and the solubility product of AgOH ( $2.0 \times 10^{-8}$ ) are exceptionally high among all the metal ions studied here.

Although the monolayer coverage depicts the competitive nature of adsorption of a pair of metal ions the correlation

40

39.75

39.5

39.25

39

38.75

38.5

3

4 5

FIGURE 9: Variation of  $\Gamma$  against pH for Ni<sup>2+</sup> ion adsorption on pyrite surfaces: in presence of none ( $\blacklozenge$ ), Zn<sup>2+</sup>( $\blacksquare$ ), Pb<sup>2+</sup> ( $\blacklozenge$ ), Ag<sup>+</sup>( $\bigtriangleup$ ), Cu<sup>2+</sup> ( $\Omega$ ), and Co<sup>2+</sup>( $\Box$ ).

pН

6 7 8

Ni

9 10 11

between fraction surface site coverage ( $\Gamma$ ) and pH as well as computed correlation coefficients (CC) would give a precise understanding of such adsorption process. A high CC indicates retardation of a particular metal ion adsorption in presence of a second metal ion and vice versa. Figure 9 shows the variation of  $\Gamma$  against pH for Ni<sup>2+</sup> ion adsorption in presence of any metal ion. Major variation of fraction surface coverage is observed at pH 8. At this pH presence of  $Cu^{2+}$  (CC = 0.962) or  $Zn^{2+}$  (CC = 0.960) in enhances while presence of Pb<sup>2+</sup> (CC = 0.969) or Ag<sup>+</sup> (CC = 0.964) ion retards the adsorption of Ni<sup>2+</sup> ion; the presence of Co<sup>2+</sup> (CC = 0.960) ion has negligible impact. In case of  $Zn^{2+}$  ion adsorption (Figure 10), significant variation of  $\Gamma$  is observed at pH 7 where the presence of Ni<sup>2+</sup> (CC = 0.903), pb<sup>2+</sup> (CC = 0.919), Ag<sup>+</sup> (CC = 0.889), Cu<sup>2+</sup> (CC = 0.921), or Co<sup>2+</sup> (CC = 0.904) ion enhances the adsorption. An interesting point to note is that the fractional surface coverage of pyrite with Zn<sup>2+</sup> ion is the highest in the presence of  $Ag^+$  whereas the CC is the lowest. This is in accordance with the highest pK1 value for aqua Ag<sup>+</sup> ion. For Pb<sup>2+</sup> ion, major variation in surface coverage is observed at pH 6 (Figure 11) where the presence of  $Ag^+$  (CC = 0.797),  $Cu^{2+}$  (CC = 0.774), or  $Co^+$  (CC = 0.853) enhances whereas the presence of  $Zn^{2+}$  (CC = 0.901) or  $Ni^{2+}$  (CC = 0.914) inhibits the adsorption. Like monolayer coverage (Table 2), a zigzag trend of curve is evident for Ag<sup>+</sup> ion adsorption on pyrite surface (i.e.,  $\Gamma$ ), in the pH range 6– 9 (Figure 12) where the presence of  $Ni^{2+}$  (CC = 0.941),  $Zn^{2+}$  $(CC = 0.969), Pb^+ (CC = 0.861), Cu^{2+} (CC = 0.946), or Co^{2+}$ (CC = 0.889) ion retards the adsorption. In case of  $Cu^{2+}$ ion adsorption, significant variation of  $\Gamma$  is observed at pH 6 (Figure 13). At this pH, presence of  $Co^{2+}$  (CC = 0.800), Pb<sup>2+</sup>  $(CC = 0.802), Ag^+ (CC = 0.809), Zn^{2+} (CC = 0.837), or Ni^{2+}$ 



FIGURE 10: Variation of  $\Gamma$  against pH for  $Zn^{2+}$  ion adsorption on pyrite surfaces: in presence of none ( $\blacklozenge$ ), Ni<sup>2+</sup> ( $\blacksquare$ ), Pb<sup>2+</sup> ( $\blacklozenge$ ), Ag<sup>+</sup> ( $\bigtriangleup$ ), Cu<sup>2+</sup> ( $\Omega$ ), and Co<sup>2+</sup> ( $\square$ ).



FIGURE 11: Variation of  $\Gamma$  against pH for Pb<sup>2+</sup> ion adsorption on pyrite surfaces: in presence of none ( $\blacklozenge$ ), Ni<sup>2+</sup> ( $\blacksquare$ ), Zn<sup>2+</sup> ( $\blacklozenge$ ), Ag<sup>+</sup> ( $\bigtriangleup$ ), Cu<sup>2+</sup> ( $\Omega$ ), and Co<sup>2+</sup> ( $\square$ ).

(CC = 0.868) ion enhances the fractional surface coverage of pyrite with Cu<sup>2+</sup> ion. For Co<sup>2+</sup> ion, major variation of fractional surface coverage is observed in the pH range 6–8 (Figure 14). In the presence of Pb<sup>2+</sup> (CC = 0.939), Ag<sup>+</sup> (CC = 0.971), or Cu<sup>2+</sup> (CC = 0.960), the adsorption of Co<sup>2+</sup> ion shows a zigzag curve (Figure 14) which strongly supports the observation of two adsorption edges with these metal ions (Table 1) whereas curves of continuous increase in  $\Gamma$  against



FIGURE 12: Variation of  $\Gamma$  against pH for Ag<sup>+</sup> ion adsorption on pyrite surfaces: in presence of none ( $\blacklozenge$ ), Ni<sup>2+</sup> ( $\blacksquare$ ), Zn<sup>2+</sup> ( $\blacklozenge$ ), Pb<sup>2+</sup> ( $\triangle$ ), Cu<sup>2+</sup> ( $\Omega$ ), and Co<sup>2+</sup> ( $\Box$ ).



FIGURE 13: Variation of  $\Gamma$  against pH for Cu<sup>2+</sup> ion adsorption on pyrite surfaces: in presence of none ( $\blacklozenge$ ), Ni<sup>2+</sup> ( $\blacksquare$ ), Zn<sup>2+</sup> ( $\blacklozenge$ ), Pb<sup>2+</sup> ( $\bigtriangleup$ ), Ag<sup>+</sup> ( $\Omega$ ), and Co<sup>2+</sup> ( $\square$ ).

pH are observed with Ni<sup>2+</sup> (CC = 0.940) and Zn<sup>2+</sup> (CC = 0.942).

It is evident that, in majority of cases, a high CC (in the range of a particular metal ion in a binary system) predicts the retardation of fractional surface site coverage of that metal ion on pyrite surface. However, the magnitude of the CC varies with respect to the nature of the metal ion. For instance, the CC for Ni<sup>2+</sup> ion adsorption in presence of any second metal



FIGURE 14: Variation of  $\Gamma$  against pH for Co<sup>2+</sup> ion adsorption on pyrite surfaces: in presence of none ( $\blacklozenge$ ), Ni<sup>2+</sup> ( $\blacksquare$ ), Zn<sup>2+</sup> ( $\blacklozenge$ ), Pb<sup>2+</sup> ( $\bigtriangleup$ ), Ag<sup>+</sup> ( $\Omega$ ), and Cu<sup>2+</sup> ( $\square$ ).

ion is in the range 0.960-0.969 whereas, for Cu<sup>2+</sup> ion, the range of CC is 0.800-0.868. It is apparent that computed CC is an important parameter to understand the extent of fractional surface coverage of a metal ion on the adsorbent surface in a binary system.

4.5. Adsorption Thermodynamics. Study of adsorption thermodynamics can provide significant insight into the nature of adsorption of metal ion on pyrite surface. The adsorptiondesorption process or more precisely the adsorption equilibrium can be described by the following equation:

$$\cdots S + M \underset{\text{Desorption}}{\overset{\text{Adsorption}}{\leftrightarrows}} \cdots S - M \tag{10}$$

where M is the metal ionic species. The potential energy of adsorption of metal ion on pyrite surface can be calculated by (11) known as the reaction isotherm [43]:

$$\Delta G = RT \ln K_c \tag{11}$$

Here  $\Delta G$  is Gibb's free energy of adsorption at equilibrium, R is the universal gas constant, T is the temperature in Kelvin, and  $K_c$  is the equilibrium constant. Every chemical process is accompanied by a chemical equilibrium. In adsorption process the position of the equilibrium may be different at different pH with a specific equilibrium constant. The equilibrium constant at a particular pH can be determined by considering the fact that the activities of the concerned species in a very dilute solution may be replaced by their corresponding equilibrium concentrations.

For the determination of the entropy of adsorption at equilibrium ( $\Delta S$ ) in the bulk [43] (12) is applied here:

$$\Delta S = -nR\Sigma X_i \ln X_i, \tag{12}$$

where *n* is the total mole numbers of the system excluding the mole numbers of solvent (water) because of bulk volume and  $X_i$  is the mole fraction of the *i*th species at equilibrium.

Once the values of  $\Delta G$  and  $\Delta S$  are known, the heat of adsorption ( $\Delta H$ ) of equilibrium can be calculated at a temperature *T* (301.2 K) by using the following Gibbs-Helmholtz equation:

$$\Delta G = \Delta H - T \Delta S \tag{13}$$

Thermodynamics parameters, namely, of  $\Delta G$  and  $\Delta S$ , are known; the heat of adsorption ( $\Delta H$ ) for individual metal ion adsorption at equilibrium is represented in Table 3; in all cases, pH range 4-8 is considered because around pH 8 the adsorption is nearing completion and the concept of equilibrium is not applicable above pH 8. The negative value of  $\Delta G$  suggests the spontaneous nature of adsorption. Since the change of potential energy of adsorption is calculated at equilibrium, a change in its magnitude with respect to the change of solution pH means the change of the position of equilibrium adsorption which is the actual representation of  $\Delta G$  in the present context. For instance, the  $\Delta G$  value for Ni<sup>2+</sup> ion adsorption at pH 4 is  $-158.95 \times 10^2$  J mol<sup>-1</sup> whereas, at pH 5, this value changes to  $-83.63 \times 10^2 \text{ J mol}^{-1}$  suggesting the shifting of the position of equilibrium to the left; that is, the desorption process is more predominant over the adsorption at equilibrium. This is strongly supported by our observation as in Figure 9. Therefore, an increase in the value of  $\Delta G$ indicates more desorption relative to adsorption and vice versa. It is evident from Table 3 that the magnitude of  $\Delta G$  is more likely to be a function of the nature of metal ion and the solution pH.

In a system containing two metal ions, the  $\Delta G$  values calculated at equilibrium for each metal ion have been found to be higher (Table 4) in most cases relative to its individual metal ion adsorption (Table 3) in the pH range 4–8. The higher value of  $\Delta G$  for each metal ion in a binary system suggests the less spontaneity of the respective metal ion adsorption. This strongly reveals that, in a binary system, both the metal ions have tendency for adsorption on pyrite surface. Thus in such a system, the adsorption of metal ions is a thermodynamically controlled process.

Entropies of adsorption ( $\Delta S$ ) at equilibrium of metal ions in bulk with pyrite surface shown in (Table 3) are all positive signifying (a) the degree of randomness of the bulk system and (b) the feasibility of the adsorption process. An increase in the value of  $\Delta S$  represents the decrease of adsorption because the decrease in adsorption makes the system more chaos by the removal of adsorbed metal ions to the bulk aqueous phase. As a result, there would be an increase of disorderness of the system in the bulk. The low positive value of  $\Delta S$  reflects the greater extent of adsorption resulting in increase of orderness because of well-defined orientation of the adsorbed metal ionic species on the pyrite surface. Low temperature might have also contributed to the low positive value of  $\Delta S$ , calculated in the bulk equilibrium, in all cases because of low collision frequency.

The increase in randomness in a binary system as revealed by the increase in value of  $\Delta S$  (Table 4) relative to their individual values (Table 3) attributes decrease in adsorption of a particular metal ion because of limited surface site concentration of pyrite. Alternately, this proves that both the metal ions competitive for their preferential adsorption on the pyrite surface.

The  $\Delta H$  values evaluated at equilibrium adsorption for all the individual metal ions (Table 3) as well as metal ions in a binary system (Table 4) are all negative. The negative value of  $\Delta H$  represents the exothermic nature of adsorption. This is supported by the fact that adsorption is an exothermic process. The exothermicity for a particular metal ion adsorption further decreases in most cases when two metal ions are present together in a system. The decrease in the value of  $\Delta H$  in such a system indicates decrease in adsorption of a particular metal ion. The occurrence of adsorption of such an exothermic process can be accounted for by gaining energy from the collision suffered by the species present in the bulk as well as with the pyrite surface. According to Le Chatellier's principle [44], the increase in temperature for an exothermic process shifts the position of equilibrium to the right, that is, resultant. Therefore, greater adsorption of metal ions on pyrite surface may be expected if the temperature is low even at low pH. High temperature will certainly accelerate the process of desorption; that is, equilibrium (10) will shift to the left because, in multilayer adsorption processes, the bonding nature between adsorbate and adsorbent is very weak, for example, Van der Waal's type. Thus it is evident that adsorption of metal ions on pyrite surface is an exothermic process and is due to the spontaneous nature of the process at low temperature.

#### 5. Conclusion

The noteworthy features of this investigation are as follows.

- (1) Although equal concentration of each individual metal ion was added to pyrite sample, the pH of adsorption (adsorption edge) for them is different suggesting that the magnitude of adsorption is more likely to be a function of the nature of the metal ion. The calculated adsorption edge for different metal ions follows the increasing order:  $Pb^{2+} < Cu^{2+} < Ni^{2+} < Zn^{2+} < Co^{2+} < Ag^{2+}$ .
- (2) The magnitude of adsorption of a metal ion varies in presence of a second metal ion. In such a system, the adsorption edge of a particular metal ion either increases or decreases. However, with Ag<sup>+</sup> and Co<sup>2+</sup> ions, two distinct adsorption edges have been found in most cases.
- (3) The mechanism of adsorption of metal ion suggested here involves the hydroxyl species formation. However, discriminatory results in some cases have shown that some other types of mechanism such as physiosorption might have been involved.
- (4) Although the Langmuir isotherm fits experimental data on chemisorptions quite well, the assumptions on which it is based are too restrictive because in few

|                    |  |  |  | •  |   |  | Lamma  |  |  | d toomn to                                     |  |  |  |  |  |
|--------------------|--|--|--|--|---|--|--|--|--|--|--|--|--|--|--|
| Metal ion          |  | pH 4   |  |  | pH 5  |  |  | pH 6   |  |  | pH 7   |  |  | pH 8   |  |
|                    | $-\Delta G \times 10^2$<br>J mol <sup>-1</sup> | $\Delta S \times 10^{-2}$<br>J K <sup>-1</sup> mol <sup>-1</sup> | $-\Delta H \times 10^2$<br>J mol <sup>-1</sup> | $-\Delta G \times 10^2$<br>J mol <sup>-1</sup> | $\frac{\Delta S \times 10^{-2}}{J  \mathrm{K}^{-1}  \mathrm{mol}^{-1}}$ | $-\Delta H \times 10^2$<br>J mol <sup>-1</sup> | $-\Delta G \times 10^2$<br>J mol <sup>-1</sup> | $\Delta S \times 10^{-2}$<br>J K <sup>-1</sup> mol <sup>-1</sup> | $-\Delta H \times 10^2$<br>J mol <sup>-1</sup> | $-\Delta G \times 10^2$<br>J mol <sup>-1</sup> | $\Delta S \times 10^{-2}$<br>J K <sup>-1</sup> mol <sup>-1</sup> | $-\Delta H \times 10^2$<br>J mol <sup>-1</sup> | $-\Delta G \times 10^2$<br>J mol <sup>-1</sup> | $\Delta S \times 10^{-2}$<br>J K <sup>-1</sup> mol <sup>-1</sup> | $-\Delta H \times 10^2$<br>J mol <sup>-1</sup> |
| Ni <sup>2+</sup>   | 158.95   | 11.98  | 158.59   | 83.64  | 15.64   | 83.16  | 89.78  | 15.00  | 89.33  | 104.81   | 13.78  | 104.39   | 122.36   | 12.86  | 121.97   |
| $\mathrm{Zn}^{2+}$ | 67.19  | 17.69  | 66.66  | 69.25  | 17.51   | 68.72  | 67.93  | 17.71  | 67.40  | 84.02  | 15.60  | 83.55  | ND   | ND   | ND   |
| $Pb^{2+}$          | 133.87   | 12.47  | 133.49   | 127.99   | 12.64   | 127.61   | 155.60   | 12.02  | 155.24   | ND   | ND   | ND   | ND   | ND   | ND   |
| $Ag^+$             | 88.39  | 15.13  | 87.93  | 95.04  | 14.52   | 94.60  | 138.19   | 12.36  | 137.82   | ND   | ND   | ND   | ND   | ND   | ND   |
| $Cu^{2+}$          | 87.72  | 15.20  | 87.26  | 86.22  | 15.36   | 85.85  | 138.19   | 12.36  | 137.82   | ND   | ND   | ND   | ND   | ND   | ND   |
| $Co^{2+}$          | 85.60  | 15.42  | 85.13  | 85.40  | 15.45   | 84.93  | 88.16  | 15.16  | 87.71  | 92.28  | 14.76  | 91.83  | 96.84  | 14.37  | 96.41  |
| ND: not det        | erminable.                                     |  |  |  |   |  |  |  |  |  |  |  |  |  |  |

TABLE 3: Thermodynamic parameters for individual metal ion adsorption.

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| Matal ion        |                    |                     | pH4                      |                     |                     | pH 5                      |                     |                     | pH 6                      |                     |                     | pH 7                                |                     |                     | pH 8                                |                     |
|------------------|--------------------|---------------------|--------------------------|---------------------|---------------------|---------------------------|---------------------|---------------------|---------------------------|---------------------|---------------------|-------------------------------------|---------------------|---------------------|-------------------------------------|---------------------|
| INTELIAT TOTI    | In presence<br>of  | $-\Delta G \times$  | $\Delta S 	imes 10^{-2}$ | $-\Delta H \times$  | $-\Delta G \times$  | $\Delta S \times 10^{-2}$ | $-\Delta H \times$  | $-\Delta G \times$  | $\Delta S \times 10^{-2}$ | $-\Delta H \times$  | $-\Delta G \times$  | $\Delta S \times 10^{-2}$           | $-\Delta H \times$  | $-\Delta G \times$  | $\Delta S \times 10^{-2}$           | $-\Delta H \times$  |
|                  | 5                  | J mol <sup>-1</sup> | $J K^{-1} mol^{-1}$      | J mol <sup>-1</sup> | J mol <sup>-1</sup> | $J K^{-1} mol^{-1}$       | J mol <sup>-1</sup> | J mol <sup>-1</sup> | $J K^{-1} mol^{-1}$       | J mol <sup>-1</sup> | J mol <sup>-1</sup> | J K <sup>-1</sup> mol <sup>-1</sup> | J mol <sup>-1</sup> | J mol <sup>-1</sup> | J K <sup>-1</sup> mol <sup>-1</sup> | J mol <sup>-1</sup> |
|                  | Zn <sup>2+</sup>   | 87.06               | 27.25                    | 86.24               | 88.16               | 27.20                     | 87.34               | 92.02               | 26.21                     | 91.23               | 104.81              | 21.11                               | 104.17              | 122.36              | 15.88                               | 121.88              |
| + 0              | $Pb^{2+}$          | 83.64               | 21.56                    | 82.99               | 85.60               | 21.33                     | 84.96               | 86.43               | 21.15                     | 85.79               | 95.93               | 18.92                               | 95.36               | 113.86              | 17.31                               | 113.34              |
| $Ni^{4+}$        | $Ag^+$             | 83.45               | 23.96                    | 82.72               | 88.39               | 22.53                     | 87.71               | 91.25               | 21.68                     | 90.60               | 95.33               | 21.14                               | 94.69               | 100.52              | 20.71                               | 06.66               |
|                  | Cu <sup>2+</sup>   | 85.19               | 24.52                    | 84.46               | 85.80               | 24.28                     | 85.07               | 92.54               | 20.69                     | 91.92               | 113.26              | 17.35                               | 112.74              | 141.55              | 16.20                               | 141.06              |
|                  | $Co^{2+}$          | 85.60               | 24.03                    | 84.87               | 86.22               | 24.15                     | 85.49               | 87.06               | 23.95                     | 86.34               | 100.52              | 21.54                               | 99.87               | 122.36              | 19.07                               | 121.79              |
|                  | $Ni^{2+}$          | 67.19               | 27.25                    | 66.37               | 66.78               | 27.20                     | 65.96               | 69.48               | 26.21                     | 69.69               | 93.62               | 21.11                               | 92.99               | 207.73              | 15.88                               | 207.25              |
| -                | $Pb^{2+}$          | 67.83               | 24.74                    | 67.08               | 67.19               | 24.31                     | 66.46               | 67.61               | 23.90                     | 66.89               | 93.35               | 18.99                               | 92.78               | 207.73              | 15.52                               | 207.26              |
| $Zn^{2+}$        | $Ag^+$             | 66.37               | 27.20                    | 65.55               | 66.98               | 26.43                     | 66.19               | 70.99               | 24.89                     | 70.24               | 180.20              | 17.69                               | 179.67              | ND                  | 18.97                               | ND                  |
|                  | $Cu^{2+}$          | 64.69               | 28.30                    | 63.84               | 64.50               | 28.19                     | 63.65               | 67.61               | 23.90                     | 66.89               | 103.57              | 18.03                               | 103.02              | 207.73              | 15.52                               | 207.26              |
|                  | $Co^{2+}$          | 64.22               | 28.73                    | 63.35               | 64.50               | 28.72                     | 63.64               | 67.83               | 27.73                     | 66.99               | 122.36              | 19.48                               | 121.77              | ND                  | 15.97                               | ND                  |
|                  | $Ni^{2+}$          | 123.22              | 21.56                    | 122.57              | 122.36              | 21.33                     | 121.72              | 124.10              | 21.15                     | 123.46              | 180.20              | 18.92                               | 179.63              | ND                  | 17.31                               | ND                  |
| ć                | $Zn^{2+}$          | 113.26              | 24.74                    | 112.52              | 124.10              | 24.31                     | 123.37              | 132.58              | 23.90                     | 131.86              | ND                  | 18.99                               | ND                  | ND                  | 15.52                               | ND                  |
| $Pb^{2+}$        | $Ag^+$             | 132.58              | 19.34                    | 131.99              | 135.23              | 19.74                     | 134.64              | ND                  | 16.82                     | ND                  | ND                  | 17.80                               | ND                  | ND                  | 17.24                               | ND                  |
|                  | $Cu^{2+}$          | 130.18              | 20.93                    | 129.55              | 125.97              | 20.99                     | 125.34              | ND                  | 15.64                     | ND                  | ND                  | ND                                  | ND                  | ND                  | QN                                  | ND                  |
|                  | $Co^{2+}$          | 123.22              | 21.22                    | 122.58              | 127.99              | 20.94                     | 127.36              | 167.39              | 20.26                     | 166.78              | ND                  | 17.49                               | ND                  | ND                  | 17.28                               | ND                  |
|                  | $Ni^{2+}$          | 91.50               | 23.96                    | 90.78               | 99.12               | 22.53                     | 98.45               | 105.24              | 21.68                     | 104.58              | 106.56              | 21.14                               | 105.93              | 105.67              | 20.71                               | 105.05              |
| -                | $Zn^{2+}$          | 88.84               | 27.20                    | 88.02               | 94.46               | 26.43                     | 93.67               | 102.77              | 24.89                     | 102.02              | 111.01              | 17.69                               | 110.47              | 119.95              | 18.97                               | 119.38              |
| $Ag^{T}$         | $Pb^{2+}$          | 100.17              | 19.34                    | 99.58               | 95.04               | 19.74                     | 94.44               | 123.22              | 16.82                     | 122.71              | 106.56              | 17.80                               | 106.03              | 115.09              | 17.24                               | 114.57              |
|                  | $Cu^{2+}$          | 97.16               | 22.88                    | 96.47               | 103.57              | 22.29                     | 102.89              | 112.68              | 17.84                     | 112.14              | 107.96              | 17.77                               | 107.43              | 112.11              | 17.24                               | 111.58              |
|                  | $Co^{2+}$          | 95.04               | 23.04                    | 94.34               | 99.12               | 22.67                     | 98.44               | 107.96              | 21.39                     | 107.32              | 158.95              | 17.91                               | 158.41              | 111.55              | 19.21                               | 110.97              |
|                  | $Ni^{2+}$          | 84.99               | 24.52                    | 84.26               | 86.22               | 24.28                     | 85.49               | 118.47              | 20.69                     | 117.84              | ND                  | 17.35                               | ND                  | ND                  | 16.20                               | ND                  |
| +0               | $Zn^{2+}$          | 83.07               | 28.30                    | 82.22               | 84.21               | 28.19                     | 83.36               | 132.58              | 23.90                     | 131.86              | ND                  | 18.03                               | ND                  | ND                  | 15.52                               | ND                  |
| Cu <sup>2+</sup> | $Pb^{2+}$          | 86.22               | 20.93                    | 85.59               | 87.06               | 20.99                     | 86.43               | 180.20              | 15.64                     | 179.73              | ND                  | ND                                  | ND                  | ND                  | ND                                  | ND                  |
|                  | $Ag^+$             | 87.06               | 22.88                    | 86.37               | 87.28               | 22.29                     | 86.61               | 155.60              | 17.85                     | 155.07              | 207.73              | 17.77                               | 207.19              | ND                  | 17.42                               | ND                  |
|                  | $Co^{2+}$          | 85.40               | 24.84                    | 84.65               | 87.50               | 24.44                     | 86.76               | 207.73              | 19.66                     | 207.14              | ND                  | 19.40                               | ND                  | ND                  | 17.60                               | ND                  |
|                  | $\mathrm{Ni}^{2+}$ | 88.39               | 24.03                    | 87.66               | 86.85               | 24.15                     | 86.12               | 87.50               | 23.95                     | 86.78               | 96.23               | 21.54                               | 95.58               | 108.44              | 19.07                               | 107.87              |
| +0 -             | $Zn^{2+}$          | 80.77               | 28.73                    | 79.90               | 80.43               | 28.74                     | 79.56               | 82.52               | 27.73                     | 81.69               | 103.17              | 19.48                               | 102.58              | 152.65              | 15.97                               | 152.17              |
| Co <sup>2+</sup> | $Pb^{2+}$          | 86.22               | 21.22                    | 85.58               | 86.85               | 20.94                     | 86.22               | 85.40               | 20.26                     | 84.79               | 111.01              | 17.49                               | 110.48              | 114.47              | 17.28                               | 113.95              |
|                  | $Ag^+$             | 87.50               | 23.04                    | 86.80               | 87.28               | 22.67                     | 86.60               | 92.02               | 21.39                     | 91.37               | 111.01              | 17.91                               | 110.47              | 115.73              | 19.21                               | 115.15              |
|                  | Cu <sup>2+</sup>   | 82.52               | 24.84                    | 81.77               | 83.45               | 24.44                     | 82.71               | 88.16               | 19.66                     | 87.57               | 89.78               | 19.40                               | 89.20               | 109.44              | 17.60                               | 108.91              |
| ND: not dete     | erminable.         |                     |                          |                     |                     |                           |                     |                     |                           |                     |                     |                                     |                     |                     |                                     |                     |

TABLE 4: Thermodynamic parameters for metal ion adsorption in binary systems.

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cases consideration of physiosorption is also taken into account to explain the adsorption process.

- (5) The monolayer coverage (Γ<sub>α</sub>) calculated from the Langmuir isotherm indicates that the extent of surface coverage changes with the change in solution pH. The monolayer coverage value coincides with the principle on which the affinity of the adsorbate towards adsorbent value (K) is based.
- (6) The fractional surface site coverage (Γ) of a particular metal ion on pyrite surface in a binary system has been found to be excellent as inferred from correlation coefficient data in understanding the competitive nature of adsorption of metal ions on pyrite surface.
- (7) This study reveals that natural pyrite is an excellent adsorbent for Ni<sup>2+</sup>, Zn<sup>2+</sup>, Pb<sup>2+</sup>, Ag<sup>+</sup>, Cu<sup>2+</sup>, and Co<sup>2+</sup> ions and, therefore, has considerable geochemical, environmental, and technological interests.
- (8) Semiquantitative thermodynamic analysis of metal ion adsorption in both individual and binary systems indicates that the adsorption process is thermodynamically controlled.
- (9) Evaluation of thermodynamic parameters indicates that the adsorption of a particular metal ion in individual and binary systems is exothermic in nature  $(-\Delta H)$ . Moreover, the exothermicity of concerned metal ion adsorption increases in majority of cases in a binary system indicating a reduction in adsorption because of limited number of coordination sites on the pyrite surface that both the metal ions compete for their preferential adsorption. The negative value of  $\Delta G$  in both the processes reveals the spontaneous nature of adsorption. Further, a low positive value of  $\Delta S$  in bulk suggests the greater extent of orderness on the pyrite surface, that is, increase of adsorption.
- (10) The exothermic nature of adsorption processes both in individual and binary systems strongly reveals that these processes are highly effective at low temperature.

Although the present study is restricted to six metal ions, it will give a foundation for mode of occurrence of trace elements in minerals of coal such as pyrite and also for purification of water containing hazardous metals and the factors (e.g., adsorption edge, mechanism, correlation coefficient, monolayer coverage, pH, temperature, thermodynamic parameters, etc.) responsible for their removal.

#### **Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.

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