

Removal of Copper (II) by Using Iron Oxide Coated Sand (IOCS) to Remediate Groundwater

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Abstract

In this study, natural sand and Iron Oxide Coated Sand (IOCS) were used to remove copper from contaminated groundwater. In the batch tests, the influence of several operating parameters such as contact time (0-90 min), initial pH of the solution (2-9), sorbent dose (0.1 to 5 g of adsorbent per 50 mL), initial concentration of copper (50-250 mg/l), and agitation speed (0-250 rpm) were investigated. The best values of these parameters that will achieve the maximum removal efficiency of Cu^{+2} were contact time was 60 min, pH=7, adsorbent dose =1 g per 50 mL, and agitation speed= 200 rpm respectively. The sorption data obtained by batch experiments have been subjected to the Langmuir and Freundlich isotherm models. The results showed that the Langmuir isotherm model described well the sorption of these Cu^{+2} ions on the IOCS in compared with Freundlich model under the studied conditions.

Keywords: Copper; Iron Oxide Coated Sand; Permeable reactive barrier; Groundwater; Heavy metal

الخلاصة

في هذا البحث تم استخدام الرمل المغلف بأوكسيد الحديد لإزالة أيونات النحاس من المياه الجوفية الملوثة. في اختبارات الدفعة (batch) تم دراسة تأثير عدة عوامل مثل زمن التماس (٠-٩٠ دقيقة)، وحامضية المحلول pH (٢-٩)، وكمية المادة المازة (٠.١ - ٥ غم) لكل ٥٠ مل، والتركيز الأولي لمحلول النحاس (٥٠-٢٥٠ مغم/لتر)، وكذلك سرعة المزج (٠-٢٥٠ دورة/دقيقة). أفضل القيم لهذه العوامل والتي حققت أعلى إزالة لأيونات النحاس من المحلول كانت كما يأتي: زمن التماس = ٦٠ دقيقة، الحامضية = ٧، كمية المادة المازة = ١ غم/٥٠ مل، وسرعة المزج = ٢٠٠ دورة/دقيقة. تم تطبيق نموذجي لانكوير وفريندلج على النماذج المتحصله وقد اظهرت نتائج الامتزاز ان موديل لانكوير هو الافضل تمثيلا للبيانات مقارنة بموديل فريندلج.

الكلمات المفتاحية: النحاس، الرمل المغلف بأوكسيد الحديد، الحاجز التفاعلي النفاذ، المياه الجوفية، المعادن الثقيلة

1. Introduction

Heavy metals pollution of ground water is caused by various metals, especially cobalt (CO), copper (Cu), nickel (Ni), chromium (Cr), mercury (Hg), lead (Pb), cadmium (Cd), and zinc (Zn), which come from different industrial activities such as mining operation, tanneries electronics, electroplating, petroleum refineries and petrochemical industries Shahlaa *et al.* (2015).

In the middle and southern regions of Iraq, the fresh water situation is especially acute, (especially, during 2014-2015 years), among other draw back, to an increase in desertification. A number of factors is to blame, foremost of which are water-important projects in river-source countries (Turkey and Iran) and scanty rainfall due to climate change, which effect on agriculture sector suffering from years of scarcity as a cited by (Faisal and Hmood, 2013).

Significant progress has been made improving air quality, cleaning up and preventing leaching from dumps and landfills, and improving surface water quality. Among the more difficult and expensive environmental problems, and often the primary factor limiting closure of contaminated sites following surface restoration, is contaminated ground water. The most common technology used for remediating ground water is surface treatment where water is pumped to the surface, treated and

pumped back into the ground or released at a nearby river or lake. These technologies are costly. Hence, the limitation of them has recently been recognized, along with the need for innovative solution to remediate groundwater contaminated with heavy metals. One of the most effective technologies is the in situ treatment of ground water contaminants by means of permeable reactive barrier (PRB). This technology is constructed of reactive materials is placed in the subsurface between waste or contaminated area and the ground water. Hence, the contaminant moves through the reactive material; the contaminant is either sorbed or chemically reacts with the material to form a less harmful substance (Moore *et al.*, 2003).

Many experimental studies concerning the migration of heavy metals through PRB were achieved as follows. The application of natural zeolite as permeable reactive barrier for lead removal from contaminated water. The values of retardation coefficient were evaluated from batch and column studies indicate the ability of zeolite barrier to retain the contaminant (Medvidovic' *et al.*, 2013). A set batch and column tests were performed the design factors for the development of PRBs against groundwater contaminated with ammonium, lead, and copper vs clinoptilolite was chosen as a reactive material (Park *et al.*, 2002). The use of Zero-Valent Iron (ZVI) as Permeable Reactive Barrier (PRB) to remove zinc from contaminated groundwater, finite difference method and Comsol Multiphysics 3.5 a software, were used to simulate the one-dimensional equilibrium transport of zinc through sandy aquifer with and without presence of PRB (Faisal *et al.*, 2014). The removal of cadmium from contaminated shallow aquifer by Zeolite was investigated; a 1D numerical finite difference model has been developed to describe pollutant transport within groundwater taking pollutant sorption on the permeable reactive barrier (Faisal and Hmood, 2013). Mechanism of lead removal is by using natural sand and clay coated with polyaniline and iron oxide as adsorbent via fixed bed column and completely mixed batch reactor. The mechanism was to be using iron oxide coated clay and sand may be applied successfully in water purification technologies in order to remove Pb (II) from aqueous solution (Eisazadeh *et al.*, 2013). The significance of the study is to assess ability of natural sand coated with iron oxide as a reactive barrier material, theoretically and experimentally for removal dissolved Cu(II) from synthetic contaminated groundwater

2. Experimental work

2.1 Materials

Sand samples obtained from a granular filter plant were used as porous medium in the experiments conducted in the present study. They were sieved through a 2- mm stainless steel mesh to remove large stones and debris to obtain soil sample with particles less than 2 mm, and oven-dried overnight at 105 °C to remove soil moisture. Depended on particle size distribution (ASTM D 422). The percentage of sand, silt, and clay were 99, 1, and 0%, respectively. Accordingly, this soil can be classified as sandy soil. The permeability of this sand, measured with a constant head permeability test was 2×10^{-4} cm/s. The measured values of the porosity and bulk density were 0.42 and 1.01 g/cm³, respectively.

Sand coated with iron oxide was prepared by using a modified precipitation method was applied in this study, as cited by Thapanapong *et al.*, (2011). The sand was collected and treated at a specified pretreatment temperature for 3 hrs before coating. The amount of 5 g sand was added to 10mL of solution containing 2.0 g Fe(NO₃)₃.9H₂O (2.77%, w/v, Fe). The pH of the mixture was adjusted to the desired value with NaOH. The mixture was stirred for 1 hr, dried at 105°C for 20 h and then washed with distilled water to remove unattached oxide until the pH of the runoff water was constant (pH 7–8). The solid was dried at 105°C for 24 hrs and finally

stored in a capped bottle for further use. The effects of pretreatment temperature, pH of ferric solution and amount of ferric nitrate were studied. The effect of coating parameters was evaluated by comparing the adsorption capacity for Cu (II) ions of the adsorbents obtained from different preparation conditions. The measured values of the porosity and bulk density for sand coated with iron oxide were 0.33 and 1.15 g/cm³, respectively.

Copper was selected as a representative of heavy metal contaminants. To simulate water pollution, a solution of Cu (NO₃)₂.4H₂O (manufactured by SELZE-HANNOVER, Germany) was prepared and added to the specimen of water to obtain representative concentration.

2.2 Batch experiments

Adsorption of Cu (II) using sand and sand coated with iron oxide was carried out using batch experiments. About 0.5 g of sand coated with iron oxide and 50 mL of solution contaminated with Cu(II) was agitated using orbital shaker for 2 hrs. with initial pH 7 at ± 25 °C temperature of lab. The Cu(II) remained was measured by atomic absorption spectrophotometer (AAS).

Kinetic studies were investigated with different values of pH (2, 4, 6, 7, 9, and 11), different values of initial concentration of Cu⁺² (50, 100, 150, and 200 mg/l), different amounts of adsorbent dosage (0.1, 0.2, 0.5, 1, 2, 3, and 5 g) according to Sulaymon *et al.*, (2014) and finally different values of agitation speed (50, 200, and 250 rpm). Eventually, geochemical calculation and batch tests were conducted pre-screen potential candidates for step of study by using column tests. The adsorption capacity, q_e (mg g⁻¹) is computed using equation (Chen *et al.*, 2015):

$$q_e = (C_o - C_e) \frac{V}{m} \quad (1)$$

where q_e is the amount of heavy metal removed from solution (mg/g), C_o is the initial concentration of heavy metal in the solution before mixing with reactive material (mg/l), C_e is the equilibrium concentration of heavy metal left in the solution at the end of the experiment (mg/l), V is the volume of solution in the flask (l), and m is the mass of reactive material in the flask (g) Wang *et al.* (2009).

The individual Langmuir and Freundlich adsorption isotherm were produced by plotting the q_e against the C_e at constant temperature. Langmuir (Eq. (2)) and Freundlich (Eq. (3)) models were used for the description of sorption data (Faisal *et al.*, 2014) as follows:

$$q_e = \frac{abc_e}{1+bc_e} \quad (2)$$

$$q_e = K_F C_e^{1/n} \quad (3)$$

Where a is empirical constant, b is the saturation coefficient (l/mg), K_F is the Freundlich sorption coefficient, and n is an empirical coefficient.

2.3 Column experiments

Dynamic flow experiments were performed using laboratory stand up constructed of Perspex cylinder having height and diameter equal to 90 and 5 cm, respectively, as the same shape adopted by (Faisal and Hmood, 2013), as shown in schematic diagram Fig(1).

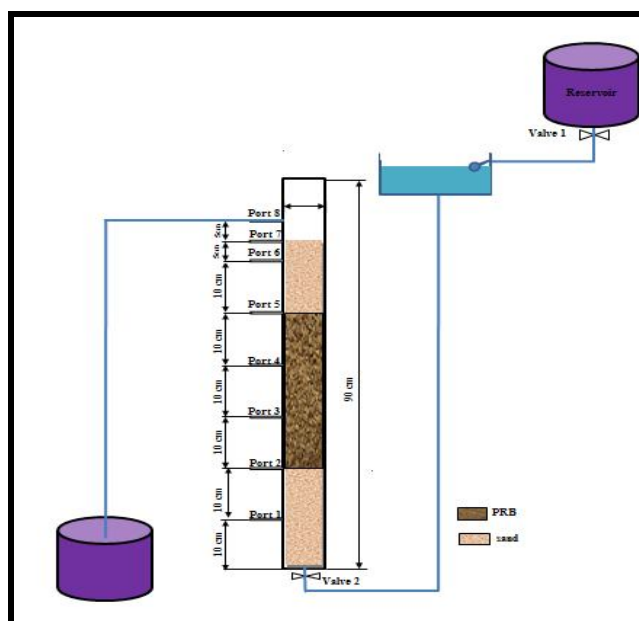


Figure1: Schematic diagram of the laboratory-scale column.

The contaminated solution with Cu^{+2} , which simulated the contaminated groundwater, was directed in an upward flow from certain reservoir. The flow from this reservoir, which is placed at the elevation higher than the level of column outlet, was controlled by 15 liters constant head tank design to provide a constant pressure to the column. The pressure drop was chosen to provide an initial flow rate of 20 mL/min according to Thu Nguyen (2012)., and pressure head drop was kept constant throughout the duration of experiment. The flow rate was measured periodically to predict the hydraulic conductivity based on the volume of the contaminated water collected during certain time periods (e.g. 15 min, 30 min, 1 h... etc.). Some of the columns used were equipped with five sampling ports at the distance of 10 cm (port 1), 20cm (port 2), 25 cm (port 3), 30 cm (port 4), 40 cm (port 5), 50 cm (port 6), 60 cm (port 7), 65 cm (port 8), 75 cm (port 9), and 80cm (port 10) from the bottom according to procedure adopted by Sulaymona *et al.* (2015). These ports along the length of the column should be constructed of stainless steel fittings which blocked with Viton stoppers. Sampling was carried out at specified periods from sampling ports using needle to be inserted into the center axis of the column according to Faisal *et al.* (2014). The influent line consisted of PTFE tubing connecting reservoir to the fitting on the bottom of the glass column. On the effluent end of the column, PTFE tubing made the connection between the column and the effluent collection bottle, about 11–15 liter of artificial contaminated water was flushed the column for each experiment.

The column specimens were packed with three different layers of porous media. The bottom 20 cm layer was packed with sand (Doina *et al.*, 2011). Then, permeable reactive barrier (iron oxide coated sand) with depth of 30 cm was placed at the top surface of the packed sand. Again, the top 30 cm of the column was packed with layer of sand. This configuration is presented a simulation for proposed theoretical as cited by (Faisal and Hmood, 2013).

Leaching of the contaminated solution with Cu^{+2} was monitored in the samples collected from the effluent port of the column. During the first 48 h of testing, frequent sampling (every 5 hr.) was performed to observe the leaching breakthrough curve of each metal studied. The samples were collected in new poly-ethylene vials, previously cleaned with acid, and analyzed by AAS (Doina *et al.*, 2011). The filling

material in the column was assumed to be homogeneous and incompressible, and constant over time for water-filled porosity. All tubing and fitting for the influent and effluent lines were composed of an inert material as a cited by Faisal *et al.* (2014)..

A solution of 1 g/l NaCl in deionized water as a tracer was continuously fed into the column at corresponding pore velocity equal to 0.017 cm/sec. Note that the injected tracer source concentration should be low enough to avoid any density effects and gravity segregation. This tracer has been widely used due to its safety, cheapness, weak propensity to adsorption, not being affected by the liquids density and viscosity, and the easy detection of the concentration changes. The concentration of ion chloride (Cl^-) was measured with time by using titration. In this case, the value of D_L is given by the following formula (Ujfaludi, 1986) as reported by Faisal *et al.* (2014):

$$D_L = \frac{1}{8} \left[\frac{(x_0 - Vt_{0.16})}{(t_{0.16})^{0.5}} - \frac{(x_0 - Vt_{0.84})}{(t_{0.84})^{0.5}} \right]^2 \quad (4)$$

Where D_L is the longitudinal dispersion coefficient, V is the mean pore velocity of seepage (volume rate of flow per unit cross sectional area of voids), $t_{0.16}$ and $t_{0.84}$ are the arrival times of $C/C_0 = 0.16$ and 0.84 relative concentration values, respectively.

In order to establish the relationship between the D_L and V , the experiment described above was repeated with another three values of pore velocity. These values were 0.2, 0.4, and 0.6 l/hr. According to Fetter in 1999.

3- Results and Discussion

3.1 Characterization of Reactive Materials

According a modified precipitation method was adopted by Thapanapong *et al.*, (2011) in coating natural sand in this study. The importance studying effect different pH of ferric solution Fe was evaluated by comparing adsorption capacity for Cu (II) ion of coated sand obtained as shown in table 1 (according arrangement by Thapanapong *et al.*, 2011). As the pH was increasing from 3 to 11, the adsorption capacity of the coated sand also increased. These result indicate that the pH higher than 3 was attributed to the adsorption of ferric hydroxide precipitate on the surface as a cited by (Thapanapong *et al.*, 2011). As can be seen when iron oxide coated natural sand at the pH 11, the removal percentage of Cu (II) (ratio of the removed Cu (II) to the initial quantity of Cu (II)) was increased from 33% of non-coated sand to 86.59 for coated sand. Therefore the pH of 11 was chosen for iron oxide coating when amount of ferric nitrate used in coating sand was 2 gm in 10 mL solution (2.77%, w/v Fe) for coating of 5g sand. Because of excessive amount of ferric nitrate was used the uncoated iron oxide would be removed by washing at the end of preparation process. Therefore the concentration of (2.77% w/v Fe) was proposed for the coating (Thapanapong *et al.*, 2011).

Table 1: Effect of pH for Fe on the adsorption capacity.

Parameters	Adsorption capacity for Cu (mg/g)	
	Non coated sand Removal efficiency (%)	Coated sand Removal efficiency (%)
Natural sand	33	
pH of ferric solution		
3		31
7		79
11		86.54

The surface morphology and fundamental physical properties of the reactive material were assessed by SEM imaging. The SEM pictures of IOCS are shown in Figure 1. It is obvious that the natural sand structure was composed of angular edge and rounded particle, in sand composites. These indicate that the surface morphology was depending on the type of substrate and coating (Eisazadeh *et al.*, 2013).

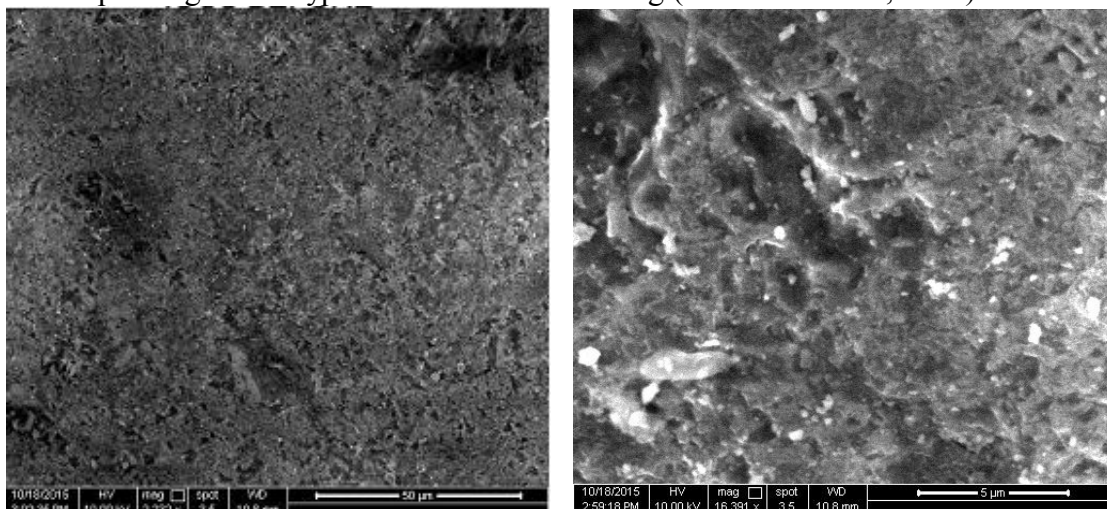


Figure 1: Scanning electron micrograph image for IOCS.

3.2 Effect of contact time and initial pH of solution

The effect of pH on the removal of Cu (II) ion from solution was investigated by varying the pH metal solution within range of 2-11 (figure 2). Copper on an aqueous solution can form various ionic species depending on the solution pH. The predominant ionic species is Cu (II) for pH between sand where copper is present mainly as Cu (II). The predominant ionic species is Zn^{+2} and $Zn(OH)_2$, and in lesser quantities as $Zn(OH)^+$ for pH < 7 as acited by (Chayapat *et al.*, 2015).

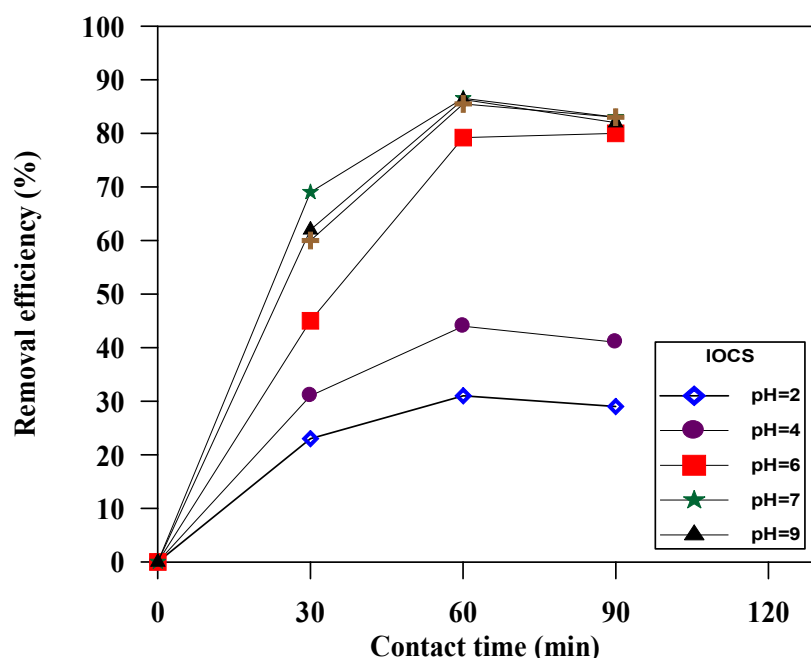


Figure 2: Effect of initial pH on removal efficiency of copper by IOCS as a function of contact time ($C_o = 50$ mg/l; IOCS dose= 1 g/50 mL; agitation speed= 200 rpm; $T = 25^\circ\text{C}$).

In strong acid solution (pH between 2, and 4), only a slight amount of metal ions could be removed. This is because at low pH the protons ions compete with Cu^{+2} for adsorption on surface hydroxyl groups resulting in low metal adsorption. Moreover, when active sites are protonated, the surface charge of IOCS would probably be positive (pH_{pzc} hematite =7.0-9.4 (Susan, 2002)), and regarding the pH_{pzc} of iron oxide (pH_{pzc} goethite =8.73) as a cited by (Thapanapong *et al.*, 2011). In solution having pH value lower than pH_{pzc} of iron oxide, the surface hydroxyl sites could be protonated and positively charged. on other hand, the active site are deprotonated when the solution pH is higher than pH_{pzc} , resulting in negative charged sites and the adsorption metal cations on iron oxide could be possibly take place via electrostatic surface ((Thapanapong *et al.*, 2011, Tushar *et al.*, 2002, and Susan, 2002). However, specific adsorption is believed to occur as well for iron oxide. This adsorption involves interaction with deprotonated surface hydroxyl group to form mono and binuclear inner sphere complexes i.e. (Tushar *et al.*, 2002)



And



Cation adsorption is accompanied by release of protons. The number of protons released per cation adsorbed i.e. termed as Z (Tushar *et al.*, 2002). At pH 6 and higher, the precipitation of Cu (II) as metal hydroxide $\text{Cu}(\text{OH})_2$ was likely to occur as shown in Figure 3.

The removal of metal ions at these pH values could be attributed to both metal hydroxide precipitation and metal ions adsorption for IOCS and natural sand were determined to be between 6 and 7, respectively. The results observed in our study are in agreement with those Thapanapong *et al.*, 2011, and Tushar *et al.*, 2002. On other hand the adsorption efficiency increased rapidly upon increasing pH attained a value of 7; there was no difference in adsorption efficiencies for IOCS. The increase in adsorption efficiencies observed as the pH increase can be attributed to the favorable change in surface charge and to the extent of hydrolysis of metal ions as a cited by (Tushar *et al.*, 2002) as a cited by Unob *et al.* As the surface charge becomes more negative with increasing pH the surface attract metal cations resulting in higher adsorption efficiencies(Tushar *et al.*, 2002).



Figure 3: Precipitation of copper salts on the surface of container when pH=8.

3.3 Effect of Adsorbent Dose

Experiments were carried out to study the effect of adsorbent dosage on the uptake of Cu (II) ions onto adsorbents iron oxide coated sand (IOCS). These experiments were conducted using varying the amount of dose from 0.1 to 5 g for adsorbent per 50 mL of metal solution for batch tests at 25°C, while keeping other parameter as follows, $C_o = 50$ mg/l, pH of IOCS as adsorbent was 7, shaking speed = 200 rpm and contact time 60 min, as shown in Figure 4. This figure reveals effect for IOCS as adsorbent on removal efficiency of copper as a function of different amounts of adsorbent it was evident that increasing the mass of adsorbent from 0.1 to 5 g has increased the final removal percent. The removal percent has shown mild decreasing changes when 1-5 g for adsorbent have been utilized, this can be due to the fact that increasing in the number of active sites as the dosage increase (Prasanta et al., 2012). Hence in all the subsequent experiments (1g) weight of IOCS, also regard (2 g) weight of natural sand were fixed as optimum dosage which could gave the maximum removal efficiency of copper (II) ions.

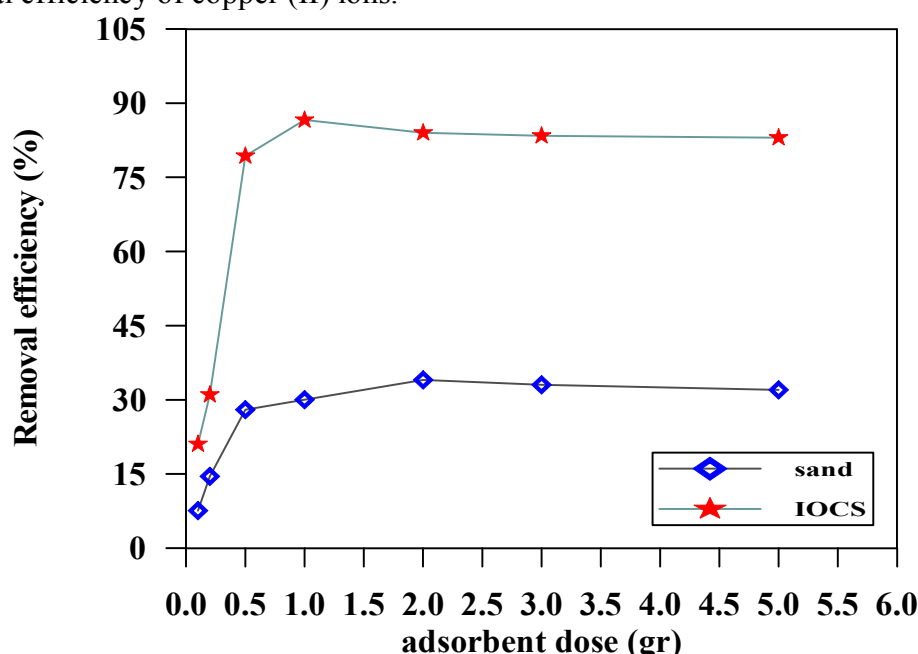


Figure 4: Effect of sorbent dosage on removal efficiency of copper ($C_o=50$ mg/l; pH=6; agitation speed= 200 rpm; contact time=60 min.; $T=25^\circ\text{C}$).

3.4 Effect of Initial Copper (II) Concentration

Batch experiments were carried out, to investigate the effect of initial copper concentration on its removal capacity by using adsorbent IOCS. These experiments were conducted using various concentration of metal range from 50 to 250 mg/l with optimum weight for IOCS (= 1 g), and sand (= 2 g) per 50 mL volume of solution shake at 200 rpm for 60 min, and initial pH of the solution is range from 7. Figure 5 presents the plot of copper initial concentration versus the copper removal efficiency by using adsorbent at equilibrium is well observed that by increasing the initial copper concentration from 50 to 250 mg/l, the removal efficiency decreased from 86.59% to 50% and 34% to 13% for IOCS, and sand respectively. This could be attributed to the fact that, at low initial concentration, the number of adsorption sites is more thus leading to increased removal of copper ions by using of adsorbent (IOCS, and natural sand). While at higher concentration, almost all the binding sites are filled and no site is available for further adsorption of Cu (II) ions thus leading to a decrease in percentage removal (Jain et al., 2015). Similar results have been reported by El-Said

et al (2010), and Chamanchi *et al.* (2012). They have also reported that the present Cu (II).

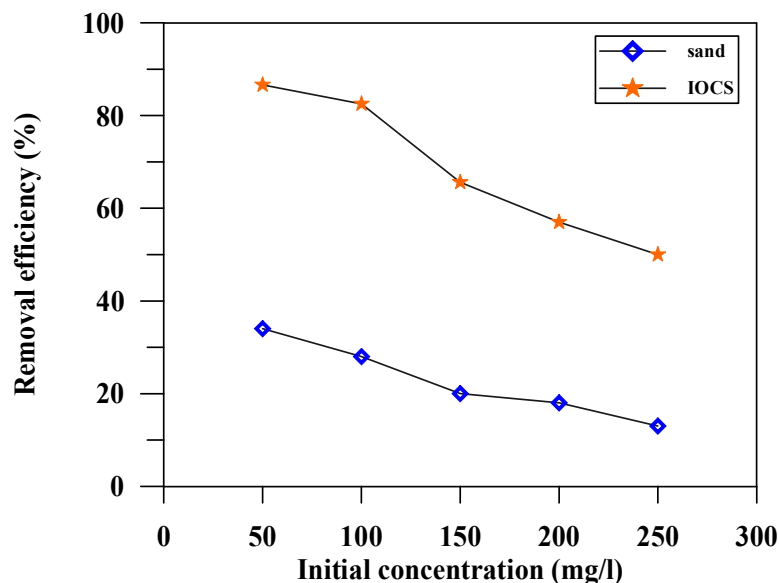


Figure 5: Effect of initial concentration on removal efficiency of copper by IOCS as adsorbent (pH=7; IOCS = 1 g/50 mL; agitation speed= 200 rpm; contact time=60 min.; T= 25°C).

3.5 Effect of Agitation Rate

A set of experimental was carried out to investigate the effect of three different agitation rates; 50, 200, and 250 rpm, on the removal of copper (II) ions by using of adsorbent (IOCS, and sand). The effect of agitation rate on the removal of copper using 50 mg/l initial concentration of copper, with optimum weight for IOCS (= 1g) and sand (= 2g) per 50 mL volume of solution, C_e time 60 min, and pH range of 7. Figure 6 shows that increasing shaking rate from 50 to 250 rpm, the removal efficiency increased from 67% to 85% and 22% to 33% for IOCS, and sand, respectively. Thus, the best equilibrium was reached at the agitation speed 200 rpm.

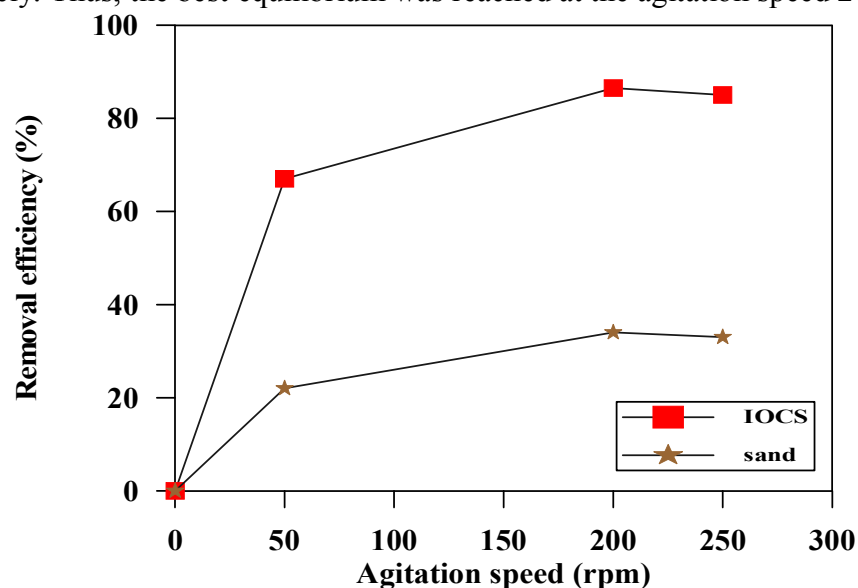


Figure 6: Effect of agitation speed on removal efficiency of copper for IOCS adsorbent (C_o =50 mg/l; pH=7; IOCS dose= 1 g and sand dose= 2 g per 50 mL; T= 25°C).

3.5 Sorption Isotherms

The adsorption isotherm were produced by plotting the amount of Cu^{+2} removed (adsorbed) from the solution (q_e in mg/g) against the equilibrium concentration of Cu^{+2} in the solution (C_e in mg/l) at constant temperature Faisal et al. (2014). The adsorption data were analyzed using Langmuir and Freundlich isotherm models are commonly used. These models are given by the eqs. 4 and 5, respectively.

$$q_e = \frac{0.7 C_e}{1+0.107 C_e} \quad R^2 = 0.985 \quad (4)$$

$$q_e = 1.32 C_e^{0.4} \quad R^2 = 0.918 \quad (5)$$

However it is clear that the Langmuir isotherm model provided the best correlation (coefficient of determination ($R^2=0.985$)) in compared with Freundlich isotherm model ($R^2 = 0.918$). Accordingly, the Langmuir isotherm model was used to describe the sorption of solute on solid in the partial differential equation governed the transport of a solute undergoing equilibrium sorption through different types of permeable reactive barrier, where used in this studying in the continuous mode Faisal et al. (2014).

3.6 Longitudinal Dispersion Coefficient

The longitudinal dispersion coefficient (D) is an important parameter needed to describe the transport of solutes in porous media. Thus accurate prediction of the spatial and temporal migration of contaminant requires accurate dispersion coefficient measurement. Result of the experimental runs concerned the measurement of longitudinal dispersion coefficient (D_L) of porous medium for IOCS acting as permeable reactive barrier in this study versus mean bore velocity are summarized in Table 2, and also shown in Figure 7 for IOCS and sand. It is clear that the curves inclined with horizontal axis. This suggests a linear relationship between the values of D_L and V for IOCS and sand, as cited by (Faisal and Hmood, 2013).

Because of the macroscopic similarity between molecular diffusion and mechanical dispersion, the coefficient D_m and D_h are often considered additive.

$$D = D_m + D_h \quad (6)$$

It is clear that longitudinal hydrodynamic dispersion coefficient consists from the molecular diffusion and from porous media flow as follows:

$$D_L = \alpha_L V + D^* \quad (7)$$

Where α_L is the longitudinal dispersivity (cm), and D^* was equal to τ (tortuosity) multiply by D_o (molecular diffusion coefficient, cm^2/s).

Table 2: calculated values of the longitudinal dispersivity for used medians as a function of mean pore velocity.

Flow rate (l/hr)		0.2	0.4	0.6
Sand	V (cm/s)	0.0067	0.0136	0.0202
	D_L (cm^2/s)	0.19	0.23	0.295
	α_L (cm)	5.8	5.8	5.8
IOCS	V (cm/s)	0.0086	0.0173	0.0256
	D_L (cm^2/s)	0.29	0.39	0.42
	α_L (cm)	11.5	11.5	11.5

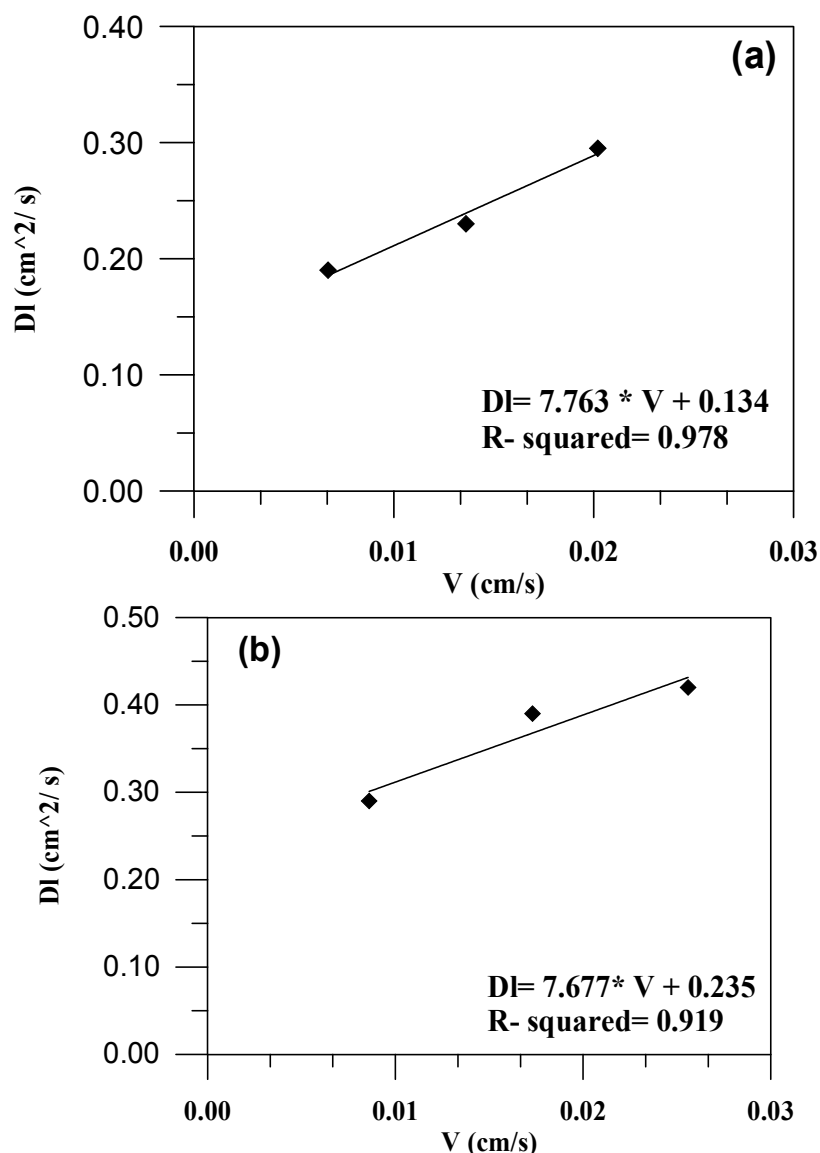


Figure7: Longitudinal dispersion coefficient versus mean pore velocity relation for (a) sand, and (b) IOCS.

3.7 Pilots-Plant Test

The pilot test results were showed in Figure 8. The variation of copper concentrations through using IOCS as permeable reactive barrier in this study measured from the sample analyzed considering the location (ports on side of column) of the monitoring for migration of copper along the column and the depth of barrier in the pilot test through different periods.

In Figure 8 which port 2 yielded observed concentration 38 mg/l at time of 5 hrs. while concentration of copper at port 6 was equal to 4.5 mg/l respectively. As seen from the same figure, it is clear that the residual concentration of copper increased with increasing the time. Whereas, decreased with increasing the distance from the bottom of column. From this Figure can be showed the evolution of barrier effect produced by the IOCS as reactive sorbent in the leaching of Cu^{+2} . Also, a significant elimination of metal of Cu is observed after reactive barrier, because of some mechanisms responsible for reducing mobilization of copper (Navarro et al., 2006).

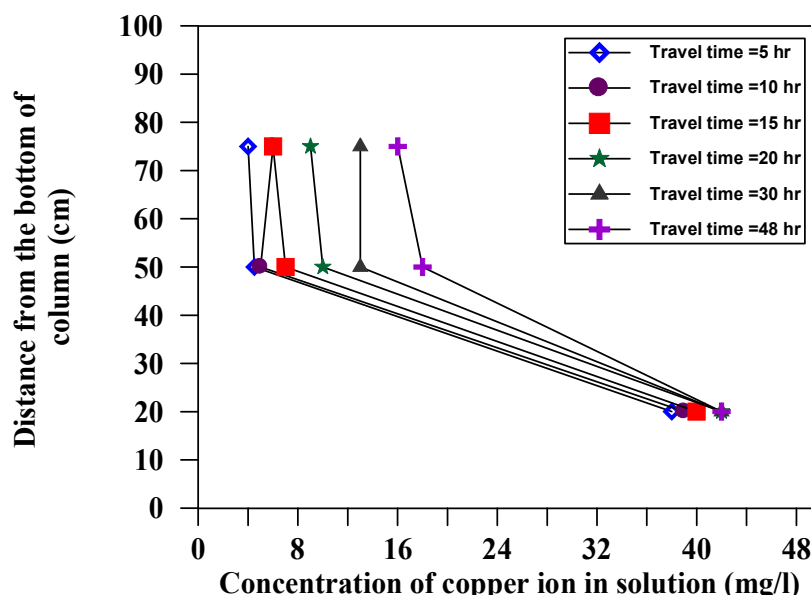


Figure 8: Column effluent concentration of Cu^{+2} in the experiment on treatment of contaminated ground water (initial concentration of 50 mg/l, and $T = 25^\circ\text{C}$) using IOCS as reactive porous media through different times of travel.

3.8 Copper Transport and Adsorption Equations

Depending on 1D numerical finite difference model has been described pollutant transport within groundwater taking pollutant sorption on the permeable reactive barrier was adopted by Faisal and Hmood (2013):

$$D_{Bz} \frac{\partial^2 C_{CB}}{\partial z^2} - V_{Bz} \frac{\partial C_{CB}}{\partial z} = \frac{\partial C_{CB}}{\partial t} + \frac{\rho_b}{n_B} \frac{\partial \left(\frac{a_b C_{CB}}{1 + b C_{CB}} \right)}{\partial t} \quad (8)$$

Where c and q_e are the solute concentrations in aqueous and on solid phases, t is the travel time, D is the hydrodynamic dispersion coefficient, V is the mean pore velocity, and z is the travel distance.

Parameters and constants related to the sand and IOCS as reactive materials adopted here for verification of model were evaluated, either through laboratory tests or through approximation using literature data (Table 3).

Table 3: Parameters, constants, boundary and initial conditions used in the transport modeling of copper in pilot plant column

Item	Location	Type/Value
Aquifer characteristics	Aquifer	Porosity (n_A) = 0.42
		Aquifer bed depth before barrier (cm) = 20
		Aquifer bed depth after barrier (cm) = 30
		Longitudinal dispersivity (α_L , cm) = 5.8
	PRB IOCS	Bulk density (g/cm^3) = 1.01
		Porosity (n_B) = 0.33
		Barrier bed depth (cm) = 30
		Longitudinal dispersivity (α_L , cm) = 11.5
Numerical model parameters	Bulk density (g/cm^3) = 1.15	
	Number of nodes = 46	
	Time step size (min)	
Boundary conditions	Initial concentration of Cu^{+2} (mg/l) = 50	
	Concentration of Cu^{+2} @ $z=0$ (mg/l)	
	$\frac{\partial C_{Cu}}{\partial z} = 0$	

Figure 9 illustrates the plotting numerical solution describing one –dimensional solute transport in homogenous, saturated porous media with introduction of the PRB. However, the barrier starts to saturate with increasing the travel time as shown when travel time were equal to 5 and 10 hrs. This means that the copper retardation factor was reduced, indicating a decrease in percentage of barrier functionality for copper retardation. This explains the increase of effluent concentration of copper from RPB with increased the travel time (Faisal and Hmood 2013).

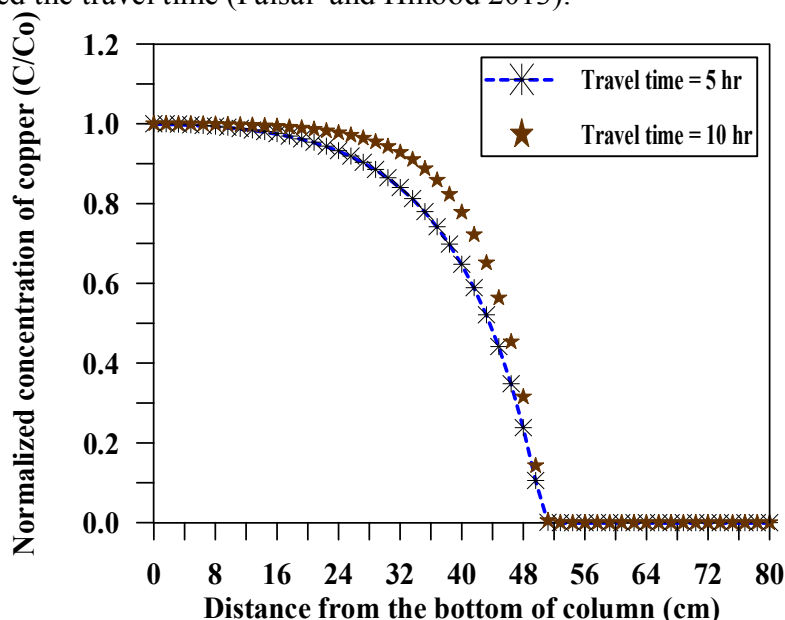


Figure 9: Copper concentration distribution in the groundwater along the length of the column with using PRB.

Figure 10 presents a comparison between the model predictions and the experimental results for total copper concentration during the migration of the contaminant plume, these concentrations seem to be almost identical however they are slightly different. The highest percentage of difference encountered between the calculated concentrations given by the experimental and prediction model were approximately 23 percent for IOCS at port 2 and approximately 15 percent at port 6. Accordingly a reasonable agreement between the predicted and the experimental results can be observed for IOCS in this study.

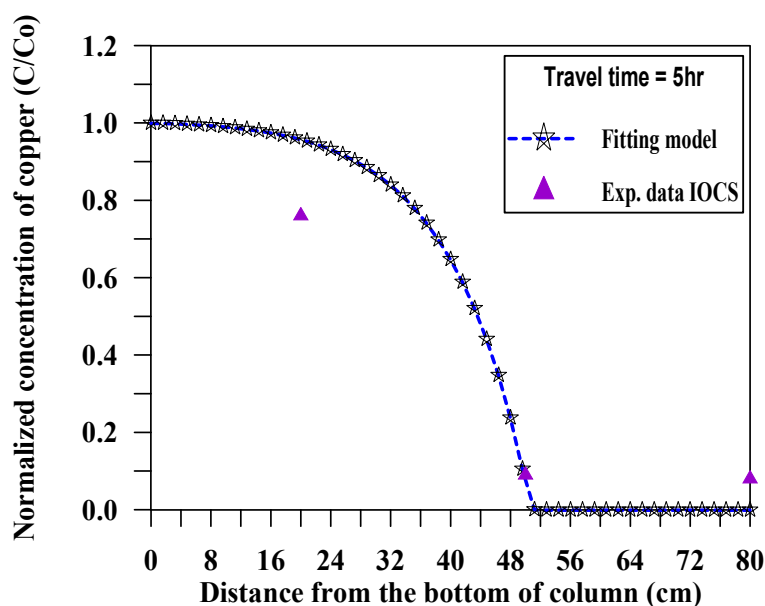


Figure 10: Comparison between model predictions and experimental results for Cu^{+2} concentrations in groundwater for travel time equal to 5 hr. for IOCS.

4. Conclusions

- 1- The batch results indicated that there are several parameters such as equilibrium contact time, initial pH of the solution; initial metal ion concentration, adsorbent dose (IOCS) and agitation speed affect the sorption process. The best values of these parameters that will achieve the maximum removal efficiency (about 87%) when IOCS used 60 min, 7, 50 mg/l, 1 g/50 mL, and 200 rpm respectively.
- 2- The sorption data obtained for IOCS applied to the Langmuir and Freundlich isotherm sorption model as calculated maximum sorption capacities (a) were equal to 6.5 mg/g for IOCS. These data were correlated reasonably well by the Langmuir sorption isotherm with coefficient of determination (R^2) equal to 0.985. While, (R^2) for Freundlich isotherm equal to 0.918.
- 3- The use IOCS appears promising for treatment polluted ground water, whereas using PDP as reactive barrier is less mature in this application and information on it still very limiting, for technical and for economic issues may be suitable.

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