



Sand Modified with Nanoparticles of Calcium, Aluminum, and CTAB in the Form of Layered Double Hydroxide for Removing of Amoxicillin from Groundwater

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Abstract

The addition of new reactive sites on the surface area of the inert sand, which are represented by layered double hydroxide nanoparticles, is the primary goal of this work, which aims to transform the sand into a reactive material. Cetyltrimethylammonium bromide (CTAB) surfactant is used in the reaction of calcium extracted from solid waste-chicken eggshells with aluminum prepared from the cheapest coagulant-alum. By separating amoxicillin from wastewater, the performance of coated sand named as "sand coated with (Ca/Al-CTAB)-LDH" was evaluated. Measurements demonstrated that pH of 12 from 8, 9, 10, 11, and 12, CTAB dosage of 0.05 g from 0, 0.03, 0.05, and 0.1 g, ratio of Ca/Al of 2 from 1, 2, 3, and 4, and mass of sand of 1 g/50 mL from 0.5, 1, 1.5, 2, and 2.5 g/50 mL are the optimal manufacturing conditions for coated sand to guarantee an antibiotic removal efficiency greater than 80. After planting the LDH nanoparticles, characterization analyses revealed that the generation of a plate-like layer composed of loosely aggregated micrometric plates had significantly altered the structure of sand. Finally, as the sorbent mass increased as well as the flow rate and inlet contaminant concentration (C_0) decreased, the longevity of coated sand in the packed column significantly increased. In comparison to the Belter-Cussler-Hu and Yan models, the Thomas-BDST model provides a more accurate simulation of measured breakthrough curves.

Keywords: Amoxicillin; Transport; Alum; Breakthrough time; Layered double hydroxide.

Received on 29/12/2022, Received in Revised Form on 06/03/2023, Accepted on 06/03/2023, Published on 30/09/2023

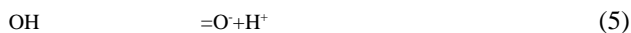
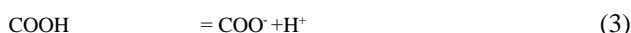
<https://doi.org/10.31699/IJCPE.2023.3.8>

1- Introduction

Antibiotic contamination of water resources is considered a global concern because these chemicals have been classified as highly harmful and toxic to human life as well as the ecosystem. Amoxicillin (AMX) in the environment can speed up the spreading of antibacterial resistance genes, eventually leading to the spread of bacteria that are resistant to beta-lactams. In addition, flucloxacillin-specific cell-induced liver injury may result from prolonged AMX exposure. As a result, in order to lessen the potential harm caused by exposure to this substance, there is a necessity to eliminate this antibiotic from the environment using a method that is both highly effective and sustainable. The AMX is a chemical that soluble in water at 37°C, having 3 values of pH 9.55, 7.11, and 2.67 because it contains several functional groups on its structure such as phenol, amine, and carboxyl respectively. It classifies weak polyprotic acid and the ionic species of amoxicillin change from a positive to a negative charge when the medium changes from an acidic to a basic medium. So, at $\text{pH} < 2.68$, its charge is positive due to the carboxyl group that has gained an ion according to equation [1].



In a basic medium, the amoxicillin molecule becomes negative according to the equations below [3].



In normal media, the amoxicillin molecule is zwitterionic [2].

Even though AMX is only available in small quantities, its toxicity can have a long-lasting impact on the sustainability of the ecosystem. Previous studies indicated that more than 80% of human-taken AMX is eliminated through urine after 2 hours. According to existing reports, the amount of AMX in wastewater produced from industrial, commercial, and residential uses as well as available within water resources can range from upper limit in mg L^{-1} to lower limit in ng L^{-1} .

For removing AMX from an aquatic environment, numerous methods, such as advanced oxidation, electro-degradation, adsorption, and photocatalytic degradation



have previously been explained in the literature related to the treatment of water [3]. The adsorption process stands out among all antibiotic abatement methods because it is cost-effective, simple to use, and able to eliminate organic chemicals from water [1]. Adsorption is highly efficient at preventing pollutants from traveling through the water system, which makes it ideal for removing AMX. Adsorption is appealing because it relies on the use of various sorbents [3], particularly those derived from industrial wastes like sewage sludge [4], dust of cement kiln [5], wastes of iron casting [6], zero-valent iron and zero-valent aluminum [7, 8] ash from rice husk [9] activated carbon and date stones [10] and others.

The permeable reactive barrier is a familiar technique used to treat groundwater contaminated with inorganic and organic compounds depending on the sorption mechanisms for restricting the contaminant migration. This barrier can be filled with reactive media that is either replaceable, semi-permanent, or permanently placed across the pathways of contamination plumes. The contaminant molecules are either degraded or removed by a series of reactions that have the ability to transform the contaminants into immobile or less hazardous compounds when contaminated water penetrates the wall under the natural hydraulic gradient.

Through the preparation of LDHs (layered double hydroxides), which are useful in the fields of magnetization, electrochemistry, and the environment, recent research has received a lot of attention. The synthesis methods are affordable and can be used in both industrial and laboratory settings. Numerous inorganic/organic chemicals, including heavy metals, dyes, and radionuclides, are well-adsorbable by the LDHs [5]. The interaction that takes place between non-framework inter-layer anions and the positively charged main lamellar makes the LDH of layered anionics that joined together by a non-covalent bond. The structure of LDH is composed of trivalent and divalent metal ions with the presence of anion that maintains equilibrium between layers. The abundance of inter-layer anions and hydroxyl groups in the LDH can increase the surface precipitation of metals [6]. Up to this point, many different kinds of LDHs have been produced and used to eliminate AMX from wastewater. One example is the synthesis of MgAl-LDH by co-precipitating Mg^{2+}/Al^{3+} with a ratio of 2 [2]. Co-precipitation was used to produce beads made of a nanocomposite (MgAl-LDH/cellulose) for treating AMX-polluted water. Sorbent and AMX both had negative charges under natural pH conditions; as a result, electrostatic forces can link this antibiotic to beads made of (MgAl-LDH/cellulose) [1]. The term "sand coated with (Ca/Al)-LDH" refers to the immobilized Ca and Al particles on the sand surfaces. A molar ratio of 2 for Ca/Al, a sand of one gram per 100 milliliters, and a pH of 8 are required for this sorbent to be prepared in the most effective manner for removing Congo red dye [5].

To minimize the impact of solid waste on the surrounding environment, the current investigation focuses on the extraction of calcium from eggshells. In the presence of a well-known surfactant (CTAB), this

element will be combined with Al to produce nanoparticles that will be planted on the inert sand. The capability of modified sand to clean up water that has been tainted with AMX will be evaluated by a set of column tests to evaluate the ability of the prepared sorbent bed as a permeable reactive barrier to restrict the propagation front of the contaminant plume in the simulated and real groundwater.

2- Experimental Approach

2.1. Materials

Chicken eggshell is composed of 4% minerals and 96% calcium carbonate; so, it can be an excellent source of calcium ions [11]. Filter sand (used in the purification of water) is provided from the nearby market. The porosity and specific gravity of sand have values of 0.45 and 1.36; respectively, with grain sizes ranging from 1 to 0.6 mm. The $Al_2(SO_4)_3 \cdot 14H_2O$ is a chemical form for "Alum" used to prepare the solution rich with Al ions. This coagulant (water-soluble) is applied to the raw water in the purification process to increase the efficacy of sedimentation tanks. The composition of the coated sand was supported by the CTAB. To mimic the target contaminant, the AMX antibiotic was used. It was provided by the Samarra Drug Organization in Iraq. The water samples containing 1000 mg/L of AMX were made by mixing 1 liter of distilled water (DW) with 1 gram of this contaminant at room temperature; however, the samples must be diluted to obtain the antibiotic concentration.

2.2. Fabrication of sorbent

To set up the current sorbent, 1 gram of washed and dried eggshells (smaller than 0.6 mm) was mixed with a blend comprised of various amounts of HCl (2, 5, 10, 15, 20, and 25) mL in 100 mL DW. This mixture was agitated at room temperature with a speed of 200 rpm for 3 hours. Using filter paper (Ashless filter paper type CHM F2040), to isolate residues of solid eggshells from the aqueous solution containing Ca ions. To get a solution with a certain molar concentration of Al, the specific mass of alum was dissolved in DW. The two Ca and Al solutions were thoroughly mixed using various molar ratios (1, 2, 3, and 4) and the CTAB dosages (0, 0.03, 0.05, and 0.1) g per 50 mL, to produce LDH nanoparticles. Manufactured calcium-aluminum-surfactant nanoparticles were precipitated on the filter sand (as an immobilized solid matrix) to establish new binding sites and functional groups that can increase the reactivity of modified sand. The utilization of sand in the manufacturing of composite sorbent-bed was to ensure the obtaining adequate hydraulic conductivity required for continuous operation. Various sand masses (0.5, 1, 1.5, 2, and 2.5) g were added to acquire the composite sorbent. The co-precipitation method was a governed approach in the preparation of LDH at room temperature. The first variable studied was pH by taking 4 grams of sand was mixed with 50 mL of a

solution containing 0.1 g of CTAB and Ca to Al ratio of 1. The solution needed to be agitated at 200 rpm for 3 hours to produce modified sand at pHs (8, 9, 10, 11, and 12). The interaction of 0.5 g modified sand (produced at a specific pH) with an aqueous solution containing 50 mg/L AMX was achieved at 3 h, 200 rpm, and pH 7.4 to track down the impact of manufacturing pH on the removal rate of AMX. 0.1 M NaOH is required for the formation of the coating layer and raising the pH of the mixture. Coated sand was separated from the solution by filtration and the unattached nanoparticles were removed by washing with DW. After that, 105°C was used to dry this sand for 3 hours. When evaluating the effectiveness of a coating process in relation to the (Ca/Al) ratio, mixture pH, and surfactant masses, the removal efficiency of antibiotics by coated sand is the only reliable indicator.

2.3. Characterization analyses

The "Siemens X-ray diffractometer, D8 Advance, Bruker, Germany" was used for the XRD analysis to examine the manufactured sorbent's crystalline structure. Functional groups liable for pollutant restriction with composite sorbent were determined through FT-IR investigation. Additionally, the "X Flash 5010, Bruker AXS Microanalysis, Berlin, Germany" SEM-EDS test was used to determine the sorbent's morphology and element percentages.

3- Column Tests

As depicted in Fig. 1, the experimental setup for representing the transport of AMX in water was composed of a single column and several accessories, including a storage tank, peristaltic pump, valves, and

pipes. The wall of the column was 5 mL thick, and its inner diameter and height were 2 and 35 cm, respectively. To represent the actual situation, the AMX transport in the coated sand bed was considered uniform and in one dimension. For the sole purpose of determining how well (Ca/Al-CTAB)-LDH nanoparticle-coated sand reduced AMX concentration, the column was tested with the presence of such sorbent. In order to prevent air from becoming trapped, distilled water was injected into the composite sorbent bed from the bottom up at room temperature. Water containing AMX (50,100) mg/L was injected into the bed at 1, 5, or 10 mL/min under fixed inlet concentration after reaching the saturation state. The ports P1, P2, and P3 are located in the column at respective distances of 10, 20, and 30 cm from the inlet with a mass of 53.595, 105.92, and 157.092 grams respectively to study the effect of the amount of adsorbents on the treatment process. In order to measure the concentrations of AMX, water samples have been withdrawn from the ports at specific times. The coefficient of hydraulic conductivity (K) is a measure of how easily water can pass through soil and it is calculated for composite sorbent bed by applying Darcy's law [12]:

$$K = \frac{Q/A}{\Delta h / \Delta l} \quad (6)$$

where A is the cross-sectional area of the cylinder (2 cm) diameter in the system of this experiment, Q is the flow rate (the volume of permeable water during a certain time), and Δh is the head drop along bed length (35 cm in this system) and (Δl) is the bed length (30 cm). High values of K indicate permeable material through which water can pass easily; low values indicate that the material is less permeable.

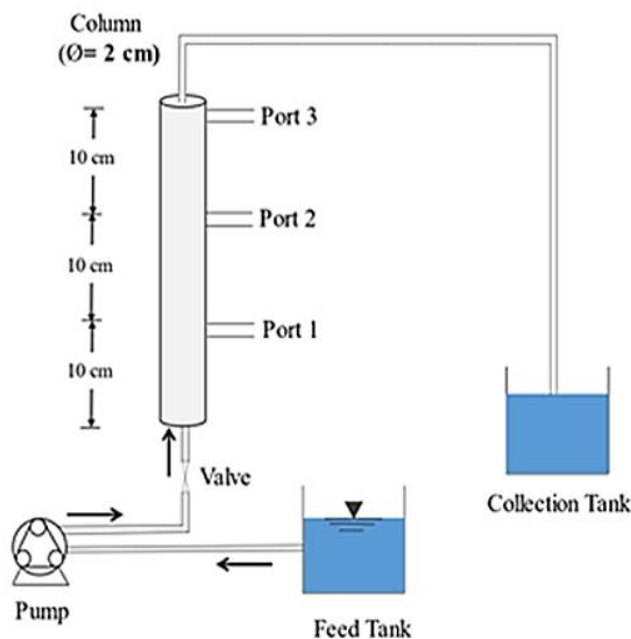


Fig. 1. Schematic Diagram and Picture of the Real System of Column Setup Used for Continuous Operation

4- Modeling of Breakthrough Curves

The propagation of the breakthrough curves provides a description of the performance of a fixed-bed column. An adsorption column's operation and dynamic response are greatly influenced by the trend of the breakthrough curve and the time taken for the breakthrough to appear [13]. There are a few observational models recorded as listed below that can be utilized to figure out such curves.

4.1. Thomas model

It is one of the most general and widely used models in previous studies such as [14, 15]. In order to derive this model, it was assumed that the Langmuir model would explain the sorption approach without taking into account dispersion in the axial direction and that the driving force would be a second-order kinetic reversible reaction. Thomas's model can be written as follows [16]:

$$\frac{c}{c_0} = \frac{1}{1 + \exp\left[\frac{(Mq_0K_{Th}) - K_{Th}C_0t}{Q}\right]} \quad (7)$$

where M is the sorbent mass filled in the column (in grams), Q is the flow rate of water pumped into the bed (in milliliters per minute), C_0 is the influent or inlet concentration (in mg/L), q_0 is the maximum sorption capacity (in mg/g) and K_{Th} is the Thomas rate constant (mL/min mg). This model can be used to estimate the values of q_0 and K_{Th} by fitting the measured breakthrough curve with the non-linear regression of Excel 2016.

4.2. Belter model

It is an empirical expression that depicts the pollutant's temporal transport at a particular point [17]:

$$\frac{c}{c_0} = \frac{1}{2} \left(1 + \operatorname{erf} \left[\frac{(t-t^{0.5})}{\sqrt{2}\sigma t^{0.5}} \right] \right) \quad (8)$$

where t is the residence time in the column, $t^{0.5}$ is the time needed for C/C_0 to be equal to 0.5, and σ is the slope of the "breakthrough curve"; however, constants of this model can be determined by non-linear fitting in the Microsoft Excel 2016.

4.3. Yan model

The previous studies also referred to this model as the "Dose-Response model" and its formula can be found as given in Eq. 9 [18] and [19]:

$$\frac{c}{c_0} = 1 - \frac{1}{1 + \left(\frac{Q \times C_0}{q_0 \times M} \right)^a \times t} \quad (9)$$

where Q is the influent contaminated water's flow rate in L/min and a is the slope of the curve between C/C_0 and t . In Microsoft Excel 2016, non-linear fitting can be used to estimate the constants q_0 and a .

5- Results and Discussion

5.1. Modification of sand

The sand surface was modified by adding LDH-shaped nanoparticles composed of Ca, Al, and CTAB. Ca was extracted from chicken eggshells solid wastes, and the results (by laboratory examination) showed that the most Ca ions concentration (1733 mg/L) was obtained when 5 mL of HCl was added, as shown in Fig. 2. The pH of the solution, CTAB quantity, ratio of Ca to Al, and sand mass all played a role in the production of the composite sorbent, which consisted of sand and nanoparticles. The highest achievable AMX removal efficiency onto the modified sand was used to determine the optimal value for each of the aforementioned parameters. After changing the pH value (8,9,10,11 and 12) at which the absorbent material was manufactured, an adsorption test for the contaminant was performed under conditions of 0.5 g modified sand (produced at specific pH) with an aqueous solution containing 50 mg/L AMX at 3 h, 200 rpm and pH 7.4 to track down the impact of manufacturing pH on the removal rate of AMX. The findings demonstrated that AMX removal at pH 12 was the highest (44%) as shown in Fig. 3 (a).

The CTAB, was another parameter affecting the coating of the sand, was varied from 0 to 0.1 g at best sand dosage of 1 g/50 mL and pH 12. However, the conditions of fabrication and batch tests utilized for studying the pH effect were also used. According to the findings, the CTAB dosage of 0.05 g resulted in the highest AMX removal 82% which was higher than coated sand without surfactant (70%) as shown in Fig. 3 (b). The remarkable increase in contaminant removal can be attributed to the fact that the presence of surfactant can significantly increase the spacing between the layers of LDH [20]. The adsorption efficiency of AMX was examined in relation to the molar ratio of calcium to aluminum. The AMX removal decreased slightly when this ratio was changed from 1 to 4, with the highest removal occurring at a molar ratio of 2 (86 percent for coated sand) as shown in Fig. 3 (c). The layered hydroxide-like structure of LDH, as well as variations in the radius difference between Ca and Al, can result in lower removal percentages for ratios ≥ 2 [21].

Finally, the coating procedure was evaluated with a sand dosage range of 0.5 to 2.5 g/50 mL and kept up pH, CTAB mass, and Ca/Al molar proportion at best values determined beforehand. This step's measurements demonstrated that, in the presence of CTAB, the maximum AMX removal (86 percent) could be achieved at a sand dosage of 1 g, as shown in Fig. 3 (d). A higher amount of sand particles implies there is an extra surface region that, even in the best preparation conditions, cannot be covered by the same nanoparticles; as a result, AMX removal decreases. Additionally, the AMX removal efficiency was likewise affected by the sand's lower mass because a number of nanoparticles were unable to bind with the surfaces of the sand and dissipated with the wash water at the end of the fabrication process [5].

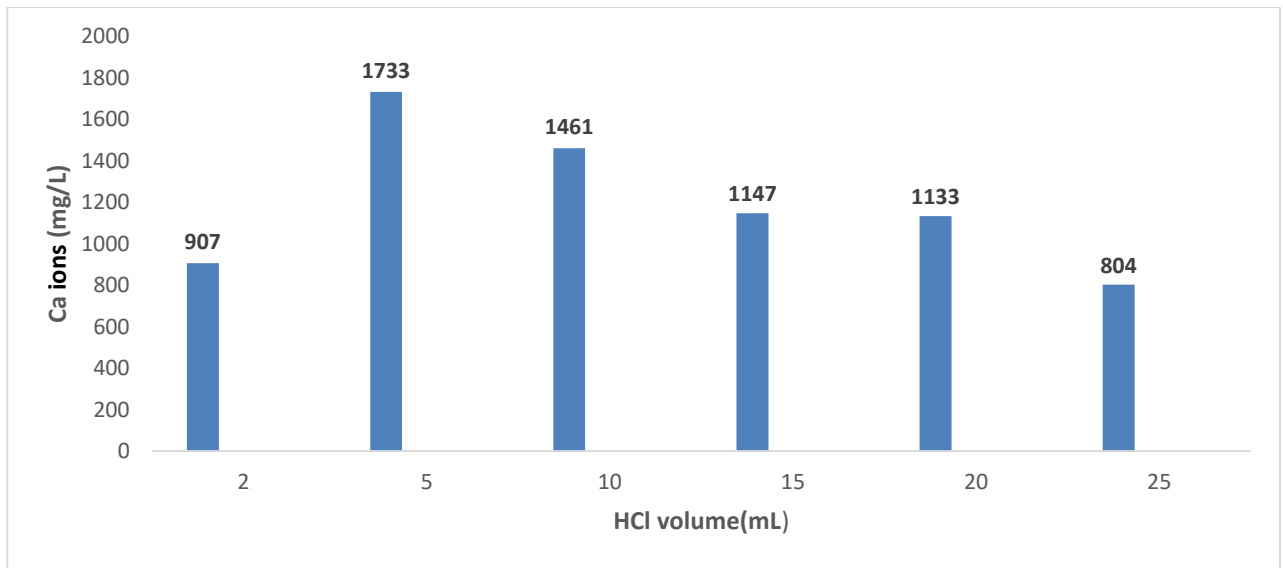


Fig. 2. Concentration of Calcium Ions Extracted from Chicken Eggshells as Function of HCl Volume

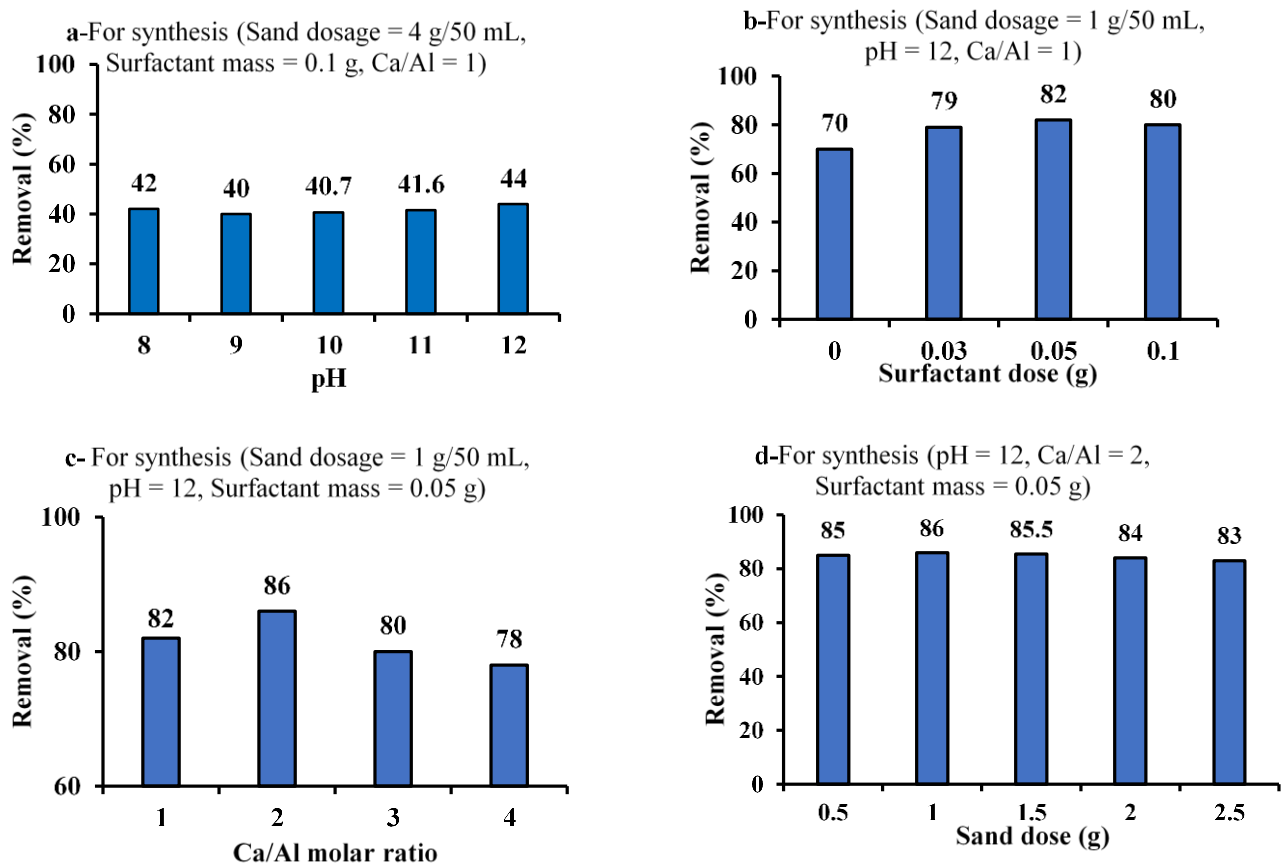


Fig. 3. Effects of a) pH, b) Surfactant Dosage, c) (Ca/Al) Ratio, d) Sand Dosage on the Removals of Amoxicillin by Sand Coated with (Ca/Al-surfactant)-LDH for Sorption Conditions (Time=3 h, $C_0=50$ mg/L, Sorbent Dosage=0.5 g/50 mL, pH 7.4, Speed 200 rpm)

5.2. Description of present sorbent

The "X-ray diffractometer, XRD" analysis was used to determine the prepared composite sorbent's crystal structure. This analysis identified the components of virgin sand and coated sand (immobilized solid particles) beyond the precipitation of LDH nanoparticles on the

surfaces of sand. Diffraction reflections appeared at different intensities that were identical to the precipitated nanoparticles. According to the "Joint Committee on Powder Diffraction Standards (JCPDS)", the primary component of the utilized sand is silica. The prepared sorbent's XRD analysis demonstrated the inclusion of

aluminum and calcium with the presence of silica oxide [22, 23] as shown in Fig. 4.

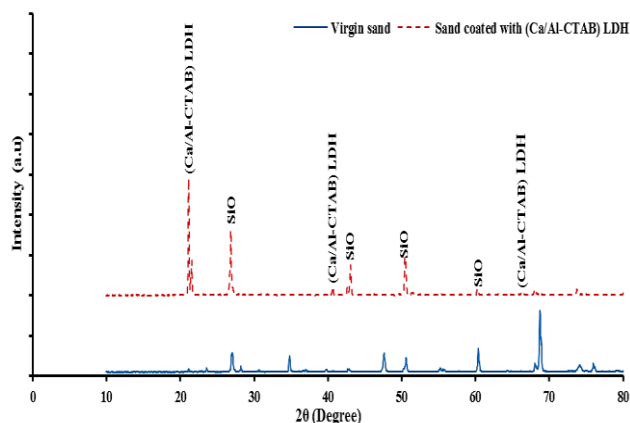


Fig. 4. XRD Profile for Virgin Sand and Sand after Coating with (Ca/Al-CTAB)-LDH Nanoparticles

The monitoring of functional groups for coated sand in comparison with virgin sand prior to the sorption and following the sorption of antibiotic was achieved as shown in Fig. 5. The peak at 3445.21 cm^{-1} represents the -OH groups vibration that bonded to the inter-lamellar water [6]. At sharp bands of 1093.44 and 1152.26 cm^{-1} , the Si-O-Si bond can be recognized; however, the Si-O bond's appearance at 778.136 cm^{-1} confirms the existence of quartz [24]. Due to the presence of LDH nanoparticles, the formation of inter-layer water molecules, hydrogen bond-stretching vibration, or OH-stretching mode can be identified by the existence of a wide peak at 3430 cm^{-1} [5]. Other bands found between 400 and 800 cm^{-1} can be attributed to "M-O, M-OH, and O-M-O (M=Ca⁺² and Al⁺³)", indicating that nanoparticles successfully modify the sand [1]. New peaks at 991.232 and 1159.97 cm^{-1} were observed on sand surfaces after AMX adsorption, and they were identical to the S-O and C-N vibrations, respectively [25].

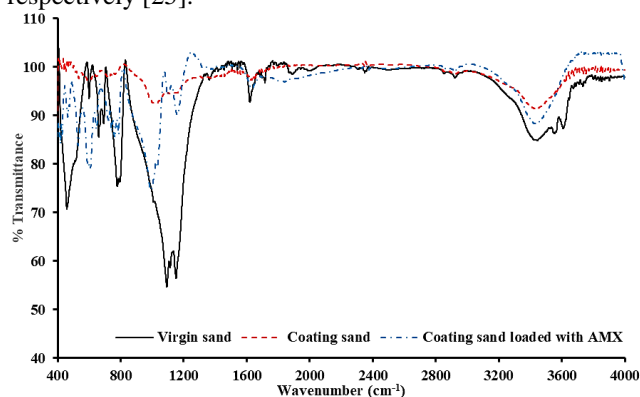


Fig. 5. FT-IR Analysis for Virgin Sand as well as Coated Sand before and after Interaction with Amoxicillin Antibiotic

The morphologies of virgin sand, coated sand, and coated sand loaded with the AMX antibiotic are depicted in Fig. 6. Fig. 6 (a) suggests that the sand contains rod particles with diversely porous surfaces that are extremely compacted and disordered. Fig. 6 (b) depicts sand

modified with LDH and explains how a plate-like layer of roughly aggregated micrometric plates of varying sizes and orientations was formed [26]. The adsorbent's efficiency was raised because of an increment in the area of the surface that interacted with AMX as a result of this layer's irregular configuration. After the sorbent interacted with the AMX antibiotic, as depicted in Fig. 6 (c), the attachment of contaminant molecules caused clear morphological variations. EDS analysis was used to determine the elemental proportions present in the composition of sand prior to and following the application of LDH, as depicted in Figure 6. A clear rise in the proportions of Al and Ca can be observed for the prepared sorbent; this indicated that the LDH coating was successfully achieved. In addition, the C content of virgin sand was 5.3%, and the addition of CTAB after coating the sand significantly raised this value to 15.3%. Additionally, because carbon is the primary component of the studied antibiotic, the sorbent's C content increased to 21% after the AMX interaction. The findings demonstrated that virgin sand had a surface area of $2.183\text{ m}^2/\text{g}$; however, the coated sand value had increased to $4.033\text{ m}^2/\text{g}$.

5.3. Transport of AMX

Under varying inlet AMX content, water flow rate, and mass of coated sand, experimental measurements were carried out on beds of modified sand. From breakthrough curves in Figure 7, it is evident the impacts of C_o variation with 50 and 100 mg/L for discharge of 1 mL/min on the propagation of the AMX front at ports from P1 to P3. This graph shows how an increase in inlet concentration resulted in the sorbent becoming saturated with contaminants within a short amount of time. This can be explained by the fact that a stronger driving force for the chemical mass transfer resulted from a high concentration gradient, which caused the adsorption sites to be exhausted more quickly [27]. From the plotted curves, it is possible to determine the breakthrough time that corresponds to five percent of the C/C_o for adopted antibiotics. The breakthrough time represents the "bed longevity" necessary to keep the concentration of chemicals in the effluent below the allowable regulation. With C_o 50 mg/L and discharge 1 mL/min, this figure proves that the "breakthrough time" for bed of 30 cm (P3) was 2 days. However, with C_o 100 mg/L, this value was significantly reduced to 0.8 days. For other ports, the relationship between "breakthrough time" and "inlet concentration" can be seen to follow a similar pattern; for P2, longevity can range between 1.7 days and 0.3 days for C_o of 50 mg/L and 100 mg/L with a flow rate of 1 mL/min. For the same flow rate, the periods of breakthrough at a depth of 10 cm (P1) were 1.5 and 0.25 days for C_o of 50 mg/L.

Effects of water discharge on the propagation of C/C_o at various ports for C_o of 50 mg/L is depicted in Figure 8. An increase in discharge from 1 to 10 mL/min speeded up the appearance of the chemical front, shortened the "breakthrough time", and made the "breakthrough curves"

steeper because before the chemical reached equilibrium, it left the bed [28]. For weak and reversible bonds, the high discharge may also desorb many attached molecules from the sorbent surface. As a result, the effluent's

contaminant concentration rose rapidly, accelerating the "breakthrough time". For instance, raising the flow rate from 1 to 10 mL/min for C_o of 50 mg/L at P3, can drop the breakthrough time from 1.75 to 0.75 days.

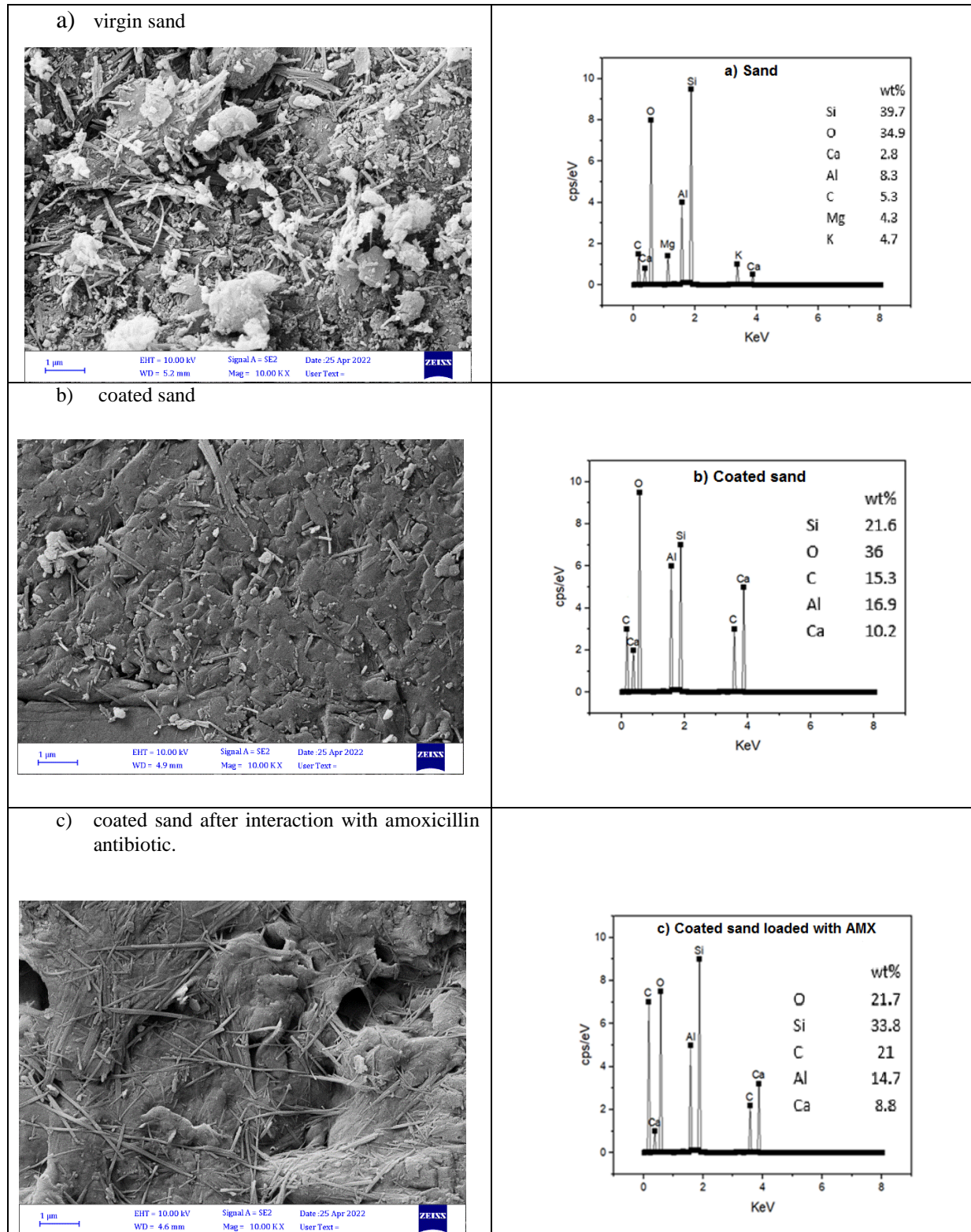


Fig. 6. SEM-EDS Images for a) Virgin Sand, b) Coated Sand and c) Coated Sand after Interaction with Amoxicillin Antibiotic

Fig. 7 and Fig. 8 demonstrate that the higher sorbent depth caused a significant delay in the appearance of the contaminant front, indicating that the bed depth may influence its propagation. As a result, the adsorption process was enhanced because the solute molecules had more time to diffuse into the particles' pores at the higher bed depth. With changing the bed depth from 10 cm (P1)

to 30 cm (P3), the breakthrough time dramatically increased from 1.5 to 1.75 days for a flow rate of 1 mL/min and a concentration of 50 mg/L at the inlet. It is essential to note that for the same C_o , increasing the bed depth resulted in a decrease in the bed's adsorption capacity because a particular concentration can spread over a higher area of surface at thicker depths.

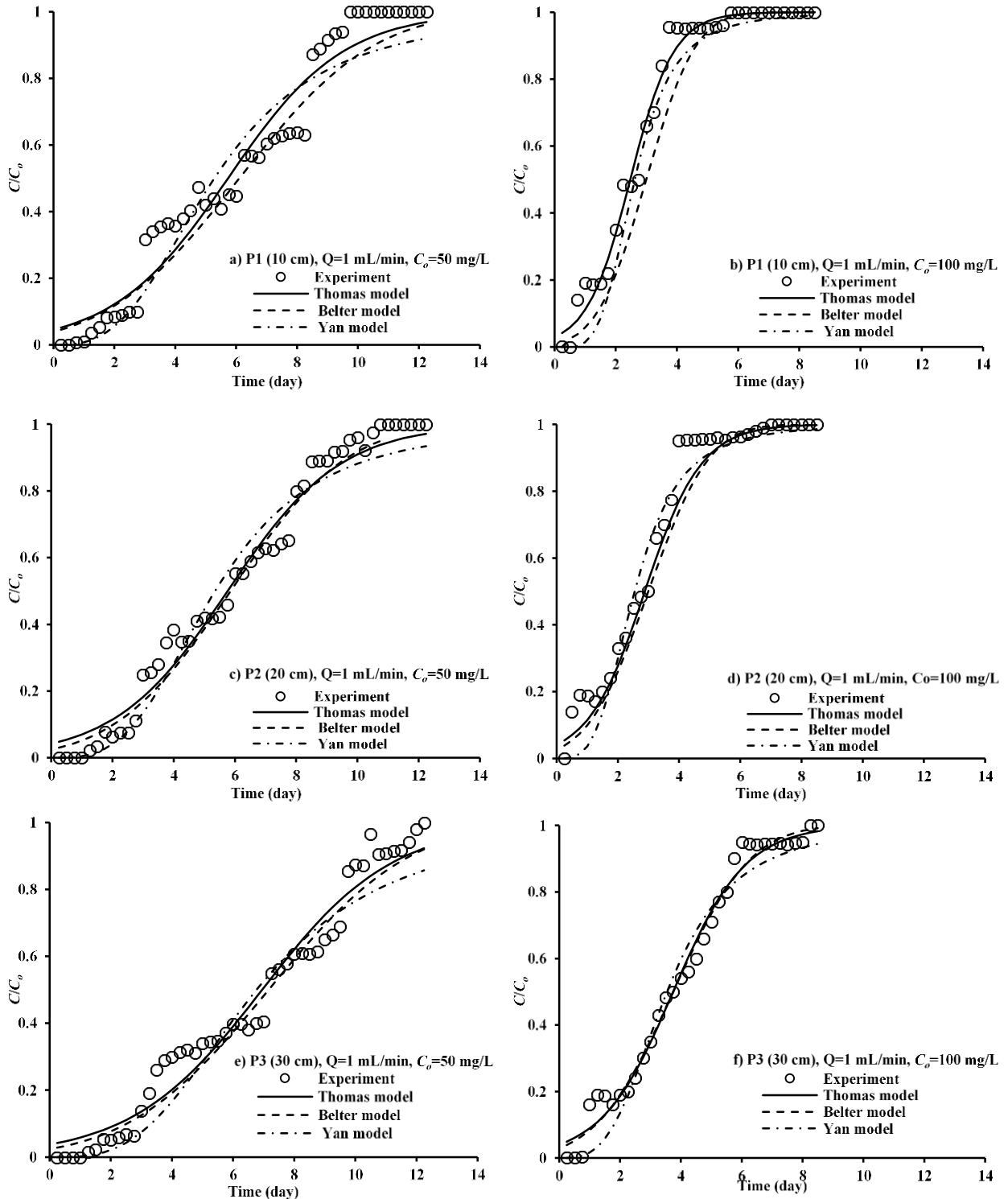


Fig. 7. Measured Breakthrough Curves of AMX in Comparison with Predictions of Models for Different Inlet Concentrations at Ports P1, P2, and P3

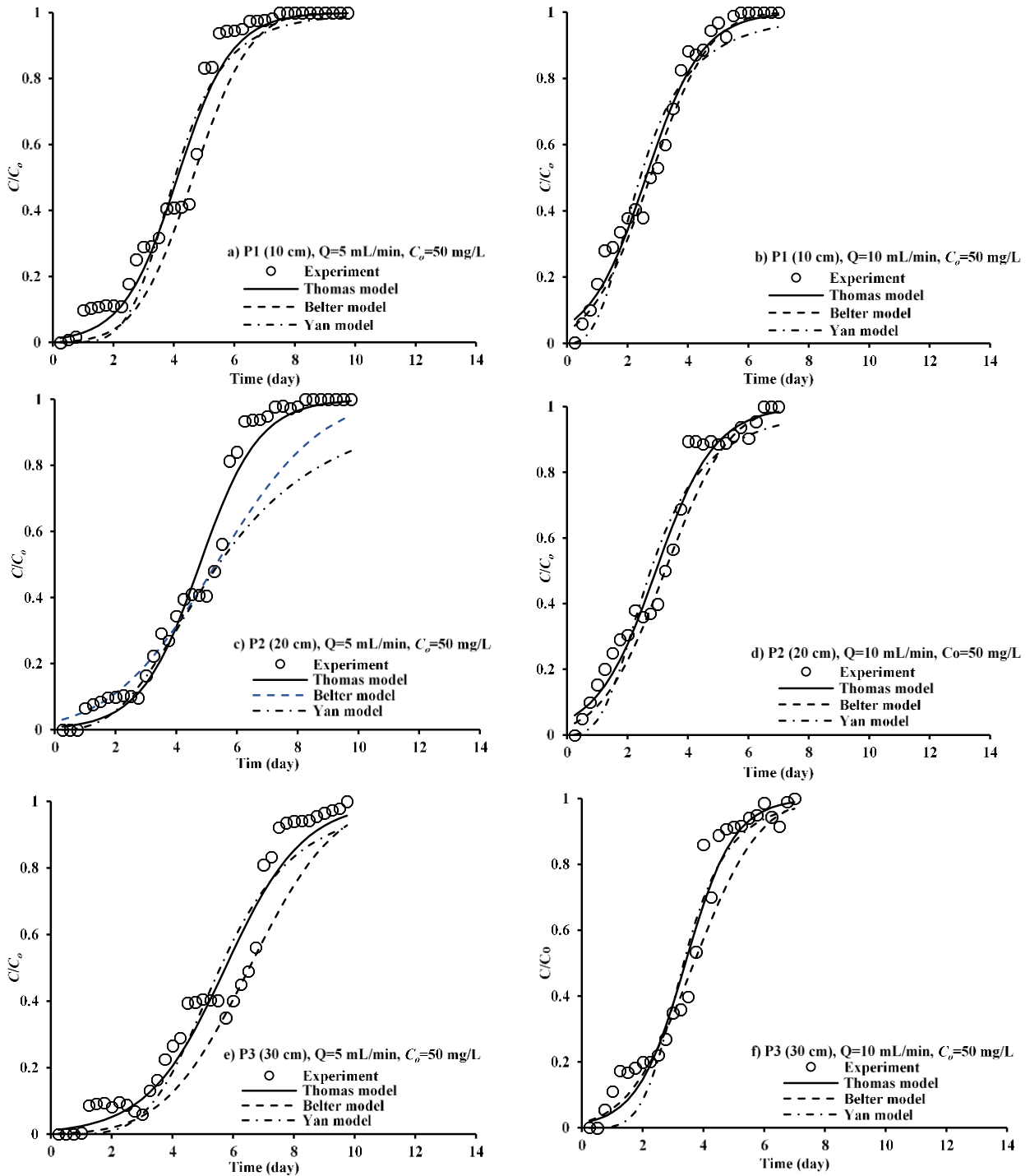


Fig. 8. Measured Breakthrough Curves of AMX in Comparison with Predictions of Models for Different Water Flow Rates at Ports P1, P2, and P3

AMX breakthrough curves along coated sand bed at different discharge and C_0 for depths ranging from 10 to 30 cm were compared with experimental measurements in Fig. 7 and Fig. 8. The Thomas-BDST, Belter-Cussler-Hu, and Yan models were used to simulate these curves at ports P1, P2, and P3. The "solver option in Microsoft Excel 2016 for nonlinear regression" was applied to determine the fit between the models mentioned and the measurements. With the lowest sum squared errors (SSE) and a coefficient of determination (R2) greater than 0.95,

the Thomas-BDST model accurately described the experimental measurements. The coefficient of hydraulic conductivity over the course of the operation is one of the most important characteristics that must be monitored for a packed bed. However, the outcomes demonstrated that these coefficients remained roughly constant throughout the experiments, with a mean value of 3.9×10^{-1} cm/s. This indicates that the voids for the movement of aqueous solutions remained accessible during solution transport and consequently, the contaminant's migration. In

Permeable Reactive Barrier (PRB), the appropriate permeability was greater than 2.1×10^{-2} cm/s [29].

5.4. Treatment of real groundwater sample

Water samples were taken from a well in the Baghdad Governorate-Iraq at the coordinates 33.2787828, and 44.2848751 to evaluate the column's ability to clean up real groundwater that was contaminated with AMX. These samples had values of 1648 mS/cm, 775 mg/L, 10 mg/L, 950 mg/L, 94 mg/L, and 40 mg/L, respectively, for electrical conductivity (EC), total dissolved solids (TDS), total suspended solids (TSS), sulfate (SO_4^{2-}), calcium (Ca^{+2}), and magnesium (Mg^{+2}). AMX was dissolved in the water samples collected from the mentioned well at a concentration of 50 mg/L, and then injected at a flow rate of 1 mL/min through the coated sand-filled column. At ports P1, P2, and P3, C/Co was monitored to determine the time it took to exhaust the packed bed (saturation time). At P1, P2, and P3, packed beds had saturation times of 6, 6.75, and 8 days for well water, respectively; whereas these values were 8.75, 9.25, and 10.25 days for the same ports when distilled water was used for stock solution preparation. Due to competition between the target contaminant and other dissolved salts in the well water, the coated sand bed performed less efficacy in treating contaminated aqueous solution prepared from well water based on saturation times [30].

6- Mechanism of Removal

Based on the surface chemistry of the sorbent and the evidence provided by the FT-IR spectrum, the mechanisms underlying the removal of AMX onto sand coated with (Ca/Al-CTAB) LDH were delineated. Even though the pH of the water and the amount of available AMX have a significant impact on the overall mechanisms of the sorption process, the functional groups supported such a process. The surface charge of the sand changed as a function of pH because the functional groups on the surface were protonated at low pH; the –OH groups on the surface can lose or gain a proton. Hence, a positive charge would be framed and the surface would be positive. At a low pH, positive charges can create an electrostatic attraction between oxygen, nitrogen, carbon, and hydrogen charges on the surface and (COO^-) groups in AMX [31]. The results of FT-IR spectra of coated sand before and after AMX interaction are consistent with this explanation. After sorption, the stretching peaks of oxygen-metal–oxygen and metal–oxygen-metal stretching appeared or changed, indicating that ion exchange occurred between the metal ions (Ca^{+2} and Al^{+3}) and AMX anions. The band at 3430.74 cm^{-1} is a property of the stretching vibration of hydrogen-bonded hydroxyl groups and water adsorbed. The removal of AMX onto coated sand was primarily governed by electrostatic interaction and hydrogen bonding [5].

7- Conclusions

A new sorbent named "sand coated with (Ca/Al-CTAB)-LDH" was created by co-precipitating these particles on the filter sand, an inert material, to remove the antibiotic amoxicillin from simulated and real groundwater. According to the findings, the optimal amount of hydrochloric acid to ensure the extraction of the highest calcium ion concentration ($=1733 \text{ mg/L}$) was 5 mL. To ensure an antibiotic removal effectiveness of more than 80%, measurements showed that a pH of 12, CTAB dosage of 0.05 g, Ca/Al ratio of 2, and sand of 1 g/50 mL were the ideal manufacturing conditions for coated sand. Characterization studies for coated sand showed that the creation of a plate-like layer made up of loosely aggregated micrometric plates had drastically changed the sand's structure. The findings demonstrated that the column's higher sorbent mass significantly delayed the emergence of contaminant fronts; however, the emergence of such fronts was accelerated by higher flow rate and inlet contaminant concentration values. The Thomas-BDST model offered a more accurate simulation of measured breakthrough curves than the Belter-Cussler-Hu and Yan models.

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تعديل الرمل بجزيئات نانوية من الكالسيوم والألمنيوم و CTAB في شكل طبقات الهيدروكسيد المزدوجة لإزالة الأموكسيسيلين من المياه الجوفية

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الخلاصة

الهدف الأساسي لهذا العمل هو إضافة مواقع تفاعلية جديدة على سطح الرمال الخاملة، والتي يتم تمثيلها بواسطة جزيئات هيدروكسيد النانوية المزدوجة، والتي تهدف إلى تحويل الرمل إلى مادة تفاعلية. يستخدم بروميد سيتيل تريميثيل الأمونيوم (CTAB) مع الكالسيوم المستخلص من النفايات الصلبة - قشر بيض الدجاج والألومنيوم المحضر من أرخص مادة تخثر - الشب. لفصل الأموكسيسيلين عن المياه الملوثة، تم تقييم أداء الرمل المطلي المسمى "بالرمل المطلي بـ LDH (Ca / Al-CTAB)". أظهرت القياسات أن الرقم الهيدروجيني ١٢، وجرعة CTAB البالغة ٠,٠٥ جم، ونسبة Ca إلى Al تساوي ٢، وكتلة الرمل ١ جم / ٥٠ مل هي ظروف التصنيع المثلى للرمل المطلي لضمان كفاءة إزالة المضادات الحيوية بنسبة تزيد عن ٨٠ بالمائة. بعد زرع جزيئات LDH النانوية، كشفت تحليلات الخصائص عن توليد طبقة تشبه الصفيحة تتكون من ألواح ميكرومترية متجمعة بشكل غير منتظم مما غير بشكل كبير بنية الرمل. أخيراً، مع زيادة كتلة المادة الماصة وكذلك انخفاض معدل التدفق وتركيز ملوث الداخل (Co)، زاد طول عمر الرمل المطلي في العمود المعبأ بشكل كبير. بالمقارنة مع نماذج Belter-Cussler-Hu و Yan، يوفر نموذج Thomas-BDST محاكاة أكثر دقة لمنحنيات الاختراق المقاسة.

الكلمات الدالة: أموكسيسيلين، انتقال، الشب، وقت الاختراق، هيدروكسيد مزدوج الطبقات.