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Simulation of the remediation of groundwater contaminated with ciprofloxacin using grafted concrete demolition wastes by ATPES as reactive material: Batch and modeling study

Ziad T Abd Ali[a], Hussein J Khadim[a *], Mohammad A Ibrahim[b]

[a]*Department of Environmental Engineering, College of Engineering University of Baghdad, Iraq*
[b]*Department of Civil Engineering, Al-Nahrain University, Baghdad, Iraq*

Abstract

This work presented a batch and kinetic study on the possibility of using concrete demolition wastes grafted with 3-aminopropyltriethoxysilane (APTES) as a reactive material in a Permeable reactive barrier PRB technology to remediate the ciprofloxacin (CPX) contaminated groundwater followed by evaluating the performance of this barrier by simulating the remediation process using two-dimensional aquifer model by COMSOL Multiphysics 3.5a program. To make this work more realistic, real groundwater was used in addition to distilled water in preparing the CPX contaminated groundwater. Several parameters that influence the sorption process were studied to achieve the highest removal percent such as contact time, pH, and sorbent dosage. Langmuir and Freundlich isotherm models were used to depict sorption data, moreover, the pseudo-first-order and pseudo-second-order models were applied in the kinetic study. The best values of the parameters that achieved the highest removal percent (93%), as confirmed by the batch experiments, were time=120min, pH=7, and dosage=1.5g/50mL. In addition, the two-dimensional aquifer model shows that the CPX propagation was restricted by a reactive barrier.

Keword:concrete demolition wastes; ciprofloxacin; Reactive barrier; Contaminant transport; Modeling.

1. Introduction

Within a few decades of their discovery, antibiotics had become environmental contaminants of concern [1]. Many studies confirmed that these contaminants are permanent and mobile in a sufficient amount that they can move from wastewater and liquid agricultural waste to uncontaminated water, and their potential to endanger the human, animal, and environment for risk, so it considered as one of the most dangerous threats of our modern age [2,3]. Quinolones are considered one of the most important synthetic antibacterial agents used in human and veterinary medicines that the CPX belongs to which. These agents are effective against pathogenic bacterial species, which selectively prohibit the fabrication of bacterial DNA. The spread of manure and its slurry on agricultural lands, or direct sedimentation by grazing livestock, led to the possibility of secreting quantities of these medicines as origin compounds or metabolites and entering the environment and reaching the groundwater [4]. One of the techniques that may be used to eliminate CPX from aqueous solutions is the adsorption process. It proved to be an engaging and efficient process because of its cost-effective nature and easiness of operation [5]. Due to the characteristics of CPX such as difficulty to remove or biodegrade from the aqueous solutions, there is limited reported information on the adsorption behaviours of ciprofloxacin. Therefore, the treatment of contaminated water and groundwater with this antibiotic has become an urgent process [6,7]. There are many methods used for remediation of contaminated groundwater, the most common one in terms of low cost and effectiveness is permeable reactive barrier (PRB) technology. It may be installed in two configurations called continuous (C-PRB) and funnel-and-gate (FG-PRB) permeable reactive barrier [8]. Design of PRB includes many steps, the selecting of the filler or reactive medium is considered one of the important steps, that should be cost-effective, efficient in the containment of contaminants, and convenient with the underground environment so that no adverse chemical reactions occur, nor should it represent as a potential source of pollutants through itself [9]. In most cities of the world, there are a lot of construction and demolition processes as a result of population growth and urban development that produce large quantities of construction and

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*Corresponding author e-mail: hussein.jabar@coeng.uobaghdad.edu.iq.

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demolition waste. It's worth noting, Iraq is one of the countries whose cities were destroyed as a result of terrorist operations, which led to the accumulation of large quantities of demolition waste such as concrete demolition waste (CDW) that require high disposal costs in addition to the inappropriate scene. Therefore, the re-use of this waste and modified it to be an effective and low-cost reactive material for remediation of contaminated groundwater is a great achievement and has offered many advantages in terms of reduced waste disposal cost and sustainable technology [10]. Many studies used natural concrete without modification in the water and groundwater remediation such as [11-15]. The APTES grafting process for the concrete demolition waste (CDW) that collected from demolition sites and attempt to reuse it as a reactive material in the PRB technique for remediation of ciprofloxacin (CPX) contaminated groundwater is the most important feature of this work. The reaction among the Al−OH or Si−OH that presents at the surface of the inorganic matrix and the silanol groups of alkoxysilanes represents the grafting process of CDW, yielding an organic-inorganic material. The mineral material such as CDW that can be grafted by an amine is considered a promising process to fabricate such effective media to use them in the remediation of contaminated water and groundwater, therefore, the research efforts were directed to develop this kind of materials [16]. Accordingly, the main goal of this work is to study the possibility of modification of concrete demolition waste (CDW) using 3aminopropyltriethoxysilane (APTES) and use it as an effective media in PRB technology for CPX contaminated groundwater remediation through a batch and kinetic study. In addition, an aquifer model, designed and solved using COMSOL Multiphysics 3.5a software, was developed under the state of equilibrium to evaluate theoretically the performance of ATPES grafted concrete demolition waste (GCDW) as an effective material in two configurations (C-PRB and FG-PRB).

2. Experimental Work

2.1. Materials

- The CDW used in this study was collected as old concrete blocks from the demolition sites of old buildings in Baghdad city. It was crushed, sieved into (1-2 mm) particle size, washed with distilled water many times, dried, and stored to use for the preparation of GCDW.
- The sandy soil was used as the default aquifer in a numerical groundwater model to simulate CPX transport in groundwater because it represents the worst case in the speed of the arrival of the contaminants into the groundwater. The characteristics of this soil were measured in the soil laboratory at the College of Engineering/University of Baghdad, such as hydraulic conductivity of 0.0022 cm/s, porosity = 0.41, particle size ranged=63 μm - 0.71 mm.
- The ciprofloxacin (CPX) was selected as a contaminant to mimic the CPX groundwater contamination. It was obtained as Ciprofloxacin hydrochloride ($C_{17}H_{18}FN_3O_3.HCI$) with purity 99.5% was bought from the local market (State Company for Drugs Industry and Medical Appliances/Samarra-Iraq), while, 3aminopropyltriethoxysilane (APTES, 98%) and ethanol (C_2H_6O) were purchased from Sigma–Aldrich (Brazil). The aqueous solutions of CPX that mimic contaminated groundwater were prepared by dissolving 0.05 gram of CPX in one liter of distilled water to acquire a concentration of 50 mg/L. The initial pH of each of the solutions was adjusted by the addition of HNO_3 or NaOH solution. The remaining CPX concentration in the solution was measured by a double beam UV-visible spectrophotometer (PG Instruments, Model UV T80, England) at λ_{max} = 275 nm.

2.2. Preparation of grafted concrete demolition wastes (GCDW)

The grafted concrete demolition wastes (GCDW) was synthesized by grafting of raw CDW with 3-aminopropyltriethoxysilane (APTES) according to the grafting method that was adopted by [17,18]. This method is summarized in mixing 10g of CDW and 100mL of ethanol, then adding 5.0g of APTES to the mixture with the proportion of (1/0.5). The mixture is stirred in a reflux system at 70 ^{O}C for 24h until the reaction is complete. This process leads to the production of organic-inorganic material in one step. Due to the alkaline nature of the CDW, the grafting process was catalyzed in a pH range of (10-11). After that, the grafted CDW particles (GCDW) were detached from the ethanol and dried at 105 °C after the mixture cooled down to room temperature. Finally, the GCDW particles are washed several times with deionized water until the pH value reaches a neutral state (pH 7), then it is dried and stored. The physical properties of the GCDW that determined at the Oil Research and Development Center, Ministry of Oil, Baghdad, Iraq included hydraulic conductivity (0.013 cm/s), porosity (0.61), surface area (10.555 m2/g), real density (2.755 g/cm^3), and bulk density (1.123 g/cm^3).

2.3. Characterization of the CDW and GCDW

The EDX analysis was employed to determine the CDW major components that may exist in it. It achieved using a TESCAN Vega III (Brno-

Kohoutovice, Czech Republic). The SEM analysis is used to study the surface morphology of materials. It applied in this study to give a clear view of the changes that may occur to the surface of CDW before and after grafting by APTES. To obtain an understanding of the grafting process of the CDW by APTES, the FTIR analysis was employed to set apart the existence of the surface functional groups of the CDW before and after the grafting process.

2.4. Distilled water leaching of CPX - bearing GCDW

The opportunity of using GCDW as a reactive material in PRB requires ensuring its ability to hold the contaminant (CPX) for as long as possible and not allowing it to turn into a liquid state, therefore, CPX - bearing GCDW specimen was tested in the distilled water leaching test that was done according to the "German Standard Methods [19].

2.5. Batch Experiments

The sorption of ciprofloxacin (CPX) using GCDW was studied through batch experiments under different conditions, the batch experiments were done by adding a specified quantity of the GCDW to 100 mL of CPX synthetic solution with an initial concentration of 50 mg/L, then the mixture was shaken using a thermostatic shaker (Edmund Buhler SM25, German) with agitation speed equal to 250rpm. The batch experiments were implemented with different contact times (0-5 hr), initial pH value (3-12), and dosage (0.1-0.8g/100 mL). A fixed volume (20 mL) of the solution was withdrawn from the flask, and filtered using filter paper type (Whatman No. 40) to detach the particles of GCDW from the aqueous solution, then the filtered solution was analyzed to determine the remaining concentration of CPX. The amount of CPX sorbed onto GCDW, qe (mg/g), was estimated from the mass balance Eq. 1 [20]:

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

Where qe is the amount of CPX sorbed per unit mass of GCDW (mg/g), Ce and C0 (mg/L) represent the equilibrium and the initial concentration of CPX, V (L) is the volume of CPX solution, and m (g) is the GCDW mass. The removal percent (R%) of CPX onto GCDW at time t was calculated by Eq.2 [21]

$$R\% = \frac{(C_o - C_e)}{C_o} \times 100 \qquad (2)$$

2.6. Sorption isotherms

The determination of the mathematical equation (isotherm model) that describes the relationship between the adsorbent (GCDW) and adsorbate (CPX) is considered one of the fundamental points in this study that contributes to the modelling of the groundwater aquifer model [22], therefore, the CPX sorption data are fitted with two isotherm models as follows:

Freundlich model: The sorption to heterogeneous surfaces or surfaces supporting sites with varying affinities was understood as this model. The stronger binding sites are thought to be occupied first, and the binding strength declines as the number of occupied sites grows. This model can be represented as in Eq. 3 [23]:

$$q_e = K_F C_e^{1/N} \qquad N > 1 \qquad (3)$$

Where, N is an empirical coefficient indicative of the intensity of the adsorption, and K_F (mg/g) (L/mg) $^{1/N}$ is the Freundlich coefficient.

Langmuir model: This model is based on the assumption that maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface. It can be represented as in the following equation [24].

$$q_e = \frac{q_m b C_e}{1 + bC_e} \qquad (4)$$

Where, qe (mg/g) is the solute sorbed amount per unit of sorbent weight at equilibrium, (qm) is the maximum sorption capacity, Ce (mg/L) is the equilibrium concentration of the solution in the bulk solution, and b is the constant related to the sorption free energy. Sorption kinetic study is helpful to understand the mechanism that dominant the sorption of CPX using GCDW. Two kinetic models are used in this study called "Pseudo-First Order Kinetic Model" and "Pseudo-Second Order Kinetic Model" as illustrated in Eq.5 and Eq.6, respectively [25]:

$$\left(\frac{dq_t}{dt}\right) = K_1(q_e - q_t) \qquad (5)$$

$$\left(\frac{dq_t}{dt}\right) = k_2(q_e - q_t)^2 \qquad (6)$$

Where q_t the quantity of CPX sorbed at period t (mg/g), *qe* is the amount of CPX sorbed at equilibrium (mg/g), K_2 is the rate constant of pseudo-second-order sorption (g.mg^{-1} min^{-1}), and K_1 is the rate constant of pseudo-first-order sorption (min^{-1}).

2.7. Development of two-dimensional aquifer model

The two-dimensional groundwater aquifer model that represents the theoretical simulation for remediation of CPX-contaminated groundwater using PRB technology establishes that the COMSOL 3.5a was applied as follows: the flow (advection) was one-dimensional (X direction) and the solute transport (dispersion) was two-dimensional transport (X and Y direction) over an unconfined aquifer. Although the velocity of flow has a component in the transverse direction (Y-direction), the unidirectional fluid flow in the X-direction only was adopted in the present simulation which is fair for such a situation as described by [26]. The model determines the spatially and temporally extent of the CPX plume in the subsurface of the model formulated in this work. The aquifer model is contained within the square shape (50×50 m) for two configurations of PRB called funnel and gate-PRB (FG-PRB) and continuous-PRB (C-PRB), as illustrated in Fig 1. The C-PRB aquifer model contained three compartments. The first, illustrated by 30 m length of the sandy soil measured from the left side of the aquifer, the second, illustrated by 3m (thickness) barrier placed beside the soil, and 17m of the sandy soil illustrated the third part was placed beside the barrier. The CPX contaminated solution was inserted into the aquifer model from a line source (10 m long) which was located on the left side of the aquifer model with velocity and an initial concentration of 3 m/d and 0.05 kg/m3, respectively. This source was simulated a continuous release of CPX contamination, therefore, at zero time, the concentration of CPX in all aquifer models, except the line source, is zero then the CPX concentrations start to increase with the increase of time indicating the spread of the CPX in the aquifer model. The concentrations of CPX at points of interest were monitored in front of, within, and behind the PRB, these points are very important because they clarify the difference in CPX concentrations before, during, and after treatment thus demonstrating the efficiency of the GCDW-barrier

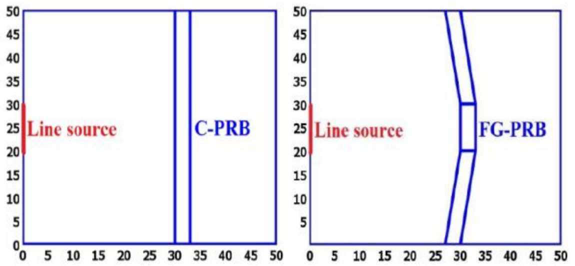


Fig. 1. Schematic diagram of the model aquifer with PRBs as plotted by COMSOL (all dimensions in m)

The advection-dispersion equation (one-dimensional) describes the contaminant transport in porous media (Eq.7).according to this equation, the mechanisms that control the dissolved contaminant transport are dispersion, advection, and sorption. The dispersion is the migration of contaminants due to concentration gradient and varied pathways, while the advection is the migration of contaminants with flowing water [27].

$$D_x \frac{\partial^2 C}{\partial x^2} - V_x \frac{\partial C}{\partial x} = \frac{\partial C}{\partial t} + \frac{\rho_b}{n} \frac{\partial (q)}{\partial t} \qquad (7)$$

Where n is the porous medium porosity, V velocity of pore water m/min, q sorbed amount of pollutant onto the sorbent substance mg/g, D is the hydrodynamic dispersion coefficient, and ρ_b bulk density Kg/m^3. The term $\rho_b/n\ \partial(q)/\partial t$ is the rate of change in the contaminant solution concentration due to sorption processes, where q is the concentration of contaminant (CPX) sorbed on the reactive media (GCDW), so, this term can be written as follows:

$$\frac{\rho_b}{n} \frac{\partial (q)}{\partial t} = \frac{\rho_b}{n} \left(\frac{dq}{dc} \frac{\partial C}{\partial t} \right) \qquad (8)$$

The description of q can be incorporated) with Eq.7, the subsequent can be present as follows:

$$D_x \frac{\partial^2 C}{\partial x^2} - V_x \frac{\partial C}{\partial x} = R \frac{\partial C}{\partial t} \qquad (9)$$

Where R represents the effect of contaminant transport retarding due to the sorption process. It is called the retardation factor and can be estimated as in Eq.10:

$$R = 1 + \frac{\rho_b}{n} \frac{\partial q}{\partial C} \qquad (10)$$

Eq.9 is utilized to depict the porous media contaminant transport in one-dimensional, it can be reformulated to depict the contaminant transport in two-dimensional as in Eq.11:

$$D_x \frac{\partial^2 C}{\partial x^2} + D_y \frac{\partial^2 C}{\partial y^2} - V_x \frac{\partial C}{\partial x} = R \frac{\partial C}{\partial t} \qquad (11)$$

In this study, for the flow of CPX-contaminated groundwater through the sandy soil (aquifer), the R-value is considered equal to 1 which is rational for this kind of soil (assumed as a non-reactive or inert medium). On the other hand, the sorption of CPX using GCDW as a reactive medium in this study is represented by the isotherm model that matches with batch experimental data (higher coefficient of determination, R^2). To solve the two-dimensional aquifer model, Eq.11 with initial and boundary conditions presented in (Table 1) solved numerically by COMSOL Multiphysics 3.5 software which is based on the finite element method.

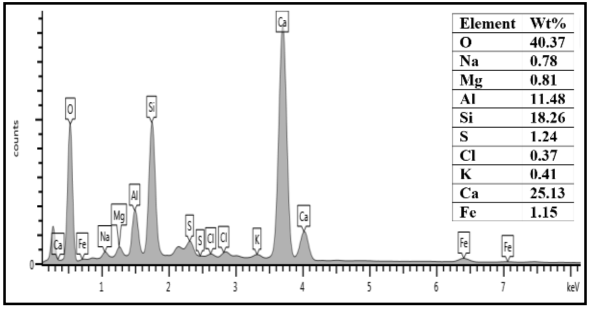
Table 1: Boundary and initial conditions used in the aquifer model

Item	Location	Type/Value	
Boundary settings	Upper boundary	No flux/symmetry	
	Lower boundary	No flux/symmetry	
	Left side boundary	Line source	Co = 0.05 kg/m3
		Except for the line source (10m)	No flux/symmetry
	Right side boundary	Advective flux	
Initial condition	(X, Y)	Initial concentration = 0	

3. Results and discussion

3.1. Characterization of GCDW

According to the EDX spectrum of CDW, the following components such as sodium, magnesium, potassium, trace quantities of chlorine, calcium, aluminium, silicon, sulfur, and iron were present in CDW, as illustrated in Fig.2. The presence of Si and Al in the composition of CDW led to support its grafting with APTES [18]. The grafting process of CDW by APTES was executed according to a chemical reaction to occur between the APTES silanol group with the aluminates and the surface oxygen groups of silicates that exist on the surface of CDW [16]. The groups that exist in APTES that can be hydrolyzed such as ethoxy groups could be condensate with groups that exist on the CDW such as Si─OH or Al─OH of the SiO_2 and Al_2O_3. According to this reaction (condensation reaction), a stable amino-grafted adsorbent was synthesized through a covalent engagement of lateral 2-dimensional sheets of APTES molecules created by intermolecular siloxane bonding and/or a covalent engagement of APTES molecule on the hydroxyl groups of the CDW oxides [28]. In addition, the existence of many components in the CDW such as inorganic oxides and silica make its grafting process by APTES result in the employment of waste material as support [29].



Element	Wt%
O	40.37
Na	0.78
Mg	0.81
Al	11.48
Si	18.26
S	1.24
Cl	0.37
K	0.41
Ca	25.13
Fe	1.15

Fig. 2. EDX Spectrum of CDW

Fig.3 illustrates the SEM images of CDW before and after grafting by APTES and the changes that may happen on the surface of CDW. It can be seen that the surface of CDW after the grafting process offered an irregular and rougher surface while the surface of CDW before the grafting process was smooth. The difference in the surface morphology, interlayer or broken edges, and polymerization that occurred on the surface indicated the success of the grafting process [29]. Due to the amine groups, the grafting process produced larger particles without direction, also, the grafting process provide a densely packed network. In addition, the presence of a higher degree of aggregation on the surface of CDW after grafting when compared to CDW before grafting indicates the presence of different surface morphology which confirms the interaction of APTES with the CDW to produce GCDW.

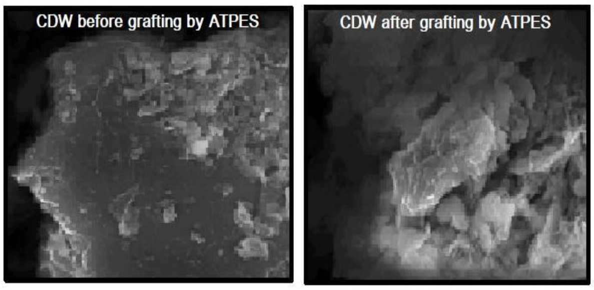


Figure 3. SEM images of CDW before and after grafting by APTES

FTIR spectra for CDW before and after grafting by ATPES was illustrated in Fig.4. It can be seen there are many differences. The CDW after grafting presented several peaks that are not observed in CDW before grafting, such as 3600, 3401, 2530, 1758, 1650cm^{-1}. These notes proved that the CDW particles had been grafted by APTES successfully. The C-N group created in the APTES chemical reaction and the Si─OH bending can be represented by a peak around 2530cm^{-1} and 1650cm^{-1}, respectively. The peak at 3401cm^{-1} may be indicated by the N H stretching vibrations of $^{-}NH_2$ and ^{-}NH groups [30]. Moreover, the stretching vibrations of

Al-O-Si and the asymmetric stretching of Si-O-Si were noted at (750 & 590cm^{-1}) and (480 & 1075cm^{-1}), respectively, for both the CDW before and after grafting by APTES, also, it can be noticed that the case of CDW after grafting (GCDW), the strength of previous bands is higher, which emphasizes the intensification among the hydroxyl groups on the CDW surface indicating the successful preparation of GCDW [31].

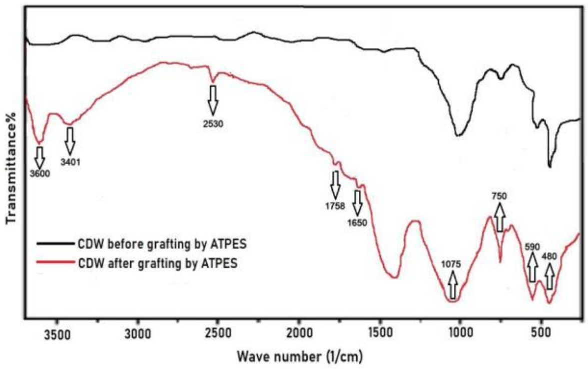


Figure 4. FTIR analysis of CDW before and after grafting by ATPES

3.2. Distilled water leaching of ciprofloxacin -bearing GCDW

According to the "German Standard Methods", the leaching test indicated that the dissolution of CPX-bearing GCDW is generally very low (below the limits of detection). This result confirms that GCDW can be an effective reactive material in PRB by bonding strongly with the CPX and prevent it to turn into a liquid phase again.

3.3. Influence of batch operating parameters on the sorption of CPX

3.3.1 Effect of contact time

Using 0.5g of GCDW that was added to 50 mL of CPX solution with an initial concentration of 50 mg/L, the effect of contact time on CPX removal percent was studied in a batch process, as shown in Fig 5a. It can be observed that with the increasing contact time, the CPX removal percent was increased, in addition, the rate of sorption was fast at the premier stage and afterwards progressively retard. This behavior can be attributed to the decrease in the sites of sorption located on the surface of GCDW that lead to a decrease in the sorption rate [32]. About 60% of CPX was removed after 120 min; while the concentrations of CPX were kept relatively constant at a time of more than 120 min.

3.3.2 Effect of initial pH of the Solution

At the initial pH of CPX solution range of 3–10, the effect of initial pH on the CPX removal percent was considered as shown in Fig.5b. It's clear that the CPX removal percent start to increase with pH increasing to reach the maximum limit of 60% at pH 7, afterward, it was decreasing to reach the minimum limit of 25% at pH10. This behavior can be attributed to the CPX that demonstrated pH-dependent as follows: at pH<7, the reduction in the removal percent was due to the increase of the electrostatic repulsion between the –NH_2+ groups of CPX and the APTES groups of the GCDW with decreasing pH value. At pH >7, the removal percent also decreased with increasing pH value due to the contest from the OH^- ions that played a key role in reducing the removal percent. While at pH=7, the highest removal percent (60%) was achieved due to an increase in some kinds of functional groups and a decrease in others that present in CPX, for example, at pH= 7 the numbers of –COO− groups increased while the number of $^-NH_2$ groups decreased [33].

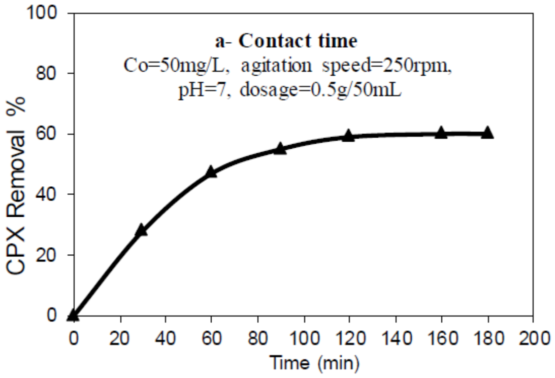
In addition, at pH<7, the COOH groups were present due to the transformation processes of some –COO− groups, therefore, the electrostatic attraction decreased between the –NH_2+ groups of CPX and the APTES groups of the GCDW which lead to decreasing the CPX sorption rate. Also, at pH>7, the numbers of –COO− groups increased while the numbers of –NH_2+ groups decreased which increased the electrostatic repulsion and decreased the electrostatic attraction, while at the neutral status (pH=7) the mechanism of sorption was governed by the forces of electrostatic attraction that leading to an increase in the sorption capacity. This interpretation was similar to what researchers have found such as [18].

3.3.3 Effect of GCDW dosage

The effect of the GCDW dosage on the CPX removal percent is considered one of the important parameters that must be studied in such a case as presented in Fig.5c. The effect of varying GCDW doses was investigated using 50 mg/L initial concentration of CPX, at initial pH=7, agitation speed = 250 rpm, and contact time of 120 min. The results showed an increase in removal percent with the increase in the dosage of GCDW up to 1.5g/50mL, where the CPX removal percent at this point was 93%, after that, there is no significant change in removal percent, therefore this value (1.5g GCDW/50mL) was adopted as the best dosage to achieve the higher CPX removal percent under the experimental conditions. An increase in the removal percent with increasing GCDW dosage is a plausible result because the increase of GCDW dosage leads to the availability of a greater number of active sites that are responsible for sorption of CPX, increasing by the removal percent [34].

3.4 Performance of GCDW using real groundwater

To evaluate the performance of the new reactive material (GCDW) at conditions that are closer to reality, natural (real) groundwater was used instead of distilled water in preparing groundwater contaminated with CPX to conduct a batch experiment under the same batch experimental conditions that achieved the highest CPX removal percent in previous experiments (initial CPX concentration=50mg/L, agitation speed= 250rpm, t=120min, pH=7, GCDW dosage=1.5g/50mL). The real groundwater was taken from a specific location in Baghdad city, it was analyzed before using to determine its contents at the Ministry of Science and Technology as clarified in Table 2. The result of this experiment depicted that the CPX removal percent was declined from 93% for the case of using distilled water to 75% for the case of using real groundwater. The reduction in the CPX removal percent in the case of real groundwater is reasonable due to the competition between the CPX and the components of the real groundwater (Table 2) on the sorption sites located on the GCDW surface. On the other hand, the use of distilled water did not add any additional compounds that may compete with CPX on the same GCDW active sites, as in the case of real groundwater, therefore, it achieved the higher CPX removal percent. This experiment proved that the GCDW can remove CPX from real groundwater although the presence of competition with other components that may be present in this kind of water on the GCDW effective sites.



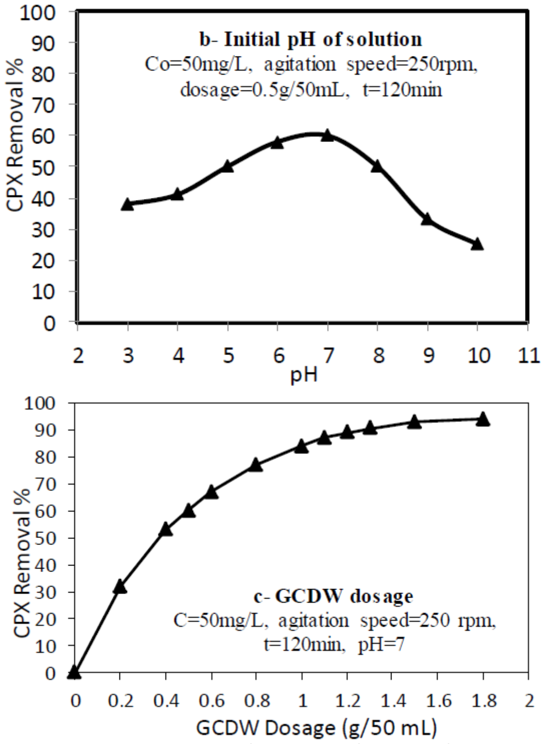


Figure 5. Removal percent of CPX as a function of (a) contact time, (b) initial pH, and (c) GCDW dosage

3.5 Sorption Isotherms

The parameters which gave the higher CPX removal percent (93%) using GCDW according to the experimental conditions of this study were t=120min, pH=7, GCDW dosage=1.5g/50mL, this experiment was conducted at a constant value of CPX initial concentration and agitation speed of 50 mg/L and 250rpm, respectively. The data of the batch experiments were fitted with two isotherm models (*Langmuir* and *Freundlich*). The constants of these models with the coefficient of determination (R^2) were estimated by non-linear estimation using "STATISTICA 8" software, presented in Table 3. In comparison with the two models, the Langmuir isotherm model obtained the higher value of the determination coefficient, therefore the Langmuir isotherm model was adopted to depict the sorption of CPX in the partial differential equation (Eq.11) that governing convey of a CPX in two-dimensional (2D) aquifer model which is solved using COMSOL Multiphysics 3.5a.

3.6 Sorption Kinetic Study

To identify the mechanism that controls the CPX sorption using GCDW, the two kinetic models called pseudo-first-order and pseudo-second-order were applied. The constants of these models with the coefficient of determination (R^2) were estimated by non-linear estimation using “STATISTICA 8” software as present in Table 4. The CPX sorption data were subjected to the second-order because the value of the experimental qe was the closest to the qe calculated for the pseudo-second-order in comparison with the pseudo-first-order model. Based on that, the prevailing mechanism of CPX sorption is closer to chemisorption.

3.7 Transport of CPX through aquifer model

Fig 6 displays the anticipated contour plot of CPX contaminated groundwater transport modelling results throughout the aquifer model in two distinct cases (without-PRB and GCDW-PRB) after 2, 5, and 75 days in two different situations (without-PRB and GCDW-PRB). It is clear that the CPX- plume is hindered by the GCDW-PRB which led to the fact that the CPX-concentrations reaching the outlet of the aquifer model region with the presence of PRB were lower than that of the first case (without PRB) for the same velocity and travel time.

Table 2: Analysis result of real groundwater

Test	Conc	Test	Conc	Test	Conc	Test	Conc	Test	Conc	Test	Conc	Test	Conc	Test	Conc
pH	7	TSS ppm	23	SO_4, ppm	2105	NO_2 ppm	0.05	H_2S, ppm	ND*	Mg, ppm	39.1	Na, ppm	0.61	Cd, ppm	0.138
TDS, ppm	1500	COD ppm	51	Cl, ppm	920	NH_3, ppm	ND*	Ca, ppm	320	K, ppm	37.9	Pb ppm	0.138	Ni, ppm	0.46

Table 3: Parameters of isotherm models for the sorption of CPX using GCDW

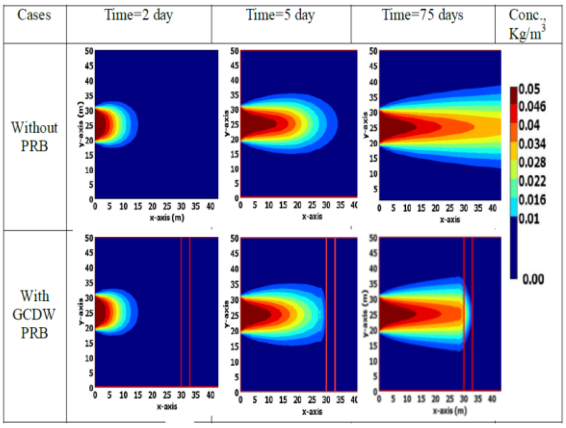
Model	Parameters	GCDW
Langmuir	qm (mg/g)	1.655
	b (L/mg)	0.101
	R^2	0.986
Freundlich	K_F (mg/g)(L/mg)$^{1/N}$	1.108
	N	1.867
	R^2	0.956

Table 4: The kinetic model constants for the sorption of CPX

Sorbent	qe (mg/g) Exp.	pseudo-first-order		pseudo-second- order	
GCDW	1.504	K_1(min)$^{-1}$	0.0363	K_2(mg g^{-1}min^{-1})	0.024
		qe (calc.)(mg/g)	3.011	qe.(calc.) (mg/g)	1.922
		R^2	0.9011	R^2	0.9923

3.8 Performance of GCDW-PRB

When the CPX-contaminated groundwater reaches the GCDW-PRB, the concentration of CPX starts to reduce due to the presence of a barrier through the sorption process. The theoretical results for this simulation were obtained in terms of the relationship between CPX-concentration and barrier operation time. The relationship between time and concentration of CPX in the contaminated groundwater that coming into (inflow) and leaving (outflow) the barrier at the points of (30, 25) and (33, 25), respectively, were illustrated in Fig.7a. The key conclusions that can be derived from this graph are as follows, were the GCDW-PRB can be used successfully to remediate CPX-contaminated groundwater, also, this barrier begins to saturate with increasing travelling time as a result of a decrease in the ability of the reactive material (GCDW) for retarding the contaminant (CPX). The barrier performance can be evaluated via the length of the period that the barrier can maintain the level of contaminant concentrations that leave it's lower than the MCL (maximum contaminant level) that could be found in drinking water (zero value was adopted to MCL for CPX). Accordingly, the operation time for GCDW-PRB is equal to 91 days as long as the outflow CPX concentration from GCDW-PRB began to increase at this time, as illustrated in Fig 7. In addition, it can be seen that the concentration of CPX entering the GCDW-PRB was constant at about 0.049 kg/m^3 which is less than the concentration at the source (i.e., 0.05 kg/m^3). This is probably due to the effect of dispersion, this result is consistent with the results of some research such as [23].



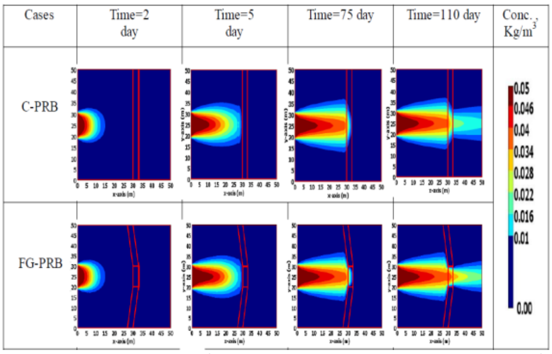


Fig. 6. Contour plot of CPX concentration across the aquifer model after 2, 5 and 75 days

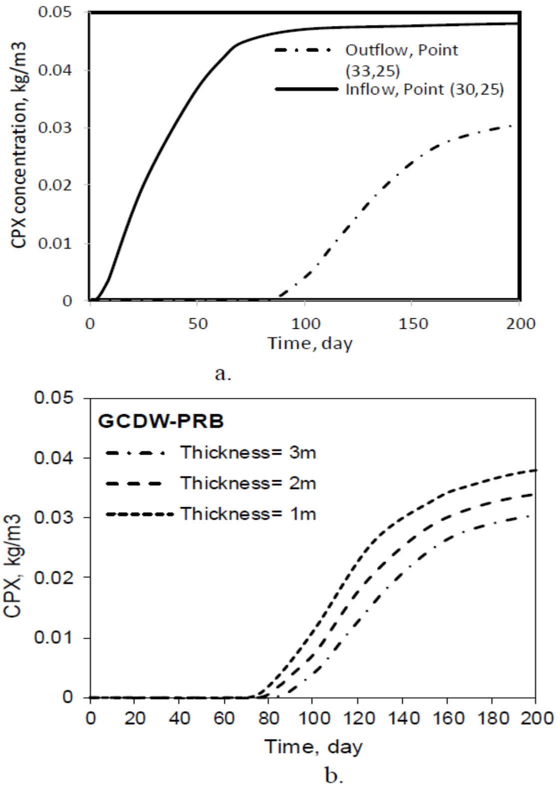


Fig. 7. CPX concentration and time (a), CPX concentration and time inside the thickness of barrier (b)

3.9 CPX- Removal within PRBs

Fig 7b. illustrates the relationship between the CPX concentration and time within the thickness of GCDW-PRB. The CPX concentration in the front parts of the PRB (e.g., 1 m) increases rapidly than the internal parts of the PRB (e.g., 2 or 3m). The increment in CPX concentration at the front parts of the PRB refers that The reactive materials, rather than the inner part of the barrier, have lost their sorption ability in remediating CPX at the front regions of the PRB; it would be in contact with an incoming contaminant of high concentration, due to that the reactive materials at these parts would be got its extreme sorption capacity first and the CPX concentrations start to increase. On the other hand, the reactive materials at the end of the PRB would be reached their maximum sorption capacity in a longer time than the front ones because it would be in contact with incoming contaminated groundwater with lower concentrations for most of the simulation time

3.10 Comparison between two configurations of PRB

There are two configurations of PRB namely continuous (C-PRB) and funnel and gate (FG-PRB) permeable barrier as shown in Fig. 1. In the C-PRB, the reactive media (GCDW) was placed along the barrier (i.e., 50 m long) with a thickness of 3 m, while for FG-PRB, shorter reactive media was installed only in the permeable gate part of the barrier (i.e., 10 m long) with the same thickness of 3m, and the impermeable material that has low hydraulic conductivity such as ebonite was installed in the impermeable funnel parts, therefore groundwater flow and contaminant transport were intentionally allowed through the gate part only. Fig 8 describes the predicted contour plot of transport of CPX - polluted groundwater with velocity = 3 m/d and Co = 0.05 kg/m^3 across the model aquifer in two cases (C-PRB, and FG-PRB) after 2, 5, 75, and 110 days. It is clear that the direction of the transport process of CPX is from a high concentration gradient on the left-hand side to the lower ones on the right-hand side, and the CPX-contaminated groundwater is transported from the contaminated site to the PRBs within 75 days without exceeding the barrier, which means that the spread of the CPX plume is confined by the reactive media (GCDW) in the barrier region. For two configurations of PRBs, the typical results for this simulation were obtained in terms of the relationship between CPX concentration and PRB operation time. Fig 9 clarifies the relationship between time and concentration of CPX entering and leaving the barrier. The important points from this diagram are that both PRB topologies can be used to successfully remediate CPX-contaminated groundwater, and the GCDW-barrier begins to saturate with time. which means a decline in its activity and the CPX retardation factor. In addition, the C-PRB has a higher operation time in comparison with FG-PRB. This result can be attributed to the fact that the C-PRB has more quantity of reactive material compared to FG-PRB, so it takes a longer time to reduce its functionality, therefore, the C-PRB has a longer operation time than FG-PRB.

Fig. 8. Contour scheme of CPX concentration through the aquifer model after various times.

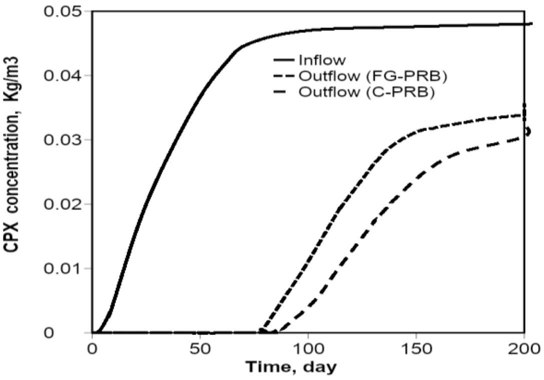


Fig. 9. CPX concentration and time relationship before (inflow) and after (outflow) remediation for C-PRB and FG-PRB

4. Conclusion

The parameters such as pH, contact time, and GCDW dosage were studied as parameters that influence the CPX sorption using GCDW at a constant CPX initial concentration of 50 mg/L and agitation speed of 250 rpm. The better parameter values that attained the higher CPX removal percent of 93% were (120min, 7, 1.5 g GCDW/50mL). The GCDW can remove CPX from real groundwater although the presence of competition with the components that may be present in groundwater on the GCDW effective sites with a removal percent of 75%. The CPX sorption data matched well with the Langmuir isotherm model with a determination coefficient of 0.986. The pseudo-second-order kinetic model showed good compatibility with the CPX sorption data, proving that the dominant removal mechanism is closer to the chemisorption. The GCDW characteristic analysis (SEM and FTIR) confirmed the success of the CDW grafting process, and the grafted material (ATPES) had interacted with CDW particles to produce a new and cheap CPX sorbent material. The two-dimensional numerical aquifer model confirmed that the GCDW-PRB was efficient in the restriction of CPX plume, and both configurations of PRBs be able to use effectively to remediate the CPX-contaminated groundwater with operation time equal to 91 and 80 days for C-PRB and FG-PRB, respectively, under the conditions of this study.

5. Conflict of Interest

The authors declare no conflicts of interest.

6. Acknowledgments

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