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Effect of pH on the performance of olive pips reactive barrier through the migration of copper-contaminated groundwater

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Adsorption data are modeled using the popular Langmuir and Freundlich isotherm models. These isotherms are primarily useful for simulating data collected at a fixed pH value. This study attempted to develop an adsorption isotherm based on the Langmuir model, to simulate pH-dependent adsorption effects. It is derived based on the results of a batch of experiments conducted under appropriate conditions using olive pips as the reactive bio-sorbent on a copper-contaminated solution. This isotherm is used as a linear correlation between the maximum adsorption capacity and the initial pH values of the feed solution, while a nonlinear power correlation is used to represent the affinity coefficient–initial pH relationship. This isotherm is integrated with the advection–dispersion equation for simulating the effect of the initial pH on the contaminant transport scenarios. The integrated model, solved numerically by the implicit finite difference method, is proven, in which the initial pH has a potential effect on the retardation factor and longevity of the bed of olive pips. This bed can be used as a permeable reactive barrier in the remediation of contaminated groundwater. A good concurrence between the integrated model predictions and experimental results for breakthrough curves was recognized with the index of agreement (d), as proposed by Willmott, not less than 0.999.

Keywords: Olive pips; Bio-sorption; Transport; Modeling; Langmuir

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1. Introduction

The production of inorganic wastes in mining- and metal-related industries has always been an important concern. These wastes are often high in heavy metals, constituting a major threat to human populations, aquatic species, plants, ecosystems, and groundwater quality because of their biological non-degradability and stability in the environment [1–3].

Permeable reactive barriers (PRBs) involve the emplacement of reactive material(s) in the subsurface to remediate the contaminated plume of groundwater as it flows through. The contaminants are then transformed into environmentally acceptable forms to achieve the remediation concentration down gradient goals of the barrier. The key element in the design and efficient *in situ* operation of a PRB system lies in the selection of an appropriate reactive medium. That is, the media is dependent upon the type of the contaminant, sufficient hydraulic conductivity, excellent environmental compatibility and availability, low-cost and long-term stability [4,5].

The mobility of the heavy metals in groundwater is controlled by reactions that cause the metals to be adsorbed or to precipitate, as well as by the chemical reactions that enable the metals to remain associated with the solid phase [6]. The pH of the feed solution is the primary parameter that affects and controls

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these reactions. It affects the sorption capacity of a sorbent for ions from the aqueous solution due to its influence on the surface properties of the sorbent and the ionic forms of the pollutants in the solutions [7]. This means that the pH parameter significantly affects the retardation of metals by PRB and its longevity.

An attempt to arbitrarily force fit the Langmuir isotherm to various datasets would yield different values of the adsorption capacity at different pH values [8,9]. A modified Langmuir isotherm to model the arsenic adsorption on amorphous iron oxide was used [10]. A modified Langmuir model was proposed to explain the pH-dependent bio-sorption of heavy metals on marine macroalgae. This model assumes that the functional groups for heavy metal interactions are weakly acidic and the biomass uptake capacities are effected through the association and dissociation equilibrium between two apparent ionic forms [11]. Different empirical and semi-empirical models have been proposed to consider the pH effect on copper uptake onto *Sphaerotilus natans* and calcium alginate sorbents. These models, originated from the Langmuir isotherm, may be useful to fit experimental data by simply monitoring the pH, thus evading its control [12]. The reduction of hexavalent chromium by scrap iron was investigated in long-term column experiments for aqueous Cr(VI) solutions with pH ranging from 2.00 to 7.30. The results showed that the initial pH of the solution significantly affects the reduction capacity of the scrap iron. The highest reduction capacity was determined to be 19.2 mg Cr(VI)/g scrap iron, at pH 2.50, which decreased with an increase in the initial pH of solution [13]. The analytical isotherm model, identified as the modified Langmuir–Freundlich isotherm, was then developed. It can simulate the effect of pH on the adsorption process in the batch of experiments. This isotherm uses a linear correlation between pH and the affinity coefficient values. It is validated by predicting the arsenic adsorption onto two different types of sorbents: pure goethite and goethite-coated sand [14].

Unfortunately, none of the current analytical or numerical models available, controlling the migration of solute transport in the subsurface, are capable of indicating the pH effect on the performance of PRB. Hence, there is a need to develop an adsorption isotherm that can describe the pH-dependent adsorption effects. If developed, such a model can potentially be integrated into a large-scale contaminant transport model represented by the advection–dispersion equation to simulate pH-dependent transport scenarios.

Accordingly, the objective of this study was to prepare an integrated model which simultaneously includes contaminant transport and pH-dependent adsorption effects. The integrated model was verified using experimental datasets of Cu^{2+} onto reactive material using olive pips. It is an efficient tool to evaluate pH-dependent adsorption effects on the retardation factor and longevity of the olive pips reactive barrier.

2. Theoretical modeling

The one-dimensional transport of dissolved contaminants in the saturated porous medium is described by the well-known advection–dispersion equation, as follows [15]:

$$D_z \frac{\partial^2 C_{\mathrm{Cu}}}{\partial z^2} - V_z \frac{\partial C_{\mathrm{Cu}}}{\partial z} = \frac{\partial C_{\mathrm{Cu}}}{\partial t} + \frac{\rho_b}{n}\frac{\partial q}{\partial t} \tag{1}$$

where D_z is the dispersion coefficient in the direction z (cm^2/s), V_z is the velocity of flow (cm/s), C_{Cu} represents the copper mass concentration in the aqueous solution (mg/L), q is the copper concentration adsorbed on the solid phase (mg/g), n is the porosity of the medium, and ρ_b is the dry adsorbing material bulk density (g/cm^3).

Under isotherm conditions, q in the second term on the right-hand side of this equation can be substituted by one of the adsorption models. The most applicable models for single-component systems at constant temperature are either the Langmuir or Freundlich models [16]. However, the Langmuir isotherm model was used to describe the bio-sorption of Cu^{2+} on the olive pips in this study. This model is based on the assumption that active surface sites exist on the solid material, on which the metals are adsorbed. The ions get fixed as a monolayer on the surface. This implies that no penetration of ions into the interior of the adsorbent occurs. The model can be expressed as follows [17]:

$$q_e = \frac{q_m b C_e}{1 + bC_e} \tag{2}$$

where q_e is the equilibrium concentration of the metal on the biomass (mg/g), q_m is the maximum adsorption capacity of the biomass (mg/g), b is an adsorption energy related constant (mg/L), and C_e is the equilibrium concentration of the metal in the solution (mg/L). The q_m corresponds to the maximum quantity of metal that the bio-sorbent can adsorb. At this point, all the active sites are occupied by the ions and the material cannot adsorb any further metal, even if the metal concentration in the solution is increased. On the other hand, b is the dissociation coefficient of the solute–adsorbent complex, which represents the affinity between the solute and the adsorbent—meaning that a higher b value corresponds to a higher affinity [16].

In order to introduce the effect of the initial pH of the feed solution on the migration of the contaminant through the reactive barrier, the value of q is the main factor used in this study. This means that the Langmuir model was fitted with experimental data and the two parameters q_m and b were related to the different pH conditions, consistent with Vegliò et al. [18].

Eq. (2) can be substituted into Eq. (1), and the resultant equation can be formulated numerically using the implicit (forward in time and center in space) finite difference method as follows [19]:

$$\left[-\frac{D_z\Delta t}{R(\Delta z)^2}-\frac{V_z\Delta t}{R\Delta z}\right]C^{n+1}_{\mathrm{Cu}i-1}+\left[\frac{2D_z\Delta t}{R(\Delta z)^2}+1\right]C^{n+1}_{\mathrm{Cu}_i} + \left[-\frac{D_z\Delta t}{R(\Delta z)^2}+\frac{V_z\Delta t}{R\Delta z}\right]C^{n+1}_{\mathrm{Cu}_{i+1}}=C^{n}_{\mathrm{Cu}_i} \tag{3}$$

where R is the retardation factor (Eq. (4)), the superscripts $n+1$ and n are the next and present time step, respectively; $\Delta t = t^{n+1} - t^n$ is the time step size, and i, $i+1$, $i-1$ are the grid identifications in the z direction. The numerical model described was solved with a computer algorithm that can integrate the developed isotherm expression modeling framework within the reactive transport code which was written in MATLAB R2009b (version 7.9).

$$R = 1 + \frac{\rho_d}{n}\left(\frac{q_m b}{(1+bC)^2}\right) \tag{4}$$

3. Experimental work

3.1. Preparation of adsorbent

The olive pips were collected from kitchen waste and ground to achieve particle size distribution ranging from 75 μm to 1 mm. This reactive material was first washed multiple times in tap water and then rinsed in distilled water. Thereafter, it was dried until it reached a constant weight at 105℃, then cooled and sealed in plastic bags [16]. The bulk density and porosity of the reactive material measured was 0.584 g/cm^3 and 0.47, respectively.

Copper was selected as a representative of heavy metal contaminants. To simulate copper contamination in the water, $CuSO_4{\cdot}5H_2O$ solution (manufactured by Germany) was prepared and added to the specimen to obtain the representative concentration.

3.2. Batch experiments

Batch bio-sorption experiments were performed using different initial pH (2–8) for the solution, contact time of 240 min and initial copper concentration of (10, 20, 30, 40, 50 mg/L). One gram of the bio-sorbent was added to 50 mL of the contaminated solution and continuously stirred in the high-speed orbital shaker at 250 rpm at a constant temperature of 25℃. The equilibration times were found to be 2 h although for practical reasons the adsorption experiments were run for 4 h. At the end of the each experiment, the solution was decanted into a sample bottle and analyzed for the residual metal ions in solution using the atomic absorption spectrophotometer (AAS) (Norwalk, Connecticut, USA). These measurements were repeated twice, and the average value was taken. The amount of metal ion retained on the reactive material, q_e in (mg/g), was calculated as follows [20]:

$$q_e = (C_0 - C_e)\frac{V}{m} \tag{5}$$

where C_0 is the initial concentration of Cu^{2+} in the solution (mg/L), V is the volume of solution (L), and m is the mass of the reactive material (g).

3.3. Continuous column experiments

The experimental setup (Fig. 1) consisted of a Perspex cylinder of height and diameter equal to 20 and

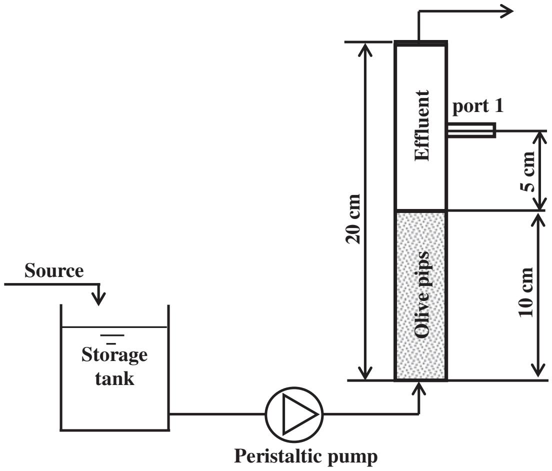

Fig. 1. Schematic diagram of the laboratory-scale column.

5 cm, respectively. This enabled visual examination of the wetting front progress and detection of the preferential flow channels along the column walls. The column dimensions were defined to minimize the occurrence of channeling by ensuring that the column diameter was not less than 30 times the maximum particle size of the material used [21]. The column dimensions also met the minimum length-to-diameter requirements [21]. This indicates that the column length (20 cm) must be four times greater than its diameter (5 cm). The column was equipped with one sampling port at a distance of 15 cm (port 1) from the bottom. Sampling from this port was achieved for monitoring variations in the Cu^{2+} concentration present in the effluent over time. The samples were taken regularly and analyzed by AAS.

The column was packed with the reactive material specimen up to 10 cm depth and then filled with distilled water, fed slowly into the bottom of the column. The water was then forced upward through the medium, pushing up the air in front of it. This procedure thus ensured no difficulties with entrapped air [22]. The up flow column test was performed at a constant temperature of 25°C.

The flow through the model bio-sorbent was accomplished by a 10-liter storage tank and peristaltic pump (Fisher Scientific, variable speed pump II- medium, model 3385, Control Company, USA). Experiments were conducted with three values of initial pH for the feed solution (2, 5, and 8) and two values of flow rate (8 and 12 mL/min). These flow rate values corresponded to the actual velocities (equal to 0.867 and 1.300 cm/min) to maintain Reynolds number <1–10 for the validation of Darcy's law [23].

A tracer experiment, adopting the same procedure of Fetter in 1999, was performed to determine the longitudinal dispersion coefficient of the olive pips reactive material [24].

3.4. Fourier transform infrared analysis

This analysis has been considered as the direct method for investigating the sorption mechanisms by identifying the functional groups responsible for the binding of copper onto the olive pips [25,26]. The characteristic bands of the olive pips before and after lead uptake at a pH 5 were used to assess the changes in the functional groups of this material. A 250 mL flask was filled with 50 mL of the contaminant solution containing 50 mg/L copper and 1 g of olive pips. The flask was agitated for equilibrium time at 250 rpm. The infrared spectra of the olive pips samples, pre- and post-copper bio-sorption, were examined using the 800 series Shimadzu Fourier transform infrared (FTIR) spectrophotometer, Japan.

4. Results and discussion

4.1. Functional groups of olive pips for copper bio-sorption

The infrared spectra of the olive pips samples, measured in the range of 400–4,000 cm^{-1}, before and after the bio-sorption of copper were examined (Fig. 2). The functional groups identified in the olive pips and their contributions in the bio-sorption process of copper are summarized in Table 1. The shifts in the infrared frequencies indicated that the alkyl halide, aromatic, alcohol, ester, amine, and carboxylic acid groups were responsible for the bio-sorption of copper onto the olive pips [27].

4.2. Development a Langmuir isotherm to model the pH-dependent adsorption effects

Fig. 3 shows an experimental data-set (symbols) measured at pH varying from 2 to 8. Each isotherm data-set corresponding with each pH was fitted to the Langmuir model (Eq. (2)) and the constants were estimated by non-linear regression using the IBM SPSS Statistics version 20 (Table 2). It is clear that the values of q_m and b vary with the initial pH of the feed solution.

In order to understand the relationship between q_m and pH and b and pH, the fitted values of these parameters against pH were plotted, as shown in Fig. 4. This implies that the values of b and q_m, fitted with the power curve and linear relationship, respectively, increase as the pH values increase until they equal to 5. Thereafter, these parameters decrease with similar types of fitted relationships with an increase in the pH values. Due to the protonation and deprotonation of the acidic and basic groups of the sorbent, the adsorption behavior for metal ions is influenced by the pH value, which in turn affects the surface structure of the sorbents, the formation of metal hydroxides and the interaction between the sorbents and metal ions [28]. This indicates that an increase or decrease in the pH from its best value (=5) resulted in a reduction in the affinity (indicated by b) for surface sites. This may be due to a competition for the binding sites between the cations and protons, at low pH values. At higher values of pH (>6), the removal was also low compared with the optimum condition. This can indicate that the binding site may not get activated in basic pH conditions [29,30].

From an initial acidic pH value of 3, the pH tends to rise as the operation progresses and remains

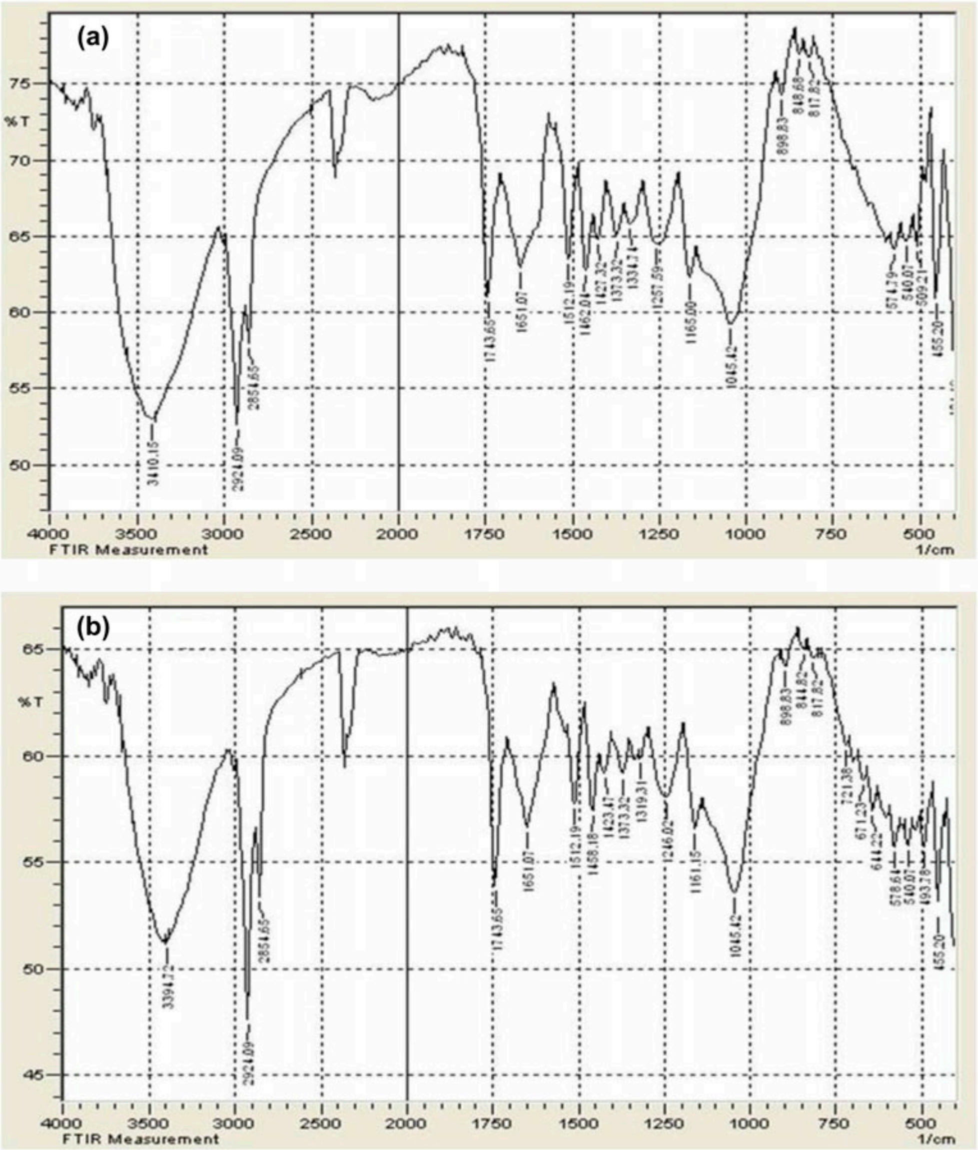

Fig. 2. IR spectrum of olive pips: (a) before Cu^{2+} loaded and (b) after Cu^{2+} loaded.

Table 1
Functional groups responsible for copper bio-sorption onto olive pips

Wave No. (cm^{-1}) before bio-sorption	Wave No. (cm^{-1}) after bio-sorption	Type of bond	Functional group
574.79	578.64	–C–Br stretch	Alkyl halides
848.68	844.82	C–H bend (para)	Aromatic
1,165	1,161.15	C–O–C stretch	Alcohols
1,257.59	1,246.02	C–C(O)–C stretch	Esters
1,334.74	1,319.31	C–N stretch	Amines
1,462.04	1,458.18	O–H bend	Carboxylic acids
3,410.15	3,394.72	N–H_2 stretch	Alcohols

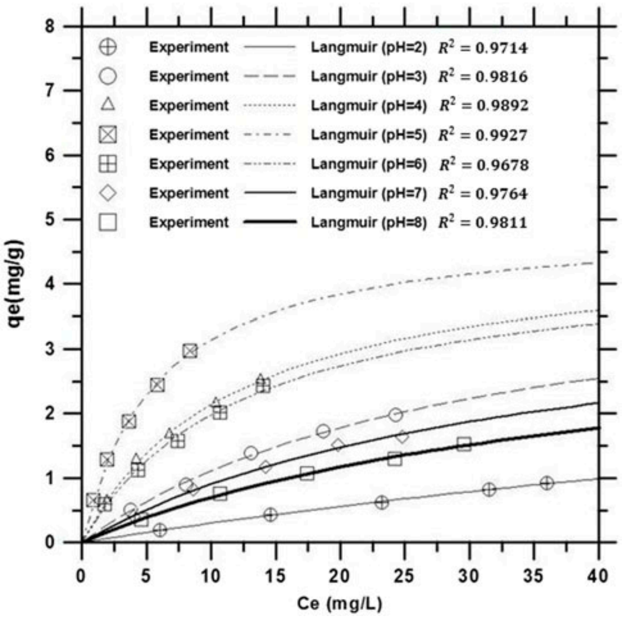

Fig. 3. Effect of initial pH on adsorption of copper ions onto olive pips reactive material.

Table 2
Values of maximum adsorption capacity and Langmuir isotherm constant as a function of initial pH of the feed solution

pH	Max. adsorption capacity (q_m, mg/g)	Langmuir constant (b, L/mg)
2	4.210934	0.007684
3	4.482777	0.032994
4	4.648093	0.085032
5	4.952972	0.17333
6	4.450081	0.080038
7	4.025408	0.029013
8	3.621876	0.023958

practically constant (=4) after around 60 min. This may be accounted for, as mentioned earlier, by the competition that arises between the cations and protons, to a point that as the protons are removed from the aqueous medium the medium tends toward a higher pH. By contrast, starting with an initially alkaline pH 8, the trend is downward as the operation progresses until the pH remains practically constant (6.2) after around 60 min. This behavior may be related to the greater presence of the $Cu(OH)^+$ ions that are retained by the solid, as well as to the precipitation of $Cd(OH)_2$, that occurs at an alkaline pH, removing the hydroxyl groups from the aqueous medium, resulting in a drop in the pH. This behavior is consistent with the findings of Blázquez et al. [31].

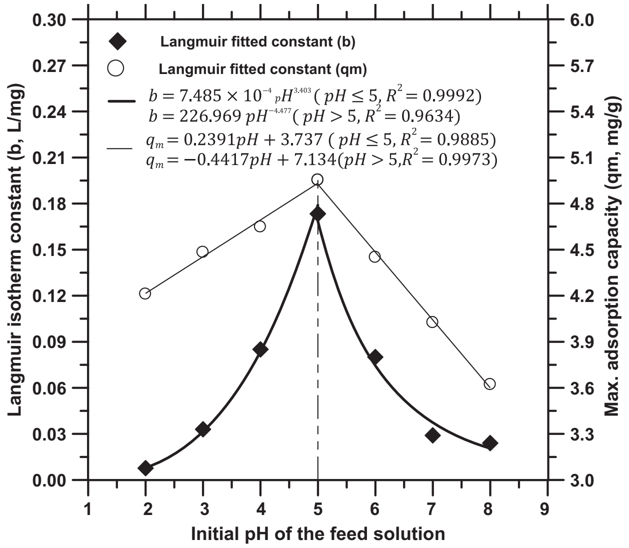

Fig. 4. Effect of initial pH on q_m and b estimated by Langmuir model for copper adsorption onto olive pips reactive material.

The relationships describing the values of q_m and b listed in Fig. 3 can be illustrated using the following general expressions:

$$q_m = \alpha_1 \mathrm{pH} + \alpha_2 \tag{6}$$

$$b = \alpha_3 \mathrm{pH}^{\alpha_4} \tag{7}$$

Inserting the above expressions in Eq. (2) yields:

$$q = \frac{(\alpha_1 \mathrm{pH} + \alpha_2)(\alpha_3 \mathrm{pH}^{\alpha_4})C_e}{1 + (\alpha_3 \mathrm{pH}^{\alpha_4})C_e} \tag{8}$$

This equation represents a flexible framework that can be used to describe the variations in the adsorption at different pH values using a consistent set of isotherm parameters. Also, this equation combined with Eq. (1) can form an integrated model that can be used to predict the pH-dependent adsorption effects on the performance, i.e. retardation factor and longevity, of the olive pips reactive barrier.

4.3. Performance of PRB under pH-dependent adsorption effects

The integrated model developed above can be solved with the initial and boundary conditions describing the status of the column experiments conducted in this study. The initial liquid and solid copper concentrations are assumed to be zero throughout the entire flow domain. The boundary conditions are represented by a concentration of Cu^{2+} equal to 50 mg/L at the bottom of the column (i.e. $z = 0$) and the advective flux of the pollutant at the top of the column (i.e. $z = 10$ cm).

As a result of the bio-sorption processes, dissolved metals will move much more slowly through the sorbent bed than the feed solution that is transporting them, an effect termed retardation [24]. Fig. 5 shows that the retardation factor of the olive pips reactive material is directly dependent upon the concentration of the hydrogen ions in the initial copper solution. It is clear that this factor increased with increasing pH values up to 5, where the highest retardation factor of the olive pips is achieved regardless of the initial or equilibrium metal concentration. Whereas this factor, after pH 5, drops with a corresponding increase in the initial pH of the copper solution. This behavior is logical and agreed with the adsorption (affinity) effects in response to the initial pH of the feed solution described above.

The breakthrough curves of the copper ions in the column effluent (Fig. 6), over the pH range of 2–8, illustrate that the predicted and experimental normalized concentrations increase in time until a steady-state concentration is observed. The time required for reaching the same normalized Cu^{2+} concentration in the effluent column decreases with decreasing or increasing the initial pH of Cu^{2+} solution from its best value. It is clear that the increased value of flow rate will increase the velocity of flow and, consequently, this will increase the propagation of the contaminant front for a given initial pH of the solution. Accordingly, the time required for achieving the steady-state concentration in the column effluent is decreased with the increased in the value of flow rate. This figure

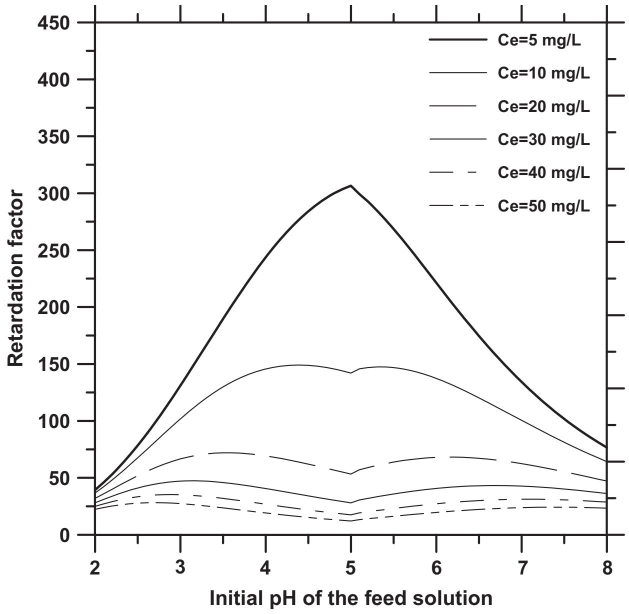

Fig. 5. Retardation of copper ions onto olive pips reactive material as a function of initial pH of the feed solution.

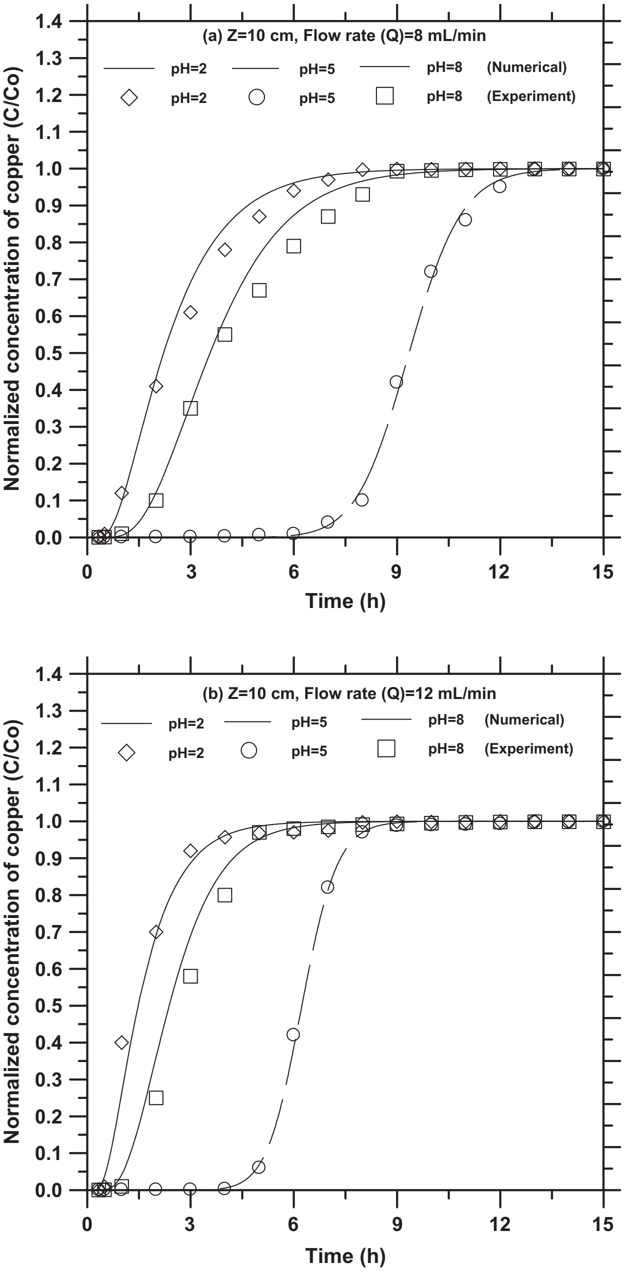

Fig. 6. Breakthrough curves as a result of the copper transport at effluent of the column for different flow rates using olive pips as PRB.

implies that there is a good concurrence between the predicted and experimental results. The Willmott's index of agreement (*d*) [32,33] is used to find the degree of agreement between the calculated and measured values. A value of 1.0 for the index of agreement indicates a perfect agreement between the calculated and measured values. Table 3 presents the values of *d* for the predicted and experimental results at different initial pH values of the feed solution and flow rates. It is clear that the values of this statistical tool are not less than 0.999.

Besides, the present integrated model developed was used to investigate the relationship between the longevity of PRB and the initial pH of the feed solution. Longevity can be defined as the time required maintaining the concentration of the contaminant down gradient of the barrier as less than the quality limit prescribed for surface waters or drinking water. The maximum contaminant level of Cu^{2+} permissible in drinking water must not exceed 1.3 mg/L, according to USEPA [34]. Fig. 7 reveals that the longevity of the barrier varies in a nonlinear trend with the initial pH of the feed solution for copper transport under the different flow rate values adopted in this study.

Table 3
The index of agreement for predicted and experimental results of copper concentrations at different values of initial pH and flow rates

	Initial pH of the feed solution		
Flow rate (mL/min)	2	5	8
8	0.999703	0.999789	0.99943
12	0.999608	0.999958	0.999377

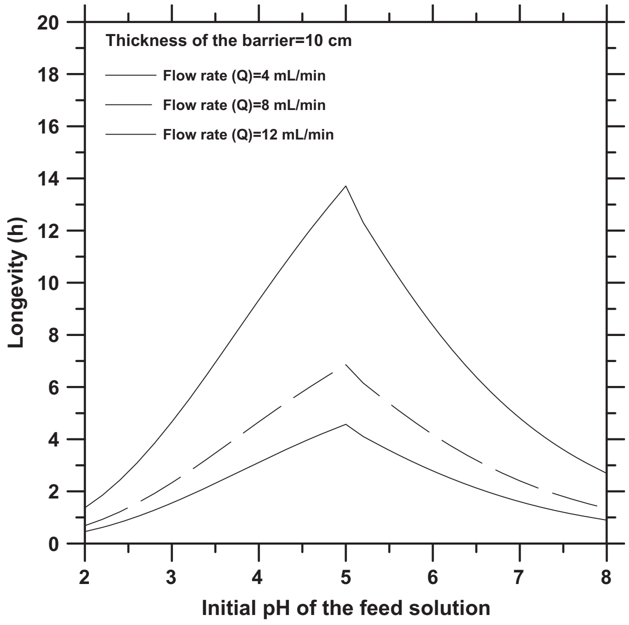

Fig. 7. Effect of initial pH of the feed solution on the longevity of the barrier for different values of flow rate as predicted by present developed integrated model.

5. Conclusions

(1) An isotherm expression for simulating pH-dependent adsorption effects was developed. Employing the Langmuir isotherm expression approach as the base model, the expression was subsequently modified by allowing the maximum adsorption capacity and affinity constant to vary with the pH values.
(2) As proven by the FTIR analysis, the alkyl halide, aromatic, alcohol, ester, amine and carboxylic acid groups were responsible for the bio-sorption process on the olive pips reactive material.
(3) A computer algorithm that can integrate the developed isotherm expression modeling framework within the reactive transport code was written in MATLAB R2009b (version 7.9). This model helped to prove that the initial pH had a significant effect on the retardation factor and longevity of the olive pips permeable reactive barrier involving a nonlinear relationship trend. Good concurrence between the integrated model predictions and experimental results for breakthrough curves was recognized, with *d* values not less than 0.999.

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