



# Characterization and Geochemical Modeling of Cu and Zn Sorption Using Mineral Systems Injected with Iron Sulfide: Case Study of Mine Waste Water, Wales, United Kingdom

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**Abstract:** Sorption of Cu and Zn was investigated using single and mixed mineral systems under sulfidic-anoxic condition to treat wastewater obtained from disused mine pits at Parys Mountain in, United Kingdom. Water courses are the recipients of these contaminants. In these water courses fishing activities exist. Attempt was made to reduce the Cu and Zn levels intake in the watercourses using mineral systems of clays and goethite. These were tested with the mine waste water for characterization of copper and zinc removal at variable pH, solid concentration and contact time. In addition, levels of saturation of hydroxyl complexes were modeled. Batch reactions conducted at ambient temperature ( $23\pm 2^\circ\text{C}$ ) reveal all systems of assorted minerals sorbed more Cu than Zn. In addition, Cu sorbed on iron sulfide exhibited increase in sorption with increasing pH. There was cross cutting effect of Cu and Zn sorbed on iron sulfide at pH 6 and Cu sorbed on goethite at about pH 7, These indicate similar metal removal characteristics. Differences in removal of copper and zinc ions may be assigned to outer sphere complexation and specific adsorption of copper and zinc ions. Non-promotive Cp effect (i.e. decrease in metal removal with increase in concentration of particle) was observed in all minerals. This effect may be assigned to increase in aggregation of the mineral particle size. Ageing characterization progresses as residence time was increased. This may be assigned thiol (=S-H) and hydroxyl (=Me-OH) groups and sites of reactions. There is no link to stable hydroxylation of copper and zinc species that could significantly contribute to the removal of these metals.

**Keywords:** Ageing, Cu-Zn, Mixed Mineral Systems, PH Solution Composition

## 1. Introduction

Pollution by heavy metals derived from acid mine drainage, and wastewater treatment are the foremost sources of sullied water chemistry [1]. Metal plating, mining and painting generate heavy metals. These metals become a severe public health concern.

This is because they are persistent and have negative effect on the environment [2]-[3]. Zn is a trace element and it is essential for nutrition. However, when taken in excess doses, it may be toxic. This could become risky in groundwater and other water resources due to accumulation in living organisms [4]-[5]. It is widely known that an overdose of Zn can lead to depression, lethargy, neurologic signs such as seizures and

ataxia, and increased thirst [6].

Therefore, elimination of Zn(II) from water sources is necessary [7]-[8]. Water bodies receive metal ions by various anthropogenic activities. These metals damage the environment and are toxic on human and other forms of life. Solution chemistry and reliable sorbents are the determinants of dissolved metal species [9].

Copper and zin removal from aquatic solution is determined by the composition of the solution [10]. These include the effect of, pH and particle concentration in the wastewater [11]-[13]. pH remains an important factor in metal removal from aqueous environments [14]. The solubilities of metals is controlled by pH.

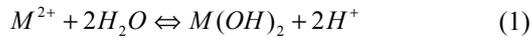
Other effect of pH includes hydrolysis characterization and

surface charge [15]. Lower pH attenuates hydrolysis and enhances metal accumulation in the solution [16]. Heavy metal adsorption is known to be dependent on the anion nature and the adsorbent surface [17]. Outer sphere complexation is reported as decrease in adsorption as particle concentration increases.

Inner sphere complexation is reported when increase in particle concentration does not significantly lead to increase in adsorption. Promotive particle concentration effects are reported when adsorption increase with increase in particle concentration [18]-[20]. The reasons for the latter is unclear. Ionic species present in solution is influenced by the dynamics of the mineral- solution ratio.

This is governed by the fact that high and new sites of reactions are formed. However, sorption of metalloids and metals does not have a linear relationship with respect to this episode [21]-[26]. The sorption mechanisms responsible removal of copper and zinc involve both slow and fast reaction phases.

The slow reaction phase is attributed to slow inter-particle diffusion and higher activation energy when compared with the fast metal removal sites. The fast reaction phase may be assigned to adsorption by electrostatic attraction [8]. Similar processes include specific adsorption and precipitation in many respects. In natural systems, adsorption generally occurs on mineral surfaces that are themselves precipitates [27]-[29]. These processes could piece together and the prevalence of one is hard to determine. This may be described by the following tentative mechanism [30]-[32].



Copper interface with mackinawite, a chalcopyrite period appeared to form, whereas interaction with pyrite seemed to produce twofold Cu sulfide (i.e. covellite at lower loadings and chalcocite at higher loadings) are provided [33]. The performance of copper in sulfidic solutions is complex.

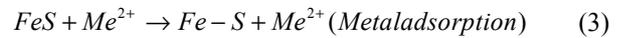
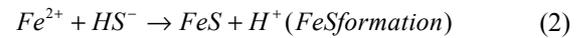
This could exist in several valence states. In addition, it is widely known that colloidal ZnS sols form during rapid precipitation of zinc sulfide from aqueous solution under sulfidic condition [34]. Heavy metal adsorption was increased with increase in initial concentration metal.

Increase in heavy metal removal as initial concentration of metal increase has been studied [35]. This adsorption increase capacity in relation to the metal ions concentration can be explained with the high driving force for mass transfer [36]-[37]. The use of wetland systems for treatment of wastewater has increased in communities without public sewage systems coupled with low economic development [38-40]. Some of these techniques are enumerated: Zn<sup>2+</sup> removal by PVA/EDTA resin in polluted water and Batch and stirred flow reactor experiments on Zn sorption in acid soils Cu competition [7]-[8].

Sorption involving sulfides sorbent reactive sites and the metal adsorbate involves three phases of reactions. These are outer sphere, inner sphere complexation and Intra-particle diffusion.

The latter involves the diffusion of the metal ions in the pore of the mineral systems [41]-[42]. Surfaces of metal sulfides contain thiol (=S-H) and hydroxyl (=Me-OH) groups and sites of reactions. Also, clays and goethite have an enormous amount of OH<sup>-</sup> groups. These easily developed protons at low pH, giving rise to positive charge [3]-[43].

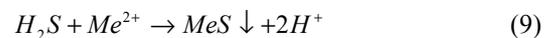
Due to its common occurrence and high reactivity under reducing conditions, mackinawite is known as a possible removal material for toxic trace metals. Authors have shown that mackinawite effectively remove heavy metals such as Cu(II), and Zn(II) [44]. These ions can have precipitated as metal sulfides, and the partition coefficient of each metal strongly increases with the decreasing solubility of the precipitated form of metal sulfides. The possible reactions for the incorporation of divalent metals into FeS are given [45]:



Concerning heavy metals adsorption onto pyrite, it widely reported that hydrolysis reaction mechanism offers a better explanation than ion exchange [3]. Pyrite surface charge can be governed by protonation- deprotonation mechanism of reactions of the surface S groups. These form hydrogen sulfide and metal precipitate as provided:



Water decomposition can occur during surface hydration. This can take place at S sites leading to hydroxyl release or at Fe sites, leading to proton release in solution as depicted in equation [75, 70].



The hydrogen sulphide produced, combines with metal cations to form insoluble precipitates of metal sulphides [46-47]. Bacteria in liquid produce iron sulfide medium with added Fe ions. These sulphides act as absorbent for heavy metals. They have specific uptake capacity for different metal ions from solutions [48]. Details of the Freundlich model isotherm and the related empirical model have been used in elucidating the copper and zinc reactions.

In this paper, the sorption relationship between Parys mine wastewater containing copper and zinc metals and mineral systems based on different solution composition, ageing under sulfidic-anoxic conditions was investigated. Copper and zinc metal investigation is based on the understanding that these metals are some of the common toxic metals in wastewaters.

## 2. Study Site

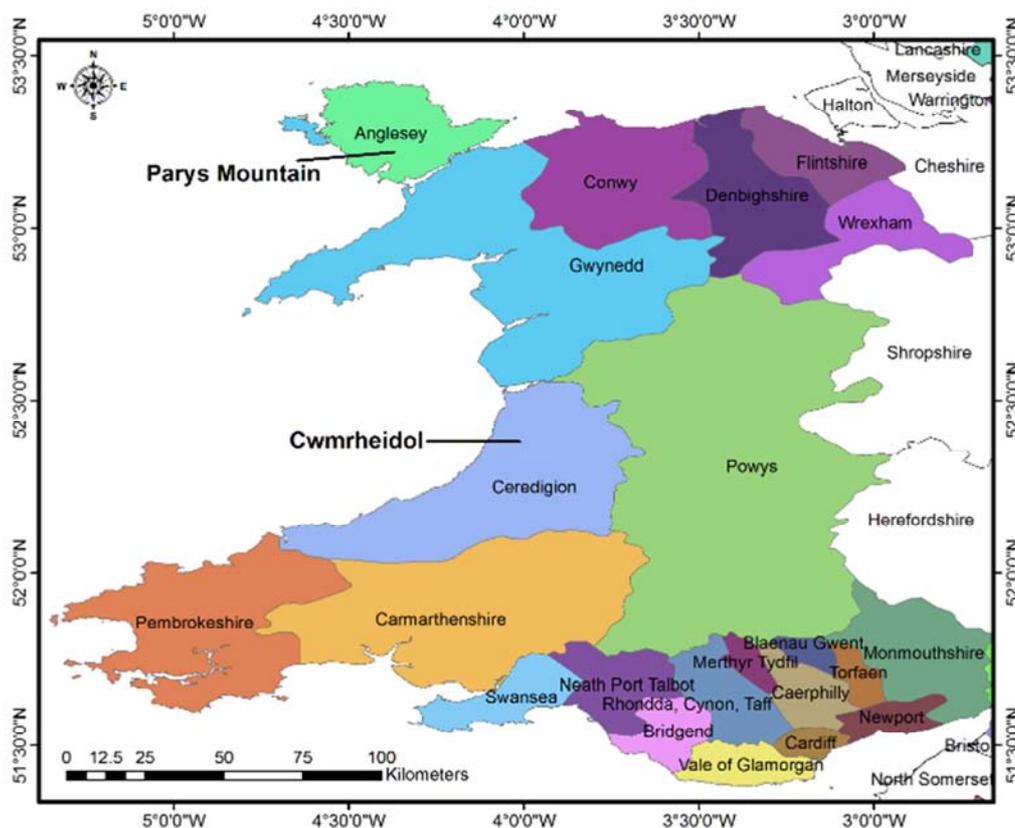


Figure 1. Location map of study sites in Wales.

Wastewaters were obtained from the mine pits in Parys Mountain mine (Grid Ref. SN 443907) and Cwmrheidol mine in Wales (Grid Ref. SN 131782) (Figure. 1). Discharges of mine wastewater from both mines contain Cu and Zn. Water courses such as River Lledr are the recipient of these contaminants in North Wales. In these water courses, commercial and local fishing activities exist. Mineralization is syngenetic and epigenetic; occurring in veins within the highly-fractured host rocks [49]-[52]. The primary mineralization comprising, sphalerite, chalcopyrite and pyrite are extensively weathered to produce colourful red and yellow ferric hydrous oxides and a different range of sulphate minerals.

These weathered minerals, forming components of the mine tailings, are rich in jarosite, anglesite, pisanite, antlerite and basaluminite [53]-[54]. Abandoned mine workings from this mineralized belt are the sources of wastewater discharged to receiving watercourses [55].

## 3. Modeling of Copper and Zinc Removal

### 3.1. Empirical Modeling of Copper and Zinc Removal

Empirical model involves the distribution coefficient ( $K_d$ ) as used in this paper and elsewhere [56].  $K_d$  (L/Kg) was calculated from the Freundlich model equation provided:

$$S = KdC^N \quad (10)$$

where  $S$  is the sorbed concentration (mg/kg),  $K_d$  (L/Kg) represents the distribution coefficient,  $C$  represents the equilibrium concentration (mg/L), and  $N$  is derived from the slope of the plot.

The Freundlich isotherm describes metal removal depicted by non-homogenous mineral surfaces over a considerable range of solute concentrations [84]. Concentration of metals used in this study are low. Adsorption isotherms were of the C type, resulting in linear isotherms. The empirical model as provided [56] to address the mineral-metal interactions is given:

$$Kd_{total} = \frac{Kd_1 + Kd_2 + Kd_n}{n} \quad (11)$$

where  $Kd_{total}$  is the theoretical coefficient of distribution for a 1:1 mixed system,  $Kd_1$  is the coefficient of distribution for first single mineral system, and  $Kd_2$  is the coefficient of distribution for second single mineral system,  $Kd_n$  is the coefficient of distribution for  $n$  number of systems of minerals and  $n$  is the number of mineral systems.

The simple empirical model used for metal-mineral partitioning in systems of mixed mineral and differences between actual and theoretical  $K_d$  may be assigned to the following:

1. Development of significant secondary mineral systems by the mixed mineral systems especially at alkaline pH.
2. Components of minerals in the mixed mineral systems act as networks of minerals and not as chemisorbed species.

**3.2. Phreeqc Modeling of Hydroxyl Complex Speciation**

*Table 1. Phreeqc modeling input for mineral systems.*

Solution parameter (mmol/Kgw)	
pH	2-8
Temperature (°C)	23°C
FeS	0.00569
Mine waste water	
Zn	0.024
Cu	0.05
SO4	0.2570

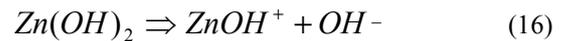
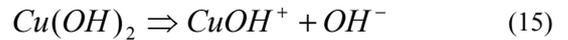
The geochemical modeling software package PHREEQC was used to simulate the mine waster containing FeS at different pH [57]. The PHREEQC model allows the basic chemistry of mixing and formation of secondary mineral. Applied reaction process was limited to the metal removal processes. This approach may be appropriate because the modeled systems are known to be essentially controlled by metal removal process. The PHREEQC modeling input and chemical composition in each system is summarized in Table 1. mine The degree of saturation (DS) for the presumed complexes Cu(OH)<sub>2</sub> and Zn(OH)<sub>2</sub> is related to the Ion Activity

Product (IAP) and the conditional solubility constant (Ksp) as follows:

$$IAP \cong [M^{2+}][OH]_2 \tag{12}$$

$$D_s \cong \frac{IAP}{K_{sp}} \tag{13}$$

$$SI \approx \log IAP - \log K_{sp} \tag{14}$$



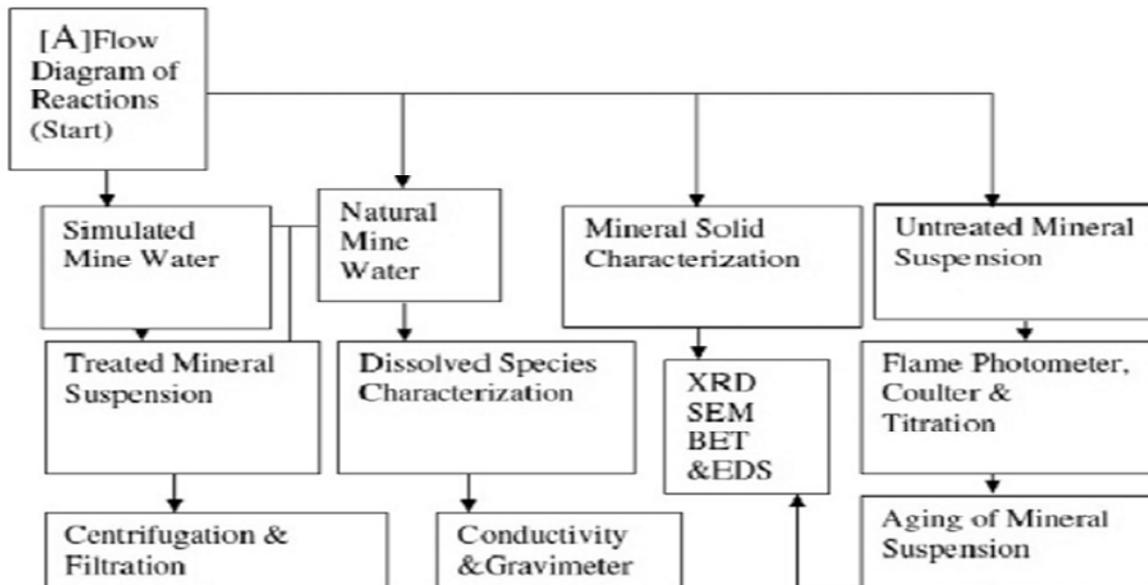
Log DS is the Saturation index (SI). Where: SI<0 the system is under-saturated with respect to the complex SI = 0, system is saturated to the complex SI> 0, system is supersaturated with respect to the complex. Where M<sup>2+</sup> is the metal molar concentration and H<sup>+</sup> as system pH [39].

**4. Materials and Methods**

Details of characterization of minerals used and experimental methods are provided in other papers [24], [88] (Table 3). The methodology is summarized (Figure. 2), characteristics of the mine wastewater provided (Table 2) and the characterization of the mineral systems are provided in Figure 3 and Figure 4.

*Table 2. Characterization of mine wastewater.*

Location	pH	Conductivity(ms/cm)	TDS(mg/L)	Salinity(g/L)	Cu(mg/L)	Zn(mg/L)	SO4(mg/L)
Cwmheidol SN131782	3.70	1.69	970.00	0.97	4.76	156.00	159.00
Parys Mt SN443907	2.50	2.60	1526.00	1.50	76.07	165.00	1234.00



*Figure 2. Flow diagram of experimental studies.*

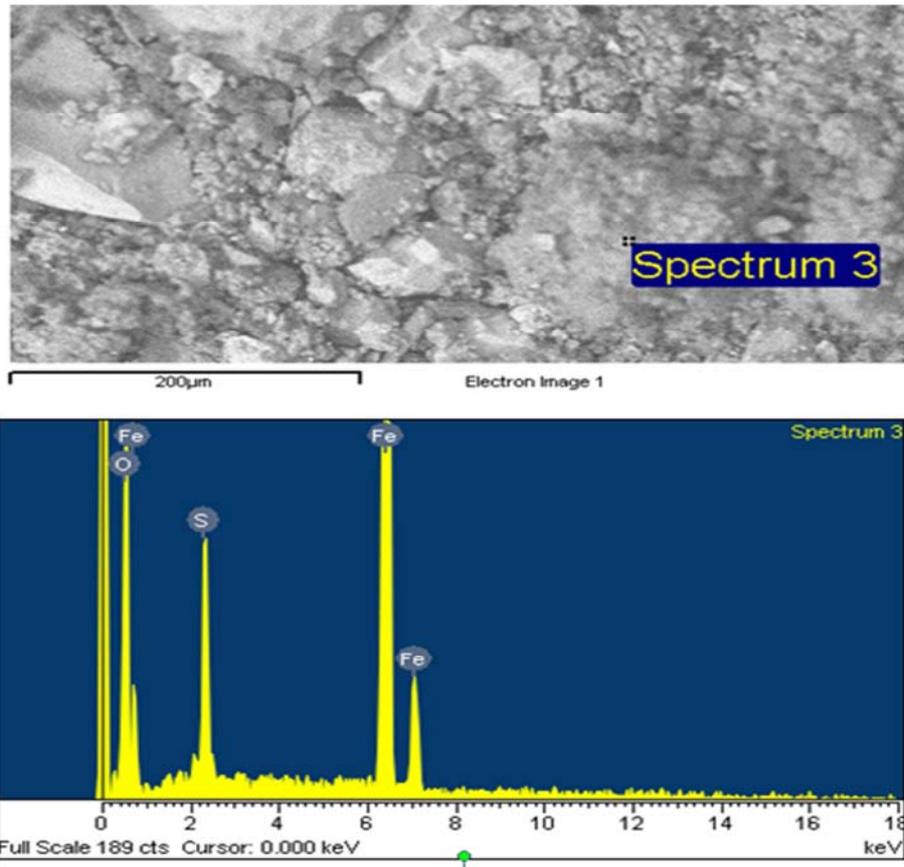


Figure 3. Scanning electron microscopy and energy dispersive spectroscopy /of iron sulfide on mineral systems.

Table 3. Characterization of clays, goethite and iron sulfide [5.6].

Mineral systems	Particle size ( $\mu\text{m}$ )	% colloid ( $<1\mu\text{m}$ )	pH $\pm\delta$	Specific Surface Area $\pm\delta$ ( $\text{m}^2/\text{g}$ )	Point of Zero Salt Effect $\pm\delta$
Kaolinite	20.5	3.00	$6.05 \pm 0.05$	$47.01 \pm 0.24$	$7.01 \pm 0.15$
Montmorillonite	80.05	0.53	$2.01 \pm 0.09$	$10.00 \pm 0.00$	$7.16 \pm 0.20$
Goethite	40.10	2.92	$8.05 \pm 0.06$	$71.05 \pm 0.17$	$7.50 \pm 0.08$
Kaolinite/Montmorillonite	80.05	0.97	$5.01 \pm 0.02$	$88.05 \pm 0.55$	$4.30 \pm 0.21$
Montmorillonite/Goethite	15.25	3.85	$3.03 \pm 0.04$	$147.10 \pm 0.50$	$4.30 \pm 0.04$
Kaolinite/Goethite	140.35	0.73	$3.05 \pm 0.01$	$79.30 \pm 0.59$	$4.70 \pm 0.13$
Iron sulfide	80.20	4.729	$4.02 \pm 0.03$	$2.00 \pm 0.00$	$4.5 \pm 0.04$

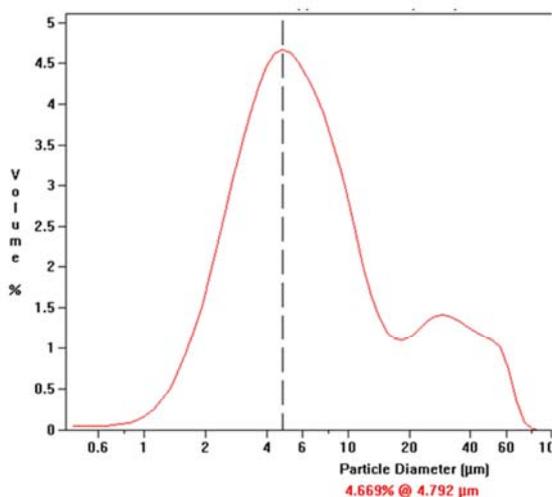


Figure 4. Particle size distribution curve of iron sulfide.

#### 4.1. Preparation of Sulfidic-Anoxic Iron Sulfide System

Sulfidic-anoxic conditions are represented by reduction of dissolved oxygen. These conditions will occur if the rate of oxidation is greater than the supply of dissolved oxygen [58]. The product of sulfate and sulfide reduction is hydrogen sulfide [58]. In this study, 1% acidified form of sulfidic-anoxic iron sulfide system was prepared. Deionized water was used, bubbled through with purified nitrogen gas. This was done continuously for 24 hours. With content secured, this was stored in the anaerobic chamber before use. The characterization of a “rotten egg” odor was evidence of hydrogen sulfide formation [59]-[60].

#### 4.2. System Characterization

The batch mode reactions: experimental design for Cu and Zn sorption by mineral systems are presented in this paper. Details of characterization of minerals used, experimental

methods and the characteristics of the wastewater are provided (Figure. 2) -(Figure. 4) and (Table 1) -(Table 3) All solutions were prepared using de-aerated and deionized water. Deionized water deoxygenated water was used, bubbled through with purified nitrogen gas. This was done continuously for 24 hours.

In an anaerobic chamber containing hydrogen and nitrogen gases at 5% and 95% respectively, the water was purged overnight C Richard Baker Harrison Company provided the clay and iron sulfide for this experimental work. Goethite was provided by Iconofile Company Inc. These were kept in anaerobic chamber after being nitrogen flushed. Particle sizes was determined using Coulter laser method. Distribution curves were used to determine % colloid.

Model 3340 Jenway ion meter was used to determine equilibrium pH. Volumetric Brunauer, Emmett, and Teller (BET) method was used to determine the surface areas [61], (e) determination of cation exchange capacity of the clay minerals was done using the Na saturation method (Table 1).

Scanning electron microscopy, energy dispersive spectroscopy and x-ray diffraction were used to identify the mineral sorbent after performing spectral analysis [10]-[11], [1], [48]. Concentrations of copper and zinc were determined using ICP-OES (Table 1).

#### 4.3. Batch Mode Experiments

Investigation of batch mode pH was done using, 1% mineral system of iron sulfide added to 1% systems of kaolinite, montmorillonite and goethite minerals. In addition, 1:1 systems of mixed minerals of kaolinite/montmorillonite, kaolinite/goethite and montmorillonite/ goethite with no added electrolyte were used. In all cases, solutions were made up to 50 ml of mine wastewater containing 76.07 ppm Cu and 165 ppm Zn. This was done after pH adjustment (i.e. pH 4 to 8) using 0.1 M HNO<sub>3</sub> and 0.1 M NaOH. The treated systems of minerals were equilibrated for 24 h a Model 3340 Jenway ion meter was used for pH measurement.

Particle concentration investigation in batch mode was done using 1% mineral system of iron sulfide added to 1% systems of kaolinite, montmorillonite and goethite mineral. Also, 1:1 mixed mineral systems of kaolinite/montmorillonite, kaolinite/goethite and montmorillonite/ goethite with no added electrolyte. In all cases, solutions were made up to 50 ml of mine wastewater containing 76.07 ppm Cu and 165 ppm Zn, containing solid concentrations (kg/L) of 0.002 to 0.01.

The systems of treated minerals were equilibrated for 24 h and adjusted to required pH. Batch mode ageing investigations were carried out from 24 to 720 h using 1% sulfidic-anoxic system of iron sulfide was added to 1% mineral systems of kaolinite, montmorillonite and goethite.

Also, the same equal amount of 1% systems of kaolinite/montmorillonite, kaolinite/goethite and montmorillonite/goethite minerals with no added electrolyte were used in the experiments. In all cases, solutions were made up to 50 ml of mine wastewater containing 76.07 ppm Cu and 165 ppm Zn. Equilibration for 24 h was done for these mineral systems after pH adjustment.

In all experimental studies samples were stored in the dark at ambient temperature (23±3°C) for a maximum of 24 h before analysis. Equilibration for 24h was based on preliminary and other reports on reaction time for adsorption [14]. Samples were treated in three replicates and metal concentration removed (S or Q<sub>e</sub>) in mgkgL<sup>-1</sup> was calculated.

This was derived from the difference between the equilibrium concentration C (the metal concentration in solution after sorption equilibrium) and initial metal concentration C<sub>0</sub> (metal concentration before metal removal) and, (17)

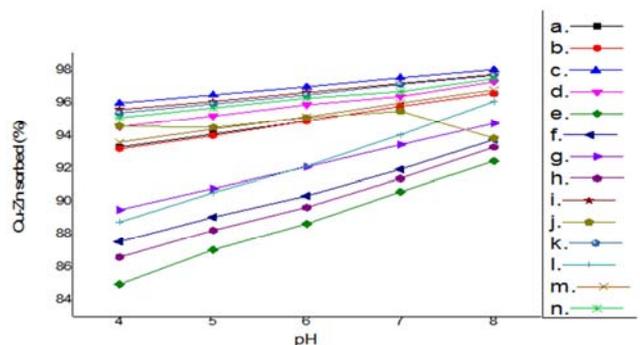
$$Q_e = \frac{(C_i - C_e)V}{W} \quad (17)$$

where V<sub>total</sub> represents the mineral suspension volume and W is the mass of mineral solid. The effect of polycarbonate tubes on the removal of metal ions is so small that it can be neglected [82].

## 5. Results and Discussion

### 5.1. Mineral Systems and pH Effects on Cu and Zn Removal

Without sulfidic-anoxic condition [56], [24], [56], mine wastewater treated with the single systems of minerals demonstrated metal removal at >pH50 (i.e. pH at which 50% of contaminant is sorbed) Cu and Zn sorption; occurring at pH 7 for kaolinite, goethite and pH 8 for montmorillonite (Figure 5). A unit change in pH i.e. from pH 6 to 7 resulted in a similar change in % sorption of both copper and zinc by montmorillonite treated Parys Mountain mine wastewater. In this study, all systems except Cu sorbed on iron sulfide revealed increase in sorption with increasing pH. Cross cutting effect (i.e. pH at which Cu and Zn removal is similar) was observed on Cu and Zn sorbed on iron sulfide at pH 6. Similarly, there was cross cutting effect on Cu sorbed on goethite at pH greater than 7.



**Figure 5.** Plots of Cu-Zn sorbed vs. pH for (a) Cu-iron sulfide (b) Zn-iron sulfide, (c) Cu-kaolinite, (d) Zn-kaolinite, (e) Cu-goethite-kaolinite, (f) Zn-goethite-kaolinite, (g) Cu-kaolinite-montmorillonite, (h) Zn-kaolinite-montmorillonite, (i) Cu-montmorillonite, (j) Zn-montmorillonite, (k) Cu-goethite-montmorillonite, (l) Zn-goethite-montmorillonite, (m) Cu-goethite, (n) Zn-goethite.

In addition, Cu sorbed on kaolinite-montmorillonite revealed cross cutting effect on Cu adsorbed on goethite at

pH 6 (Figure. 5). Iron sulfide characterization in this condition for Cu and Zn sorbed was different from that of the non-sulfidic solution for all systems, displaying higher Cu sorption than Zn. Increase in copper and zinc removal on systems as pH increases is assigned to deprotonation of reactive sites [15].

This may be assigned to thiol (=S-H) and hydroxyl (=Me-OH) groups and sites of reactions on mineral surfaces. Zn sorbed on kaolinite/ montmorillonite exhibited the lowest behavior of metal removal for all mixed systems. Zinc metal sorbed on montmorillonite exhibited the lowest metal removal behavior.

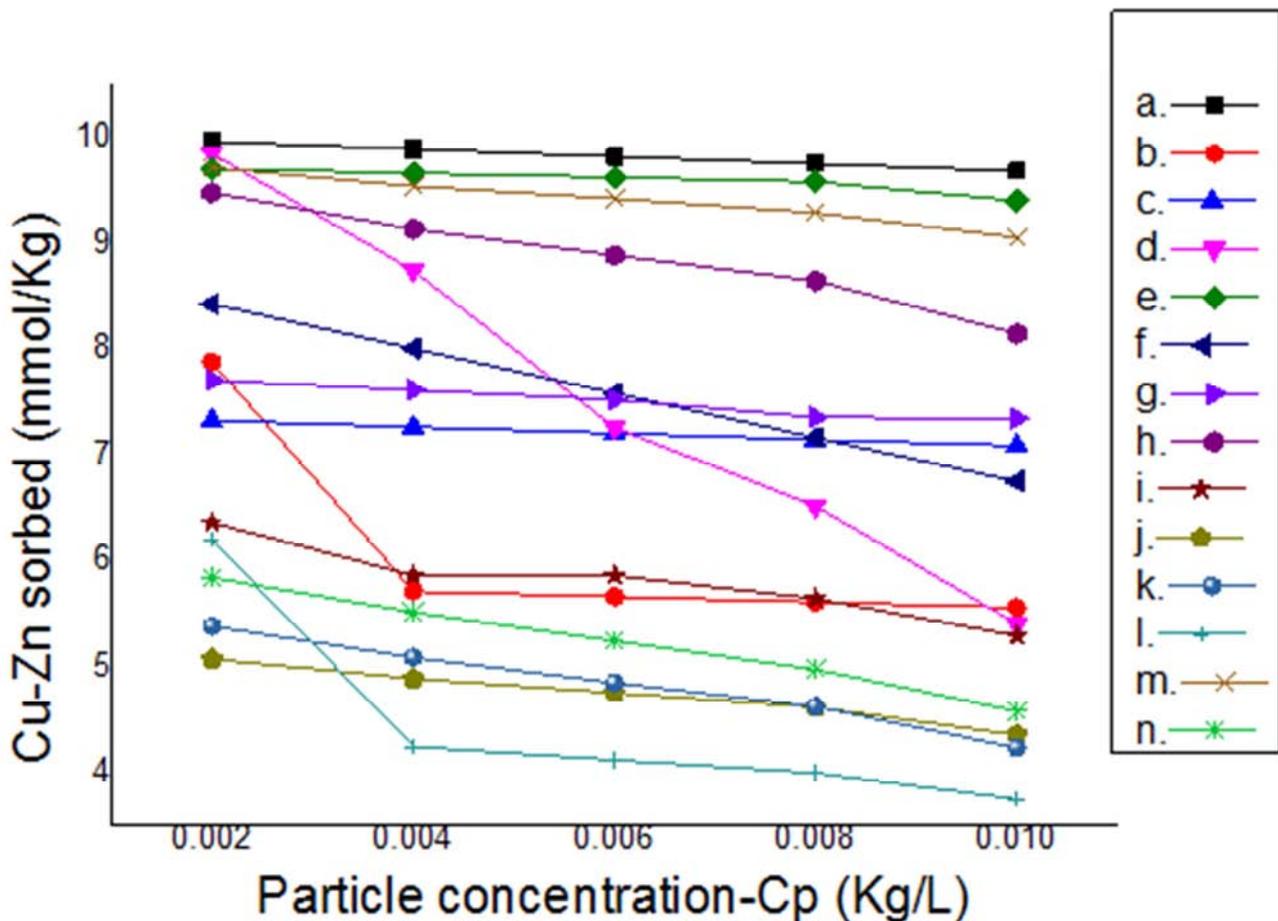
Differences in sorption behavior of these mineral sorbents may be assigned to particle size of the systems, altering the specific surface area. Mixing of minerals could lead to aggregation of flocs blocking copper and zinc transfer. This could account and can account for the low efficiency of the mixed mineral systems to sorb metals by ion exchange [42]. In addition, reactive sites of the system surfaces are masked by mineral mixing thus impeding sorption. These findings do not completely agree with the view that system mixing does not reasonably affect removal of heavy metal.

## 5.2. Mineral Systems and Solid Concentration Effects on Cu and Zn Removal

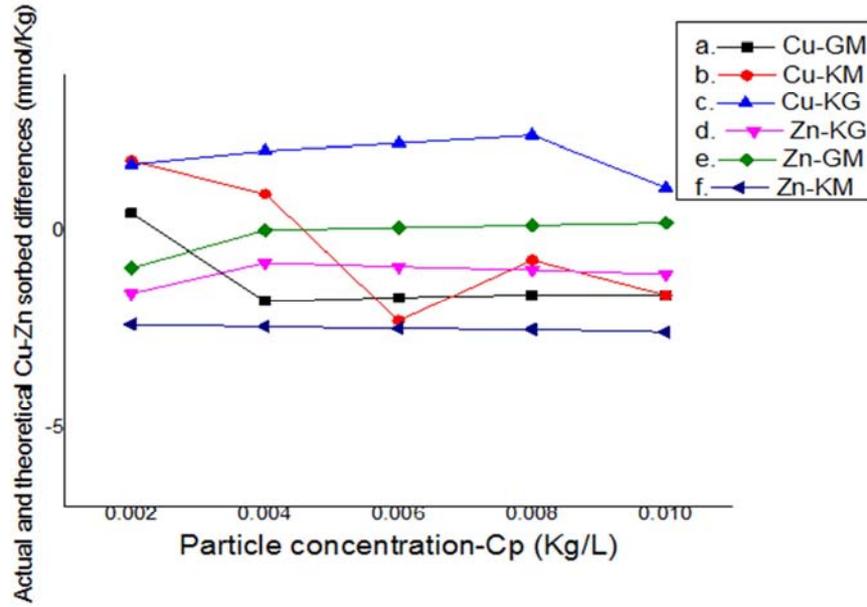
Study without sulfidic-anoxic condition revealed that Changes in Zn removal as particle concentration increased was not statistically (chi-square) significant ( $P \leq 0.01$ ) for the kaolinite/montmorillonite and kaolinite/goethite mixed systems.

Also, differences in sorption between the mixed and single systems showed enhanced metal removal. This decreases with increase in Cp effect for for copper ions attached on kaolinite/montmorillonite and kaolinite/goethite systems. In this study, all systems showed non-promotive Cp effect (i.e. metal removal decreased with increase in concentration of particle (Figure. 6).

Decrease in metal metal removal as Cp was increased may be linked to aggregation of mineral flocs leading to increase in particle size of mineral systems [56]. Also, cross-over sorption exists for copper attached on kaolinite-montmorillonite, goethite-montmorillonite and montmorillonite. Zinc attached on sorbed on systems exhibited cross-over sorption on montmorillonite and kaolinite-goethite.



**Figure 6.** Plots of ion sorbed versus particle concentration for (a) Cu-iron sulfide., (b)Cu- goethite/montmorillonite., (c)Cu- goethite., (d)Cu-kaolinite/montmorillonite., (e) Cu-kaolinite/goethite., (f)Cu-kaolinite; (g) Cu-montmorillonite;(h) Zn-iron sulfide, (i) Zn-kaolinite-goethite, (j) Zn-goethite-montmorillonite, (k) Zn-kaolinite-montmorillonite, (l) Zn-goethite, (m) Zn-kaolinite, (n) Zn-montmorillonite sulfidic-anoxic mineral systems.



**Figure 7.** Plots of actual and theoretical  $K_d$  differences versus particle concentration- $C_p$  for: (a) Cu-goethite-montmorillonite; (b) Cu-kaolinite/montmorillonite; and (c) Cu- kaolinite/goethite (d) Zn-kaolinite-goethite, (e) Zn-goethite-montmorillonite, (f) Zn-kaolinite-montmorillonite sulfidic-anoxic mineral systems.

These indicates that sorption by these metals at cross-over points are similar in characteristics. The  $C_p$  effect is linked to mineral surface area considered effective at the mineral/water interface. The presence of (=S-H) and hydroxyl (=Me-OH) functional group could lead to increase in  $C_p$  effect and subsequent decrease in the diffusion of metal ions

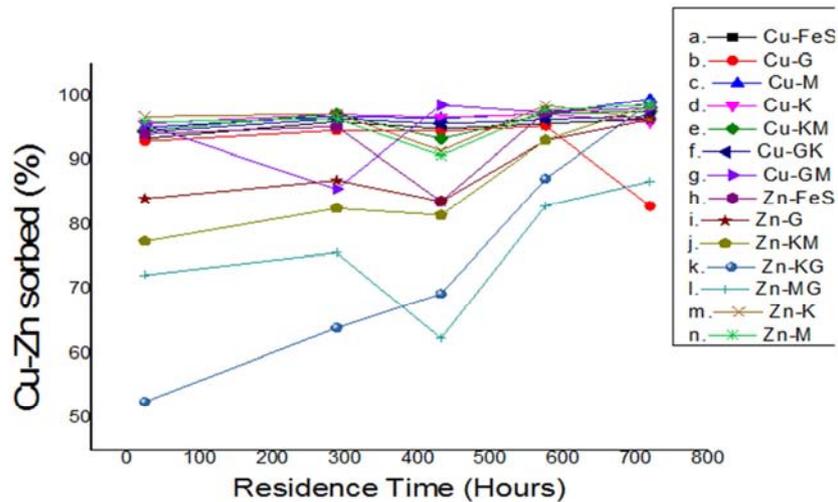
Enhancement of copper removal on the mixed systems could be assigned to increased number of reactive sites which favor Cu rather than Zn. Goethite in mixed systems could develop particles that are separate and discrete. This could be the reasoning for copper and zinc removal differences on mixed systems containing goethite.

Differences in actual and predicted sorption for ions sorbed

on mixed systems exhibited complex behavior with copper attached on kaolinite-montmorillonite and goethite-montmorillonite exhibiting step-wise decrease from the positive territory to the negative terrain (Figure 7). Also, zinc attached on goethite-montmorillonite, kaolinite-goethite and kaolinite-montmorillonite rested on the negative terrain indicating higher predicted  $C_p$  effects.

Only copper attached on kaolinite-goethite exhibited positive  $C_p$  effect indicating lower predicted  $C_p$  effects. This could be assigned to the effects of thiol (=S-H) and hydroxyl (=Me-OH) functional groups and reactive sites.

### 5.3. Mineral Systems and Aging Effects on Cu and Zn Removal



**Figure 8.** Plots of metal sorbed versus Ageing (residence time) for (a)Cu- Iron sulfide., (b) Cu-goethite, (c) Cu-montmorillonite, (d) Cu-kaolinite (e) Cu-kaolinite/montmorillonite., (f)Cu- goethite/kaolinite., (g) Cu-goethite/montmorillonite. (h) Zn-iron sulfide, (i) Zn-goethite, (j) Zn-kaolinite-montmorillonite, (k) Zn-kaolinite-goethite, (l) Zn-montmorillonite-goethite, (m) Zn-kaolinite (n) Zn-montmorillonite, sulfidic-anoxic mineral systems.

In previous papered work without, mineral systems, copper and zinc removal by the aged mixed systems increased with increasing residence time. In this study under, copper attached on iron sulfide, goethite, kaolinite and kaolinite-montmorillonite exhibited similar sorption characteristics, indicating high sorption % values.

However, the rest of the systems exhibited complex sorption behavior, increasing at the onset of sorption and declining after 432 hours for zinc attached on kaolinite-montmorillonite, montmorillonite and iron sulfide. On the contrary, zinc attached on kaolinite-goethite exhibited a graduated increase as contact time was increased (Figure 8). These changes could be assigned to hydroxylation of the mineral surfaces. This may lead to resulting formation of new sites of reactions.

Cross-over sorption exists for zinc attached on kaolinite-goethite, montmorillonite and Cu sorbed on goethite-montmorillonite. At these cross-over points, it is assumed that sorption is similar and could be linked to differences in the modes of particle association such as (a) edge-to-edge (EE); (b) edge-to-face (EF); and (c) face-to-face (FF).

Sorption characterization as ageing progresses is linked to presence of thiol (=S-H) and hydroxyl (=Me-OH) groups and sites of reactions [83]. These hydroxyl complexes probably occurred as ion pairs and not as precipitates of  $\text{Cu}(\text{OH})_2$  and  $\text{Zn}(\text{OH})_2$ . This is because speciation of the solutions related to these complexes is under-saturated related to  $\text{Cu}(\text{OH})_2$  and  $\text{Zn}(\text{OH})_2$ .

#### 5.4. Phreeqc Modeling of Geochemical Complexes

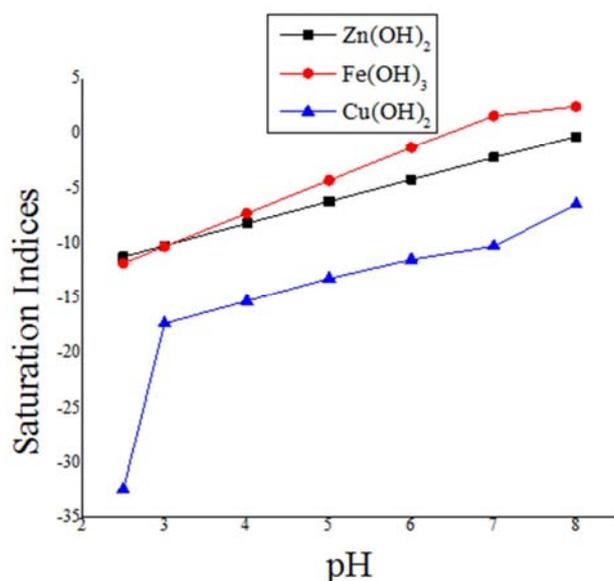


Figure 9. Plot of saturation indices versus pH.

Plot of saturation indices versus pH Speciation of the mine wastewater with respect to copper hydroxide and zinc hydroxide indicated under--saturation to these hydroxide species at all pH investigated (Figure 9). Saturation indices

increases with pH. Iron hydroxide is under saturated at lower pH, becoming super-saturated between pH7-8.

Speciation for these hydroxyl complexes are in the order  $\text{Fe}(\text{OH})_3 > \text{Zn}(\text{OH})_2 > \text{Cu}(\text{OH})_2$  and are dependent on pH. Complexes of iron hydroxide and hydroxide of zinc cross cut at pH 3, becoming dissimilar as pH increases. Cross cutting of saturation indices indicates similar saturation indices for these complexes at pH3. for these complexes. Neither Cu nor Zn appears to develop stable hydroxyl complexes. An alternative explanation could be that copper and zinc hydroxyl complexes were formed but became destabilized over time due to hydrolysis.

## 6. Conclusions

In this work the results of experimental characterization and modeling for copper and zinc sorption from Parys mine wastewater are presented.

- The experiments were performed in a laboratory using different mixed systems injected with iron sulfide mineral system.
- The model isotherm used in predicting the effects of composition of the solution and pH on copper and zinc removal are discussed,
- The results derived from the modeling are compared with work from other authors without the absence of sulfidic-anoxic condition.
- This work revealed the possibility of using empirical models to characterize complicated effects of Cu and Zn interaction with mixed systems under sulfidic-anoxic.
- Cross cutting pH effect has been observed on both copper and zinc sorption.
- Cp effect was non-promotive in all mineral systems.
- Stable hydroxylation of copper and zinc did not significantly contribute to copper and zinc removal.

## References

- [1] Egirani, D. E. Andrews, J. E Baker, A. R. (2013). "Characterization of Sorption and Quantitative Analysis of Hydroxyl Complexes of Cu and Zn In Aqueous Solution: The Interactive Effects of Mine Wastewater mixed Mineral Systems," *Inter. J. Recent Scientific Research*, 4, 469-475.
- [2] Ayari, F. Srasra, E. Trabelsi-Ayadi, M. (2007). "Retention of lead from an aqueous solution by use of bentonite as adsorbent for reducing leaching from industrial effluents," *Desalination*, 206, 270-278.
- [3] Brower, J. B. Ryan, R. L Pazirande, M. (1997). "Comparison of ion exchange resins and biosorbings for the removal of heavy metals from plating factory wastewater," *Environmental Science & Technology*, 31, 2910-2914.
- [4] Veli, S. Alyüz, B. (2007). "Adsorption of copper and zinc from aqueous solutions by using natural clay," *J. Hazard. Mater.*, 149,226-233.
- [5] Megateli, S. Semsari, S. Couderchet, M. (2009). "Toxicity and removal of heavy metals (cadmium, copper, and zinc) by Lemna gibba," *Ecotoxicol. Environ. Saf.*, 72, 1774-1780.

- [6] Chan, S. S. Chow, H. Wong, M. H. (1991). "Microalgae as a bioabsorbents for treating mixture of electroplating and sewage effluent," *Biomed. Environ. Sci.* 4, 250–260.
- [7] Zhang, Y. Yang, Y. L. L. Ma, X. Wang, L. Ye, Z. (2010). "Characterization and adsorption mechanism of Zn<sup>2+</sup> removal by PVA/EDTA resin in polluted water," *J. Hazard. Mater.* 178,1046–1054.
- [8] Fernández-Calviño, D. Pérez-Novo, C. Bermúdez-Couso, A. López-Periago, E. Arias-Estévez, M. (2010). "Batch and stirred flow reactor experiments on Zn sorption in acid soils Cu competition," *Geoderma*, 159, 417–424.
- [9] Terminghoff, E.J. M. Van Der Zee, S. A. Keizer, M. G. (1994). "The desorption and speciation of copper in a sandy soil," *J. Soil Sci.*, 158, 398–407.
- [10] Altin, O. Özbelge, H. Ö. Dogu, T. (1999). "Effect of pH in an aqueous medium on the surface area, pore size distribution, density, and porosity of montmorillonite," *J. Colloid Interface Sci.*, 217, 19–27.
- [11] Kitano, Y. Okumura, M. Idogaki, M. (1980). "Abnormal behaviour of Cu<sup>2+</sup> and Zn ions in parent solution at the early stage of calcite formations," *Geochem. J.*, 14, 167–175.
- [12] Banks, D. Burke, S. P. Gray, C. G. (1997). "Drainage and other ferruginous waters in north Derbyshire and south Yorkshire, U. K.," *J. Eng. Geol.*, 30, 257–280.
- [13] Schlegel, M. L. Manceau, A., Charlet, L. Chateigner, D. Hazemann, J.-L. (2001). "Sorption of metal ions on clay minerals. III. Nucleation and epitaxial growth of Zn on the edges of hectorite," *Geochimica et Cosmochimica Acta*, 65, 4155–4170.
- [14] Younger, P L, Banwert, S A, Hedin, R S. (2002). "Mine water, hydrology, pollution and remediation," *Springer* [Ed.], London, 16, 442 p.
- [15] Appel, C. Ma, L. (2002). "Concentration, pH, and surface charge effects on. Cd and Pb sorption in tropical soils," *J. Environ. Qual.*, 31, 581–589.
- [16] Song, H. Yim, G-J. Ji, S-W. Neculita, C. M. Hwang, T. (2012). "Pilot-scale passive bioreactors for the treatment of acid mine drainage: Efficiency of mushroom compost vs. mixed substrates for metal removal," *J. Environ. Mgt.*, 111, 150–158.
- [17] Holan, Z. R. Volesky, B. (1994). "Biosorption of lead and nickel by biomass of marine algae," *Biotechnol. Bioengery*, 43, 1001–1009.
- [18] Akar, T. Kaynak, Z. Ulusoy, S. Yuvaci, D. Ozsari, G. Akar, S. T. (2009). "Enhanced biosorption of nickel(II) ions by silica-gel-immobilized waste biomass: biosorption characteristics in batch and dynamic flow mode," *J. Hazard. Mater.* 163, 1134–1141.
- [19] Shao, W. Chen, L. Lu, L. Luo, F. (2011). "Removal of lead (II) from aqueous solution by a new biosorption material by immobilizing Cyanex272 in cornstalks," *Desalination*, 265, 177–183.
- [20] Dzombak, D. A. Morel, F. (1999). "Surface complexation modeling: hydrous ferric oxide," Wiley, New York, pp. 20.
- [21] Lutzenkirchen, J. (2001). "Ionic strength effects on cation sorption to oxides: macroscopic observations and their significance in microscopic interpretation," *J. Colloid Interface Sci.* 65, 149–155.
- [22] Devotta, I. Mashelkar, R. A. (1996). "Competitive diffusion-adsorption of polymers of differing chain lengths on solid surfaces," *Chem. Eng. Sci.* 51, 561–569.
- [23] Kamei, G. Ohmoto, H. (2000). "The kinetics of reactions between pyrite and O<sub>2</sub>-bearing water revealed from in situ monitoring DO, Eh and pH in a closed system," *Geochim. Cosmochim. Acta* 64, 2585–2601.
- [24] Ridge, A. C. Sedlak, D. L. (2004). "Copper and zinc complexes with EDTA during municipal wastewater treatment," *J. Water Res.* 38, 921–932.
- [25] Fotovat, A. Naidu R. Sumner, M. E. (1994). "Ionic-strength and ph effects on the sorption of cadmium and the surface-charge of soils," *European J. Soil Science*, 45 (4), 419–429.
- [26] Philips, I. R. (1999). "Copper, lead, cadmium and zinc sorption by waterlogged and air-dry soil," *J. Soil Contam.*, 8, 343–364.
- [27] Medina, M. Tapia, J. Pacheco, S. Espinosa, M. Rodriguez, R. (2010). "Adsorption of lead ions in aqueous solution using silica-alumina nanoparticles," *J. Non-Cryst. Solids*, 356, 383–387.
- [28] Tripathy, S. S. Kanungo, S. B. (2005). "Adsorption of Co<sup>2+</sup>, Ni<sup>2+</sup>, Cu<sup>2+</sup> and Zn<sup>2+</sup> from 0.5 M NaCl and major ion sea water," *J. Colloids Interface Sci.*, 28, 30–38.
- [29] Naeem, A. Siddique, M. T. Mustafa, S. Kim, Y. Dilara, B. (2009). "Cation exchange removal of Pb from aqueous solution by sorption onto NiO," *J. Hazard. Mater.*, 168, 364–368.
- [30] Morrison, S. J. Metzler, D. R. Dwyer, B. P. (2002). "Removal of As, Mn, Mo, Se, U, V and Zn from groundwater by zero-valent iron in a passive treatment cell: reaction progress modeling," *J. Contam. Hydrol.*, 56, 99–116.
- [31] Benjamin, M. M., (1983). "Adsorption and surface precipitation of metals of amorphous iron oxyhydroxide," *Environ., Sci., Technol.*, 17, 686–692.
- [32] Safdar, M. Mustafa, S. Naeem, A. Mahmood, T. Waseem, M. Tasleem, S. Ahmad, T. Siddique, M. T. (2011). "Effect of sorption on Co (II), Cu (II), Ni (II) and Zn(II) ions precipitation," *Desalination*, 266, 171–174.
- [33] Parkman, R. H. Charnock, J. M. Bryan, N. D. Livens, F. R. Vaughan, D. J. (1999). "Reactions of copper and cadmium ions in aqueous solution with goethite, lepidocrocite, mackinawite, and pyrite," *American Mineralogist*, 84, 407–419.
- [34] Gammons C. H. Frandsen, A. K. (2001). "Fate and transport of metals in H<sub>2</sub>S-rich waters at a treatment Wetland," *Geochem. Trans.* 2, 1–15.
- [35] Kumar, R. Barakat, M. A. Daza, Y. A. Woodcock, H. L. Kuhn, J. N. (2013). "EDTA functionalized silica for removal of Cu(II), Zn(II) and Ni(II) from aqueous solution," *J. Colloid and Interface Sci.*, 408,200–205.
- [36] Gomes, E. C. C. de Sousa, A. F. Vasconcelos, P. H. M. Melo, D. Q. Diogenes, I. C. N. de Sousa, E. H. S. (2013). "Synthesis of bifunctional mesoporous silica spheres as potential adsorbent for ions in solution," *Chem. Eng. J.*, 214, 27–33.
- [37] Wu, S. Kuschik, P. Wiessner, A. Müller, J. Saad, R. A. B. Dong, R. (2013). "Sulphur transformations in constructed wetlands for wastewater treatment: A review," *Ecological Engineering*, 52, 278–289.

- [38] Brix, H. (1999). "How 'green' are aquaculture, constructed wetlands and conventional wastewater treatment systems," *Water Sci. Technol.* 40 (3), 45–50.
- [39] Gopal, B. (1999). "Natural and constructed wetlands for wastewater treatment: potentials and problems," *Water Sci. Technol.*, 40 (3), 27–35.
- [40] Vymazal, J. (2005). "Horizontal sub-surface flow and hybrid constructed wetlands systems for wastewater treatment," *Ecol. Eng.*, 25, 478–490.
- [41] Gubbuk, I. H. (2011). "Isotherms and thermodynamics for the sorption of heavy metal ions onto functionalized sporopollenin," *J. Hazard. Mater.*, 186, 416–422.
- [42] Blesa, M. A. Magaz, G. Salfity, J. A. Weisz, A. D. (1997). "Structure and reactivity of colloidal metal particles immersed in water," *Solid State Ionics*, 101–103, 1235–1241.
- [43] Tombacz, E. Filipcseis, G. Szekeres, M. Gingl, Z. (1999). "Particle aggregation in complex aquatic systems," *J. Colloids Surf.*, 15, 233–244.
- [44] Bonnissel-Gissinger, P. Alnot, M. Ehrhardt, J. J. Behra, P. (1998). "surface oxidation of iron sulfide as a function of pH," *Environ. Sci. Technol.*, 32, 2839–2845, 1998.
- [45] Morse, J. W. Arakaki, T. (1993). "Adsorption and coprecipitation of divalent metals with mackinawite (FeS)," *Geochim Cosmochim Acta*, 57, 3635–3640.
- [46] Morse, J. W. Luther, G. W. (1999). "Chemical influences on trace metal-sulfide interactions in anoxic sediments," *Geochemical Et Cosmochimica Acta*, 63 (19-20), 3373-3378.
- [47] Odom, J. M. Singleton, J. R. (1983). "The sulfate-reducing bacteria: Contemporary perspectives," Springer- Verlag, New York, ISBN 0-387-97865-8.
- [48] Zagury, G. J. Kulnieks, V. I. Neculita, C. M. (2006). "Characterization and reactivity assessment of organic substrates for sulphate-reducing bacteria in acid mine drainage treatment," *Chemosphere*, 64, 944-954.
- [49] Neal, A. L. Techkarnjanaruk, S. Dohnalkova, A. McCready D. Peyton, B. M. Geesey G. G. (2001). "Iron sulfides and sulfur species produced at hematite surfaces in the presence of sulfate-reducing bacteria," *Geochimica et Cosmochimica Acta*, 65, 223-235.
- [50] Barrett, T. J. MacLean, W. H. Tennant, S. C. (2001). "Volcanic sequence and alteration at the Parys Mountain Volcanic-Hosted Massive Sulfide Deposit, Wales, United Kingdom: Applications of Immobile Element Lithogeochemistry," *Economic Geology*, 96: 1279-1305.
- [51] Cooper, D. C. Nutt, M. J. C. Morgan, D. J. (1982). "Reconnaissance geochemical survey of Anglesey," *Institute of Geology Science Report*, 90, 4.
- [52] Swallow, M. (1990). "Parys Mountain a mine in prospect," *Mining Magazine*, 163, 334–336.
- [53] Nelson, Y. M. (2002). "Effect of oxide formation mechanisms on lead adsorption by biogenic manganese (hydr) oxides, iron (hydr) oxides, and their mixtures," *Environ. Sci. and Technol.*, 36, 421-425.
- [54] Pointon, C. R. Ixer, R. A. (1980). "Acid mine drainage in Wales and influence of ochre precipitation on water chemistry," *Transactions of the Institute of Mining and Metallurgy*, 89, 143-155.
- [55] Engler, R. Patrick, W. (1973). "Sulfate reduction and sulfide oxidation in flooded soil as affected by chemical oxidants," *Soil Science*, 119, 217-221.
- [56] Walter, K. Johnson, D. (1992). "Microbiological and chemical characteristics of an acidic stream draining a disused copper mine," *Environ. Pollution*, 76: 169-175.
- [57] Egirani, D. E Baker, A. R. Andrews, J. E. (2005b). "Copper and Zinc removal from aqueous solution by mixed mineral systems I: Reactivity and removal kinetics," *J. Colloid and Interface Sci.*, 291, 319–32.
- [58] Parkhurst, D. L. Appelo, C. A. J. (1999). "User's Guide to PHREEQC (Version 2), A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations," U. S. Geological Survey *Water-Resources Investigations Paper*, 99-4259, 312.
- [59] Dunnette, D. A. Chynoweth, D. P. Mancy, K. H. (1985). "The source of hydrogen sulfide in anoxic Sediment," *Water Res.*, 19 (7), 875-884.
- [60] Wilkin, R. T. Barnes, H. L. (1996). "Pyrite formation by reactions of iron mono-sulfides with dissolved inorganic and organic sulfur species," *Geochim Cosmochim Acta*, 60, 4167.
- [61] Brunauer, S. Emmett, P. H. Teller, E. (1938). "Adsorption of gases in multimolecular layers," *J. Am. Chem. Soc.* 60, 309–319.