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Research Article

Removal of Manganese and Copper from Contaminated Groundwater Generated from Mines Landfills Waste Using ZV-I, AC and NZ in PRB Technology

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Abstract: In this study, Zero Valent Iron (ZV-I), Activated Carbon (AC) and Natural Zeolite (NZ) were utilized as reactive material for testing its effectiveness for removal manganese and copper in the waste of Mine Landfills. Hereby, four parameters were taken in this study which is initial concentration of metal, initial groundwater alkalinity PH and dosage of reactive ZV-I, AC, or NZ. Batch results show that ZV-I is the most effective materials for removal manganese and copper up to 48 ppm at low concentration of ZV-I 1990-4990 ppm while initial pH range varies between three through seven. The study discovered that ZV-I reactive compound can be used effectively for manganese removal through settling and adsorption on ZV-I, while copper is basically removed by ZV-I through direct reductive settling. Also, ACcompared to ZV-I reactive material has not significant effect on manganese removal whereas AC basically removed manganese by adsorption while Copper is removed basically by settling. The removal of Copper and manganese can be increased by increasing detention time and dosage of carbon. The study showed that manganese and copper are removed slowly and ineffective by NZ compound.

Keywords: Activated Carbon (AC), manganese and copper, Natural Zeolite (NZ), Permeable Reactive Barrier (PRB), Zero Valent Iron (ZV-I)

INTRODUCTION

Permeable reactive barriers have been developed and demonstrated to be effective for the treatment of dissolved metals (David and Carol, 1992; Powell *et al*., 1995; Kirk *et al*., 1995; Puls *et al*., 1999), acid-mine drainage (Waybrant *et al*., 1998; Benner *et al*., 1997; Benner *et al*., 1999) and dissolved nutrients (Baker *et al*., 1997). A wide range of reaction mechanisms can be employed to remove both negatively charged and positively charged inorganic species from flowing groundwater.These include simple adsorption (Morrison and Spangler, 1993), simple precipitation (McMurtry and Elton, 1985), adsorptive precipitation (Baker *et al*., 1997), reductive precipitation (David and Carol, 1992) and biologically mediated transformations (Waybrant *et al*., 1998; Benner *et al*., 1999). The use of permeable reactive barriers provides an alternative in situ approach to replace or supplement these existing techniques. Permeable reactive barriers are placed in the path of a migrating plume of contaminated groundwater. Reactive materials within the barrier are selected to promote geochemical reactions that result in the destruction or stabilization of the groundwater contaminants. Soils, Groundwater and surface water are polluted through acid seepage of mine called AS. AS is generated by oxidation of sulfide minerals, air, water and bacteria whereas AS causes high acidity H+ and high sulfates and heavy metals concentration. The treatment of polluted groundwater is expensive and has high sludge disposal therefore the groundwater is treated through using permeable reactive compounds. These compounds allow chemical reactions which is associated with polluted groundwater treatment. The previous studied in the last decade years showed the advantage of using reactive materials technic for treatment of acid seepage of mine (McMurtry and Elton, 1985). Polluted ground water with hazardous ions is remediated effectively by using ZV-I (Blowes *et al*., 2000) whereas reductive settling is main phenomena for ion removal by ZV-I. Settling in ZV-I permeable reactive barriers of iron oxidizing on the surface of iron minimized its re-activity. Settling accumulation of precipitates also decreases groundwater discharge through the barrier due to decreasing in its porosity. AC is used basically for organic matter removal and sometimes for inorganic materials. Activation process is carried out through by burning organic materials such as palm date. AC is porous and has high internal surface area which is optimum place for adsorption. Polluted ground water can be treated effectively from Copper, Zinc, carbon

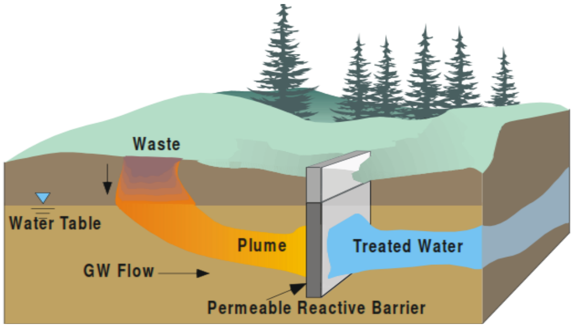


Fig. 1: Permeable reactive barriers

oxidize, mercury, Pb, cadmium and Nicle by AC (Hegazi, 2013). Zeolites compound has high surface area that can exchange cat-ions from their chemical structure like calcium, sodium, potassium and Manganese with metal cat-ions which is found in its groundwater. Previous experiments showed that heavy metal in wastewater can remove easily by zeolites compound (Park *et al*., 2002; Ouki and Kavannagh, 1997; Mier *et al*., 2001). Mines waste is found in Iraq due to many wars, (Iraq and Iran, Iraq-USA and Iraq-Daesh tourist in present time). Pollution risk by manganese and copper is coming from passing rain water through the waste of mine landfills to groundwater. So, this study aims to investigate ZV-I, AC and NZ for testing its effectiveness for removal manganese and copper in the waste of Mine Landfills. Also aims to study the using of these compounds for groundwater and AS remediation.

MATERIALS AND METHODS

This study is laboratory study.

Materials: ZV-I, AC and NZ are used as a reactive material for PRB technology (Fig. 1). Within this technology, the contaminants are removed from the groundwater aquifer by the flow of groundwater through a Permeable Reactive Barrier (PRB) filled with a reactive material. Simulated groundwater contaminated with manganese and copper ions is used in batch experiments. Reactive materials, ZV-I (Fig. 2), AC and NZ, are characterized to its chemical properties as shown in Table 1. Other properties are shown in Table 2. This section is variously called Methods or Methods and Materials. It should give essential details, including experimental design and statistical analysis.

Methodology-Kineticexperiments: For kinetic experiments, 1000 mL of batch glass reaction flasks which are containing two sampling ports

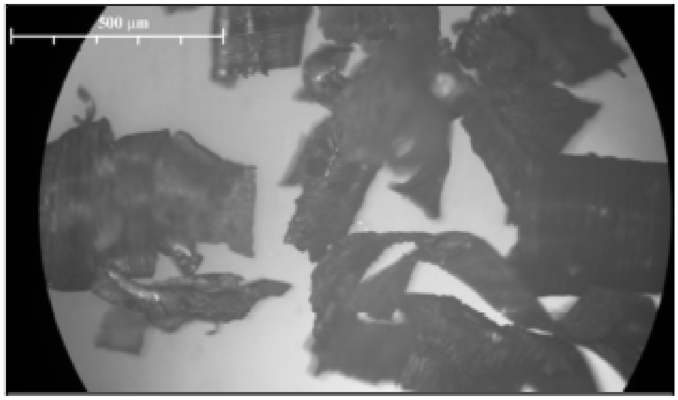


Fig. 2: ZV-I used in batch experiment (Tomasz, 2013)

Table 1: chemical analysis of ZV-I, AC and NZ

Element	ZV-I -W%	AC-W%	Compound	NZ-W%
Iron	92.93		Silicon dioxide	69.82
Carbon	3.29	80.38	Aluminum oxide	14.68
Silicon	2.15		Calcium oxide	5.66
Manganese	0.57		Potassium oxide	1.91
Aluminum	0.19		Iron (III)oxide	1.08
Sulfate	0.08	0.29	Magnesium oxide	1.01
Nickel	0.07		Sodium oxide	0.99
Crum	0.06		Titanium dioxide	0.32
Phosphor	0.03		Water	4.53
Water	0.63	4.88		

Table 2: Other properties of ZV-I, AC and NZ

Item	ZV-I	AC	NZ
Density (g/cm3)	2.65-2.89	0.46	0.86-1.09
Surface area (m2/g)	0.05-1	899.83	16.08
Granular Geometry (mm)	0.19-1.00	1.48-3.97	0.19-1.00
Acidity pH	5.2-5.4	10.19	7.91

Table 3: Experimental condition

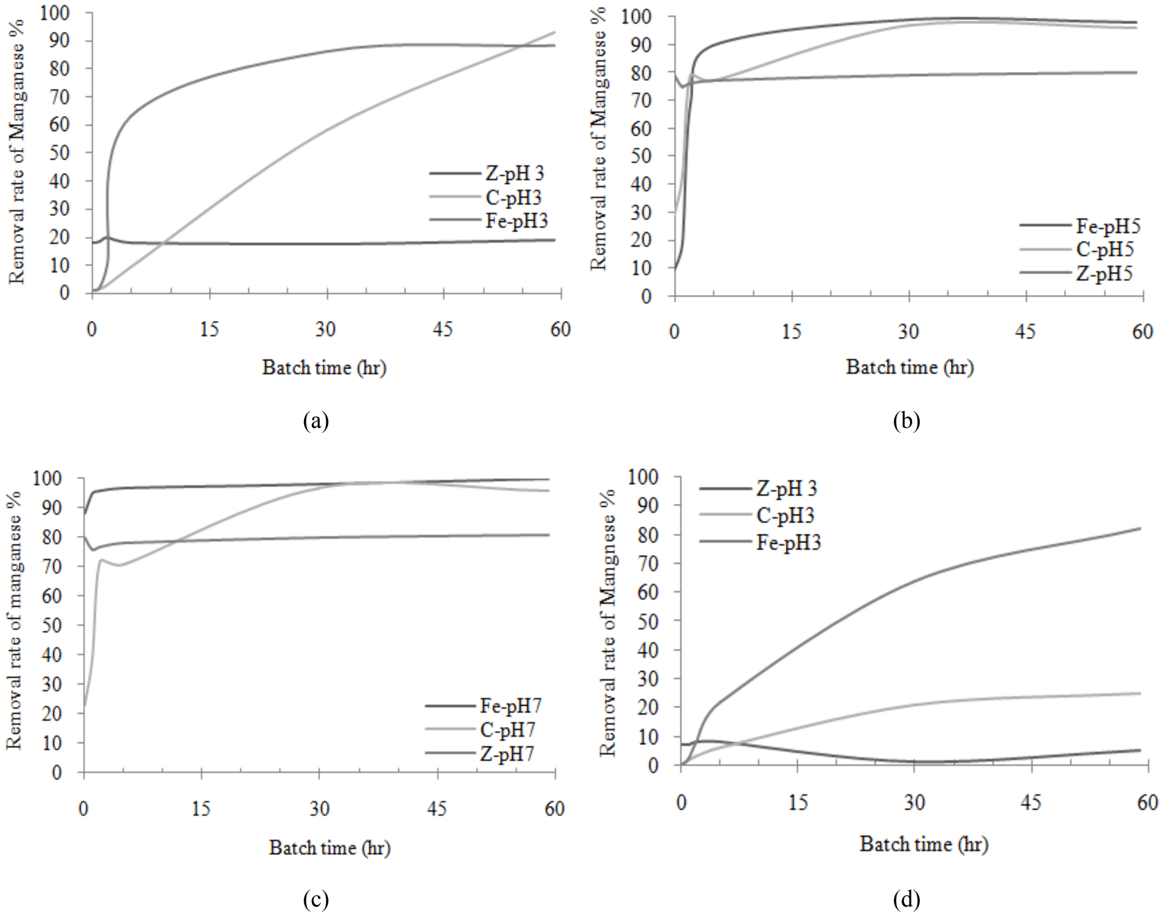
Item	Values
Material dosage	1990-4990 ppm
Initial concentration of manganese and Copper	6-48 ppm
Initial pH of $MnSO_4$ groundwater	3, 5 and 7
Initial pH of $CuSO_4$ groundwater	3 and 5

fitted with Teflonlined septa are utilized so materials could be removed or added by penetrating these septa with a syringe. Three parameters are studied which are Ion concentration, groundwater pH and reactive dosage. Atomic Adsorption Spectrophotometry, HGA-700, is used to calculate metal concentration while sulfate is calculated gravimetrically. Experiments condition is mentioned in Table 3.

RESULTS AND DISCUSSION

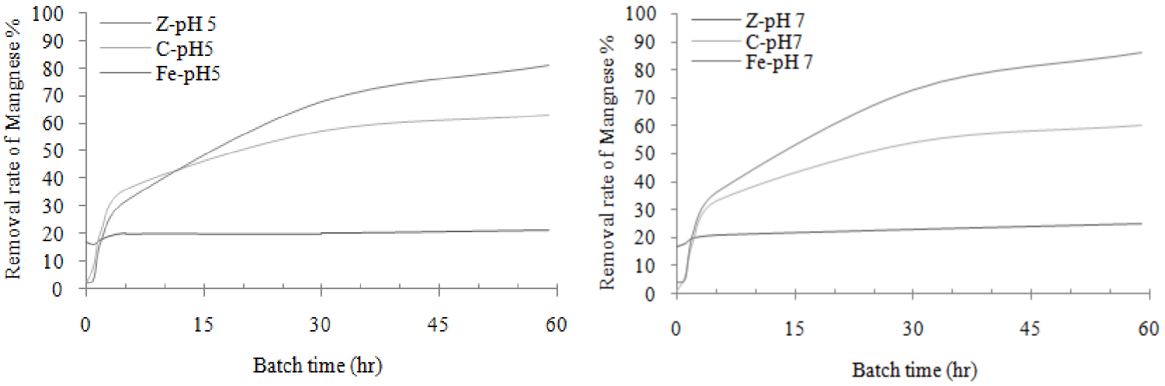
Removal rate of manganese: Removal of manganese in groundwater can be classified to three parts according to type of reactive materials used in batch experiments.

Removal by ZV-I: The kinetics results illustrated that reactive ZV-I causes rising in the Groundwater pH to natural value. When initial manganese concentration 6 ppm and ZV-I 4990 ppm, pH of groundwater reaches to 7.6 and 8.7 after two days but when the initial manganese concentration changed to 48 ppm, final groundwater pH reaches to 6.69 during two days, regardless the initial pH of groundwater. Regardless of reactive dosage of ZV-I and the initial manganese, ZV-I drops Eh of the groundwater to low values. This drop took place rapidly when the initial groundwater pH values are high. Eh values varied between 111mv and 221mV during one day. This indicates that moderate decreasing conditions is prevail in all studied systems after a short time period of 0.25 to 0.5h. For different initial pH of groundwater and manganese; reactive material dosage is 4990 ppm; the effect of seepage time on manganese removal is shown in Fig. 3a to 3f. The result proved that, only when pH be equal or more than 5, ZV-I has a significant effect on manganese removal. Manganese removal efficiency reached to 46% during two days at initial manganese concentration 6 ppm and ZV-I dosage is 1990 ppm while it changed to 85% when ZV-I dosage increasing to 4990 ppm during same period. It can be concluded from that, when the initial pH of groundwater is varied between 5 and 7, manganese removal efficiency increases dramatically for 1990 and 4990 ppm ZV-I dosages. Manganese



(a) (b)

(c) (d)



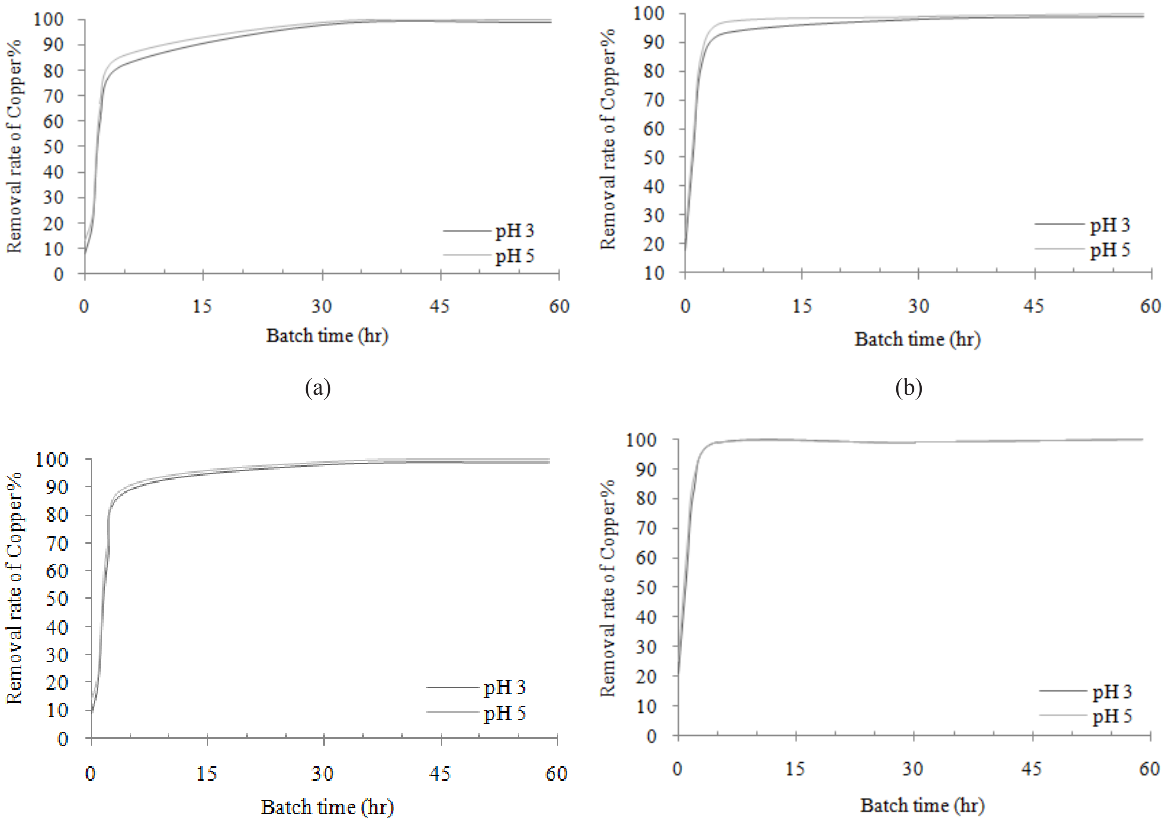
(e)

(f)

Fig. 3: Removal of manganese from polluted groundwater using ZV-I, AC, NZ; (a): At groundwater pH 3, initial manganese concentration 6 ppm and reactive dosage 4990 ppm; (b): At groundwater pH 5, initial manganese concentration 6 ppm and reactive dosage 4990 ppm; (c): At groundwater pH 7, initial manganese concentration 6 ppm and material dosage 4990 ppm; (d): At groundwater pH 3, initial manganese concentration 48 ppm and reactive dosage 4990 ppm; (e): At groundwater pH 5, initial manganese concentration 48 ppm and reactive dosage 4990g/l; (f): At groundwater pH 7, initial manganese concentration 48 ppm and dosage 4990 ppm

removal efficiency reaches 100% in less than two days and can reaches to 93% at 5h whereas ZV-I dosage is increased from 1990 ppm to 4990 ppm for minimizing time. Also, manganese removal efficiency reaches 100% after 1 day when ZV-I dosage is increased from 1990 to 4990 ppm, manganese removal efficiency approaches 64% during 1day and 87% during two days whereas this happen when the initial manganese raised straightly to 48 ppm and initial groundwater pH of 3 and ZV-I dosage of 4990 ppm. Similar efficiency is obtained, when the initial groundwater pH is 5 or 7 while manganese removal efficiency is obtained 93% during one day when the initial groundwater pH is 3, manganese removal efficiency is obtained 96% during 5h when the initial groundwater pH is high. It concluded from experimental results the increasing of initial manganese and ZV-I dosage lead to higher rates of electrochemical ZV-I corrosion while the conductivity of the groundwater increases due to high dissolved salts is higher. Therefore, higher rates of electrochemical corrosion are anticipated. At low pH of groundwater, ZV-I concentration rises with time. When groundwater pH equal or more than five, ZV-I concentration drops because of settling and manganese removal is commenced by precipitation /adsorption on iron oxhydroxide products where iron oxhydroxide displays excellent properties of sorption. The results revealed that when initial pH groundwater is higher (more than 5), Manganese is quickly removed by higher rate. Another view, when groundwater is diluted with pH 3 ZV-I, almost all precipitated manganese at the first stage will be solubilized. It is noticed that ZV-I takes out groundwater sulfate and this be more efficient at a wide range of groundwater ph. When manganese 48 ppm and pH varied between 3 to 7, more than 91 % of sulfate is taken out during four days. This can be explained as sulfate improves ZV-I oxidization therefore when ZV-I reaches Groundwater MnSO4, manganese and sulfates are effectively removed. Regardless of the initial manganese concentration, activate carbon absorber effects strongly on pH compared to other absorber like ZV-I where the Activate carbon absorber compared to ZV-I is a substantial absorber but not has high effect on manganese removal.

Removal by AC: It is observed in the laboratory, at the initial manganese is 6 ppm and the active carbon dosage is 4990 ppm, pH raised during one day from 3 to 7.9. Also it is observed, at initial pH of 5 to 7 and active carbon dosage is 1990 ppm, manganese removal exceeds only 23% after two days. Manganese removal reaches 79 and 97%, respectively, when initial manganese is 6 ppm and initial pH is 3. Manganese removal rose to 60 and 97% at initial pH 5, 7 respectively and when the absorbent dosage is raised to 4990 ppm within one day and is almost completed within two days. But, Manganese removal decreased to 21, 55 and 57% at initial pH 3, 5 and 7 respectively at same absorbent dosage within two days and to 48, 87 and 92 % respectively after eight days. As a result, the main mechanisms responsible for manganese removal is adsorption through the surface of activate carbon where pH and surface area effect on manganese removal. The efficiency of adsorption by AC is related to the absorbent dosage when the initial manganese is 6 ppm. At PH 3, manganese adsorption at absorbent dosage 1990 ppm is approximately equal twice that of



(a)

(b)

(c)

(d)

Fig. 4: Removal of copperfrom polluted groundwater using ZV-I; (a): Initial copper concentration 6ppm and ZV-I dosage 1990 ppm; (b): At initial copper concentration 6 ppm and ZV-Idosage 4990 ppm; (c): At initial copper concentration 48 ppm and ZV-I dosage 1990 ppm; (d): At initial copper concentration 48 ppm and ZV-I dosage 4990 ppm

4990 ppm. when the initial manganese raises to 48 ppm and the activate carbon dosage to 4990 ppm, the adsorption efficiency raised to 23% mg manganese/1000 m2 of activate carbon. There is more complexes surface are generated due to decreasing of hydrogen (pH increases) and therefore this causes increasing in the removal of manganese.

Removal by NZ: NZ has low effect on manganese removal especially at low pH whereas at initial pH 3 and manganese 6 ppm, manganese removal is not exceeded 21 % after two days. It is observed from laboratory results at pH range from 5 to 7, manganese removal can be achieved 59% after two days when NZ dosage is 1990 ppm and 81% when NZ dosage is 4990 ppm. It is concluded that manganese removal by NZ is completed within a very short time period of 0.25-0.5 h whereas the ion exchange is the main mechanism by NZ. Ion exchange be effective when potassium ion is available and also other ions like sodium, calcium and magnesium are available in groundwater.

Removal rate of copper: Removal of copper in groundwater can be classified to three parts according to type of reactive materials used in batch experiments.

Removal by ZV-I: Figure 4a to 4d showed the effect of groundwater batch time on removal of Copper at different concentrations of Copper.

The experimental results showed that ZV-I can be removed Copper immediately and effectively during one day and under all variations of groundwater pH. The increasing of ZV-I dosage raised slightly removal rate of Copper. There are different mechanisms for removal of Copper because it is low reactivity than ZV-I and the main mechanism is reductive precipitation (Fig. 5).

The experimental results confirmed that ZV-I is the best reactive material for the removal of Copper from acidic groundwater over a wide variation range of pH. Sequential additions of copper sulfates with copper 48 ppm each 1.2 or 3.6ksec after separation phase of solid liquid discovered that ZV-I, at a dosage of 1990 ppm, maintains its removal efficiency of Copper for fifteen groundwater phases at 3 of initial groundwater pH.

Removal by AC: Experimental results revealed that Copper removal rate depends strongly on groundwater pH. When the initial concentration of Copper is 6 ppm, AC dosage is 1990 ppm and the initial groundwater pH is 3, removal of Copper gets only 11% during two days.

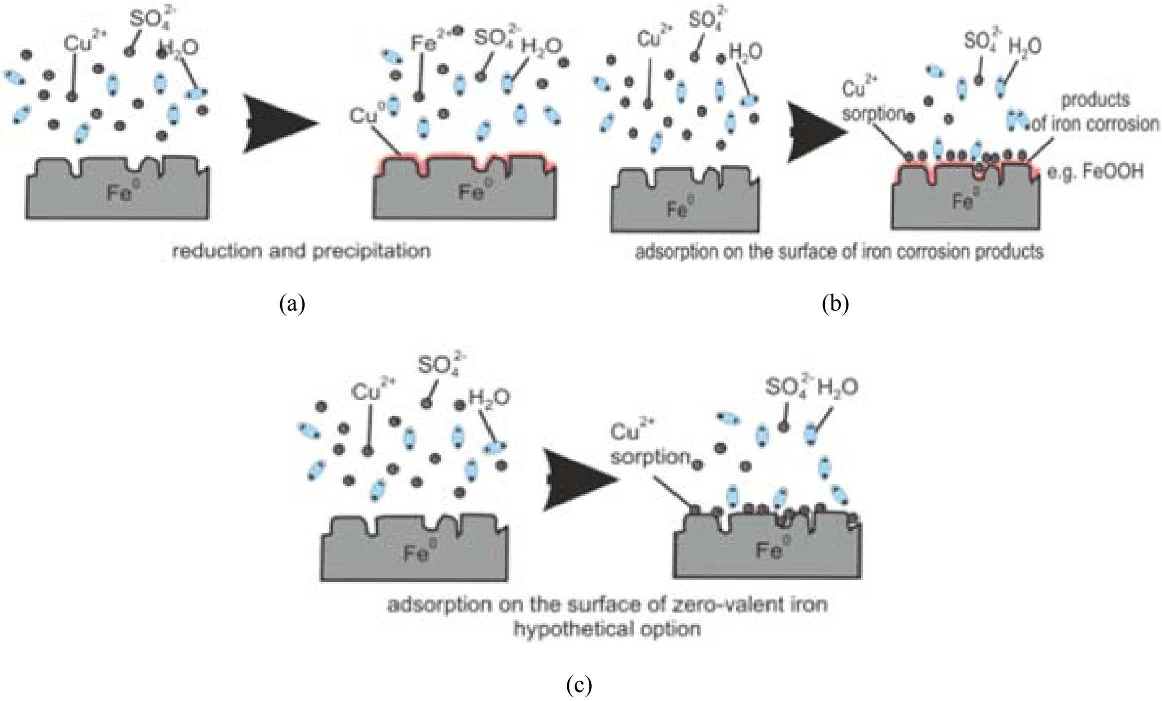


Fig. 5: Mechanism of copper removal from groundwater using ZV-I

At a dosage 4990 ppm, removal of Copper raised extremely to reach 99% during one day. At initial groundwater pH 5 and a dosage of 1990 ppm, removal of Copper was 94% while the removal rate reaches to 99% at a dosage of 4990 ppm. At initial Copper concentration 48 ppm, the removal rate of Copper doesn't exceed 21.5% when a reactive dosage 1990 ppm during two days but the removal rate increases to 72.9% when a reactive dosage 4990 ppm. At initial groundwater pH 5, the removal rate is enhanced where the removal rate exceeds 98.5 % during two days at a dosage 4990 ppm during all initial Copper concentration.

At low dosages, ACis not effective in removing Copper ion from acidic groundwater. The analysis of thermodynamic implemented discovered Copper precipitation is commenced at pH varied from 5.6 to 6.3 at initial Copper 6 or 48 ppm. The experimental result approved that Copper is removed from groundwater because of precipitation of Copper more than adsorption process on AC because it increased groundwater pH to required level of precipitation. Copper removal is inadequate at low dosage of ACwhere this dosage does not raise groundwater pH from 3 to required value for copper precipitation.

Removal by NZ: Removal of Copper by NZ is limited and not effective in acidic solutions. At initial Copper of 5 ppm and initial groundwater pH 3, the removal rate of Copper doesn't exceed 25.6% even at a dosage 4990 ppm during two days. The removal rate of Copper is 70% at pH 5 and a dosage 1990 ppm while it is reached to 93% when dosage increased to 4990 ppm. At initial Copper of 48 ppm and initial solution pH of 3 or 5, removal rate of Copper reach to 21 and 38% during two days respectively. It is observed that Ion exchange was the main mechanism for removal of copper by NZ. That is proved by the presence of Potassium, sodium, Calcium and Magnesium ions in groundwater.

CONCLUSION

In this study three reactive materials (ZV-I, AC and NZ) have been investigated for testing its effectiveness for removal manganese and copper in the waste of Mine Landfills. The experiments results discovered the following.

NZ reactive material:

- NZ is the low efficient reactive material in removing manganese and copper in the waste of Mine Landfills.
- Ion exchange is the main mechanism for removal of manganese and copper by NZ.

AC reactive material:

- AC has a positive influence on manganese and copper removal, particularly when manganese and copper are found in little concentrations.
- Adsorption is the main mechanism for removal of manganese by AC whiles the precipitation more

than adsorption is the main mechanism for removal of Copper by activated carbon.

ZV-I reactive material:

- ZV-I is the best reactive material among them for the removal of manganese and Copper from sulfate groundwater over a wide range of pH.
- Precipitation and/or adsorption on iron oxy-hydroxide formed are the main mechanisms for removal of manganese.
- Direct reductive precipitation is the main mechanism for Copper removal.

It is concluded for groundwater containment by manganese and Copper, ZV-I can be quickly built reactive barriers to clear-out manganese and Copper from acidic groundwater or containment groundwater.

Conflict of interest: The author declares that there is no conflict of interest regarding the publication of this manuscript.

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