Research Article

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Removal of paracetamol from aqueous solution by containment composites

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Abstract: Storage of wastes leads to severe problems of water pollution and neighboring matrices due to the infiltration of landfill leachate. Uncontrolled landfill and waste storage can lead to groundwater pollution, which can lead to serious health problems for the living. Engineered barriers can be a solution to these pollution problems. The purpose of this study was to develop novel composite materials – clay-based, activated carbon, cement, and PVA polymer. These composites were intended for the containment of waste in landfill. The clay (70–80%) and activated carbon (5–15%) contents were varied to obtain three different geomaterials – GM1, GM2, and GM3. In the preparation of GM3, the content of activated carbon used was higher than for GM1 and GM2, paracetamol removal capacity tested by adsorption, experiments were influenced by parameters such as the adsorbent mass, the initial solute concentration, contact time, temperature, and pH effect. The parameter of initial paracetamol concentrations was studied using a range of 50, 100, and 150 mg L^{-1}. For a GM3 mass of 80 mg, the adsorbed amount is 14.67 mg g^{-1}, and the contact time is 180 minutes. This study revealed that composites are efficient for the treatment of landfill leachates.

Keywords: geomaterials, activated carbon, clay, adsorption, wastes, landfill

1 Introduction

The industrial development of certain industries such as pharmaceutical, chemical, petrochemical, and agrifood industries leads to the waste generation. This is an inevitable outcome, which represents a risk for the environment and the human health when they are not recoverable (recycling, energetic recovery). Therefore, the burying of these wastes can lead to groundwater pollution problems leading to leachate infiltration. Thus, these effluents require prior treatment to retain toxic pollutants. Drug consumption in developing and developed countries is becoming increasingly intense. The release of these pollutants in the environment affects water and soil. These drugs are present in trace amounts. Among the drugs detected in trace amounts are antidepressants, antibiotics, contraceptives, antiepileptics, anti-inflammatory, aspirin, and paracetamol. Numerous paracetamol-based medications are available over the counter and commonly used for pain and fevers [1]. Drug use is the main source of release to the environment. After administration, the drug is absorbed, metabolized (transformed by the body), excreted, and then released to wastewater [2]. Several studies have shown the presence of drugs in drinking water at a concentration of 211 ng L^{-1} [2,3]. Indeed, paracetamol is metabolized in the liver and excreted in the urine and then released in wastewater. In the case of paracetamol overdose or if the time of taking the drug is wrong, some of them (paracetamol molecules) are directly excreted. The metabolization process occurred by a biochemical process that transformed the original molecules [2,4,5]. The new products called metabolites are excreted and released into the natural environment and then transported to urban treatment plants [4,6,7], which partially degrades. Excreted molecules are found in wastewater systems via sewage treatment plant effluents and pollute water. Therefore, stream get loaded with residues, then aquatic organisms are infected. Thus, paracetamol is the priority drug in

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the aquatic environment based on criteria of toxicity, persistence, and fate in the environment [8]. The paracetamol overdose can attack the liver and induce liver failure (hepatotoxicity) and hepatic coma in animals and humans [4,9,10]. Paracetamol overdose induces the formation of a metabolite form (*N*-acetyl-*p*-benzoquinone imine, NAPQI) toxic to the liver. Since the neutralization capacity of NAPQI by glutathione is exceeded, oxidative stress is produced causing mitochondrial dysfunction, mediated by the activation of a cascade of cytosolic kinases and followed by DNA fragmentation [11]. The risks associated with paracetamol, such as cardiovascular, gastrointestinal, and kidney diseases, have increased. Risk of kidney problems increases when paracetamol is taken cumulatively over a lifetime, as reported in a recent study [12]. Therefore, efficient and low-cost methods to deal with the environmental and health problems of paracetamol must be implemented. To remedy the problem of pollutant infiltration, researchers carried out a study using the cellulosic waste product to improve the physicochemical properties of the soil. [13,14]. This study attempts to show the possibility of reducing risks in the environment. Therefore, the development of landfills requires a permanently sealed barrier to protect the surrounding natural environment by preventing leachates from polluting soil and groundwater. The engineered barrier of a waste storage site is intended to prevent the discharge of landfill juices into groundwater by collecting leachate. Functions are active sealing and drainage. For drainage, granular and synthetic materials are used and geomembranes to improve sealing. This barrier must be permanently sealed and has a high capacity to retain organic and inorganic pollution [15]. Clay minerals have very low permeability, due to the small particle size and complex porous structures; they also have a large surface area that gives rise to strong interactions with liquids and dissolved species [16]. These interactions allow the retention of various leachate components. The montmorillonite clay smectite has a layered structure – an octahedral layer between two tetrahedral layers. The atom substitution in clay structure produces a negative charge compensated by the ions in the interlayer space (Li^+, Na^+, Ca^{2+}, K^+). Metal ion retention such as heavy metals is due to the electrostatic between negatively charged montmorillonite and compensating ions facilitated by cation exchange called Cation Exchange Capacity (CEC) [17,18].

The clay can be negatively or positively charged depending on the environment where it is located either acidic or basic. This property can promote the adsorption of organic pollutants by the formation of strong hydrogen bonds with Si–OH groups on the clay surface or by dispersion forces, as is the case with polar aromatic organic compounds or aliphatic organic compounds [19–22]. Similarly, activated carbon with a large porous surface and thermostability is one of the treatments frequently used against the infiltration of landfill leachates [14,23,24]. The surface of activated carbon with several functional groups plays a significant role in the removal of organic pollutants [25–27]. The interaction of the material with organic compounds is classified into three types [27–29]:

Organic compound-activated carbon.
Organic compound-solution.
Activated carbon-solution.

The removal of organic compounds by activated carbon is due to the attraction that occurs between the π orbitals of the base planes of carbon and the electron density of aromatic rings (π–π interactions) [30–33]. The activated carbon properties provide a high capacity to remove organic pollutants; hence, the choice to be used as an engineered barrier.

The clay-based engineering barrier has been the subject of the work of several authors [34–37]. Studies have revealed that clay is very effective in removing heavy metals [38–41].

Clay and activated carbon characteristics confer retention properties to the engineered barrier. To improve the retention properties of pollutants and isolate the groundwater from the source of pollution in the landfill sites, authors mixed clay and activated carbon and added the cement and the polyvinyl alcohol PVA polymer to increase the strength and the lifespan of the barrier. However, by mixing these constituents with different mass percentages, a range of materials called geomaterials. The removal of paracetamol by adsorption in an aqueous medium is tested on these materials and their mineral constituents.

2 Materials and methods

2.1 Reagents

Paracetamol ($C_8H_9NO_2$) – purity >99%; CAS Number: 103-90-2 – was purchased from Sigma-Aldrich. All other reagents used in this study are analytical grade and purchased from Riedel de Haën with a purity of 99%. A stock solution of 1 g/L paracetamol was prepared. A range of dilute solutions (25–700 mg/L) is prepared from the stock solution. Geomaterials used were prepared based on clay from western Algeria (Maghnia), activated carbon powder made from coconut purchased from Merck, Portland cement from Chlef (western Algeria), and PVA polymer from Fluka.

2.2 Geomaterial synthesis

The synthesis of geomaterials follows the following path. First, the clay was purified according to the Van Olphen process [42]. Then, a solution of NaCl 1 N was added to the purified clay. This step was performed to obtain a mono ionic clay. Then, the constituents of the geomaterials were added at different percentages by mass, mixed with 100 mL of distilled water with stirring for 48 h. The mixture was dried in an oven at 60°C, the resulting product was crushed. The final product is less than 1 μm in size. Figure 1 illustrates the geomaterial compositions.

2.3 Characterization

2.3.1 Nitrogen adsorption–desorption method

The studied adsorbents were previously degassed for 15 h at 150°C, then nitrogen adsorption–desorption was measured with the micrometric instrument ASAP 2010 at 77 K. The specific surface area of the samples was determined by the BET method [43].

2.3.2 X-ray diffraction (XRD)

Samples were analyzed by X-ray diffraction, curves recorded on an Xpert Pro Panalytical diffractometer using copper radiation of wavelength $\lambda = 0.15418$ nm. The crushed materials were placed on metal plates. Measurements were carried out in an angular range of 2θ from 0.03 to 70°, using a step of 0.02°.

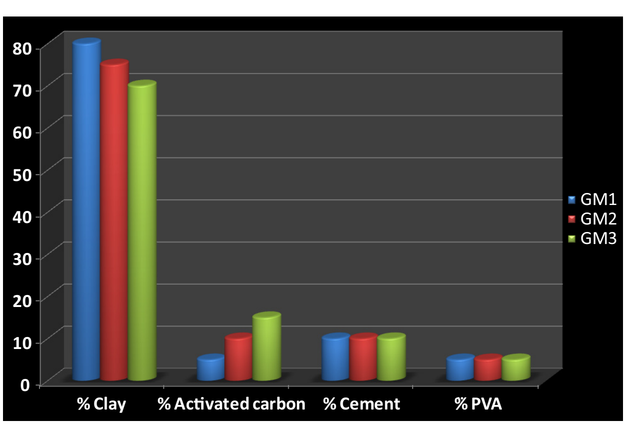


Figure 1: Composition of geomaterials.

2.3.3 Scanning electron microscopy (SEM)

The morphology of the samples was observed on a PHILIPS XL-30 FEG scanning electron microscope. Samples were powdered on an aluminum support previously covered with a self-adhesive pellet containing graphite.

2.4 Adsorption procedure

The stock solution of 1 g/L paracetamol was prepared with a purity of 99%. The studied solutions were prepared by dilution from the stock solution until the desired concentrations were obtained. The mass of the adsorbent is an important factor because of its effect on the adsorbent's ability to fix the adsorbate. The experiment was performed by mixing a mass of adsorbent with a volume of 10 mL of 150 mg/L of paracetamol solution. The mass of adsorbent was 10, 20, 40, 60, 80, and 100 mg in batch mode.

The adsorption kinetic was studied at the pH of the solution in a thermostated bath at 25°C, using 10 mL of different concentrations of polluted solution put in contact with an adsorbent matrix (GM1, GM2, and GM3) with a mass of 80 mg. The samples were shaken for different times (2 min to 24 h), and then the samples were filtered and analyzed by the UV spectroscopy analysis using a Perkin Elmer Lambda 35 spectrophotometer at a detection wavelength of 241.7 nm. The adsorption isotherms were carried out at pH of the solution; a volume of 10 mL of 25, 50, 100, 150, 200, 300, 400, 500, 600, and 700 mg L^{-1} of paracetamol solution. The pH effect was studied only with GM3. Using flasks that contain a volume of 10 mL of the paracetamol solution with a concentration of 150 mg L^{-1} at pH values from 2 to 12, by separation put in contact with GM3 with a mass of 80 mg. The samples were shaken for 24 h at 25°C. The initial pH values were adjusted by adding 0.1 N hydrochloric acid HCl or 0.1 N potassium hydroxide KOH solutions. The temperature effect was carried out at 25, 35, and 45°C at the same operating conditions to the adsorption isotherm at 25°C. The adsorption capacity and the removal efficiency were expressed by the relations (1) and (2), respectively:

$$Q_a = \frac{(C_0 - C_e)V}{m} \quad (1)$$

$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \quad (2)$$

where, Q_a is the adsorbed amount of pollutant per gram of adsorbent (mg/g), C_0 is the initial solute concentration (mg/L), C_e is the residual concentration of the solute (mg/L), V is the solution volume (L), m is the mass of the adsorbent (g).

2.5 Error measurement

Reproducibility of paracetamol adsorption results on GM1, GM2, and GM3 was studied. Experiments were repeated three times under the same operating conditions used in this study. The uncertainty was calculated using the following expression:

$$\sigma_x = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(X_i - \bar{X})^2} \quad (3)$$

$$\bar{X} = \frac{1}{n}\sum_{i=1}^{n} X_i \quad (4)$$

Hence $n = 3$.

Ethical approval: The conducted research is not related to either human or animal use.

3 Result and discussion

3.1 Characterization

3.1.1 XRD and SEM methods

Numerous studies used new materials in the landfill to isolate the source of pollution from groundwater and reduce the toxicity of pollutants until their removal [44–49]. In this section, the characterization of the synthesized geomaterials in Section 2.2 was carried out. The studied geomaterials were analyzed by X-ray diffraction. The XRD patterns showed contain montmorillonite, kaolinite, quartz, and calcite, as shown in Figure 2. Scanning electron microscopy analysis allows visualization of the morphology of the studied materials as shown in Figure 3.

The pure clay is in the form of leaves, shows particles of very variable sizes, and is most often aggregated (Figure 3a). With the addition of the geomaterials constituents, a smooth surface is obtained, which is pronounced in Figure 3d due to the activated carbon deposit [44,50].

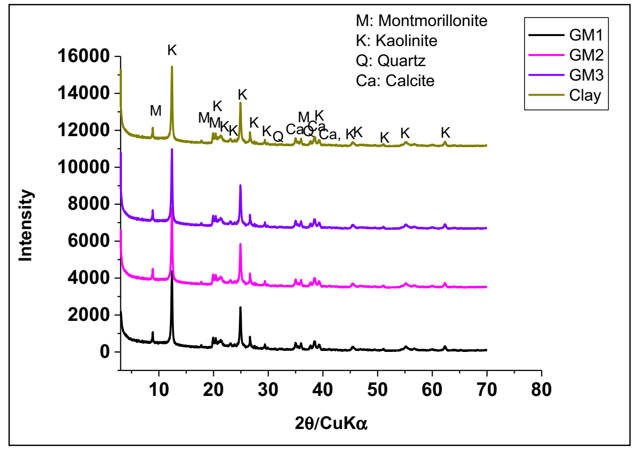


Figure 2: X ray diffraction patterns of geomaterials and clay.

3.1.2 Nitrogen adsorption–desorption isotherms

The nitrogen adsorption–desorption isotherm was studied. The result presented in Figure 4 shows that the adsorption isotherms were type 4 according to the IUPAC classification, which corresponds to mesoporous materials. It is also noticed that at low pressures, the volume of adsorbed nitrogen increased sharply and this is due to the microporosity which is related to the addition of activated carbon.

The specific surface areas of the studied materials were calculated by the BET method, from linear forms of nitrogen adsorption–desorption isotherms; the results are shown in Tables 1 and 2.

From the results presented in Tables 1 and 2, it was noticed that the specific surface areas and pore volumes of the geomaterials increased by increasing the mass percentages of activated carbon.

3.2 Paracetamol adsorption

3.2.1 Adsorbent mass effect

Adsorption may be influenced by several parameters. In this section, the adsorbent mass effect on paracetamol adsorption was investigated and the result was reported in Figure 5.

The curve shown in Figure 5 indicates that the removal yield increases by increasing the mass of the geomaterials until a maximum was reached. It is noted that the yield rate decreases for higher adsorbent dose [51]. This decrease in rate remains constant according to a previous study, due to the increase in the adsorbent

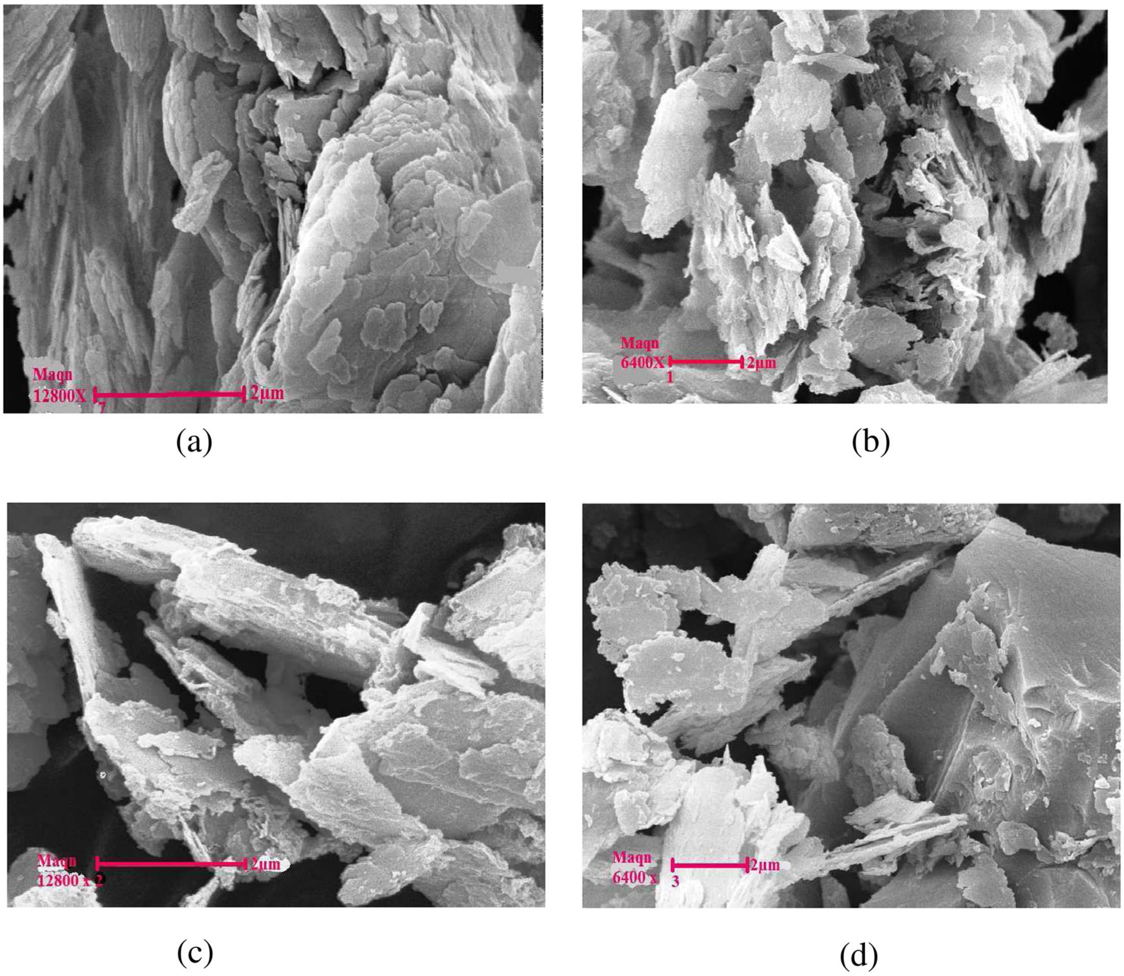


Figure 3: SEM images of ATMa clay (a), GM1 (b), GM2 (c), GM3 (d).

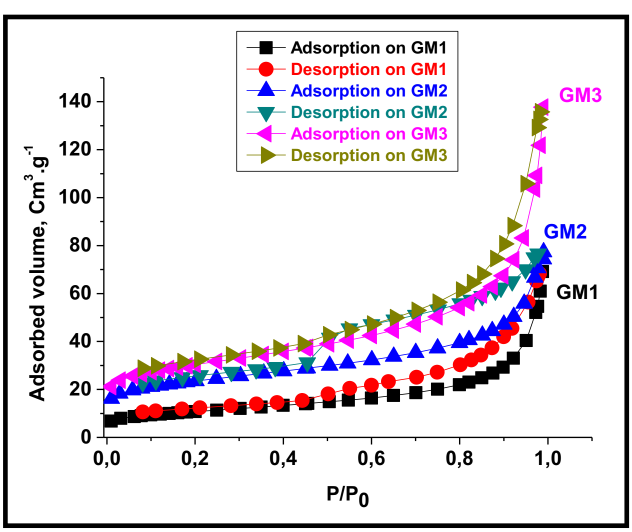


Figure 4: N_2 adsorption–desorption isotherm on GM1, GM2, and GM3.

mass, which creates an obstruction to prevent pollutant molecules to access adsorbent sites.

3.2.2 Adsorption kinetic

The contact time effect on paracetamol adsorption is shown in Figure 6.

The stages of the paracetamol adsorption kinetic are shown in Figure 6. First, a fast increase of the adsorbed amount was observed due to the availability of sites on the adsorbent surface [52], then a plateau was reached, which can be explained by saturation of the adsorbent sites. These curves were used to determine the equilibrium time (t_{eq}) and the adsorbed amount (Q_a), which follow the succeeding order: t_{eq} (GM3) = t_{eq} (GM2) < t_{eq} (GM1), Q_a (GM1) < Q_a (GM2) < Q_a (GM3); with values: 120 and 180 min, 4, 5.42, and 5.96 mg g^{-1}, respectively. This is

Table 1: Source of reagents and characterization of the geomaterial constituents

Constituents	Origin	S_{BET} (N_2/77 K)	V_p ($cm^3 g^{-1}$)	CEC meq/100 g	Size of particles (μm)	Moisture (%)
Bentonite	Maghnia	56.23	0.10	86.5	<2	9
Cement	Chlef	6.68	0.01	92.8	200–250	2.5
Activated carbon	Shell of coconut	658.52	0.55	—	<20	7.8

Table 2: Physicochemical characteristics of geomaterials

Geomaterial	S_{BET} (N_2/77 K)	V_p ($cm^3 g^{-1}$)
GM1	63.82	0.10
GM2	79.89	0.12
GM3	102.9	0.21

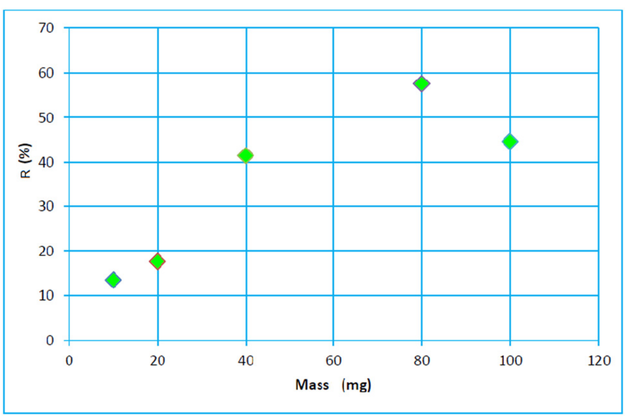


Figure 5: Influence of geomaterial mass on paracetamol removal yield.

related to the characteristics of geomaterials. Indeed, GM3 has a specific surface area of 102.90 $m^2 g^{-1}$ and a pore volume V_p of 0.21 $cm^3 g^{-1}$, which are 63.82 $m^2 g^{-1}$ and 0.1 $cm^3 g^{-1}$ and S of 79.89 $m^2 g^{-1}$ and V_p of 0.12 $cm^3 g^{-1}$, respectively, for GM1 and GM2. It has been demonstrated in a previous study [48] that the adsorption of pollutants on geomaterials is the contribution of mineral constituents, namely, clay, activated carbon, and cement.

3.2.3 Adsorption isotherm

The adsorption isotherm is a curve relating the equilibrium concentration of a solute on the surface of an adsorbent. The adsorption isotherms of GM1, GM2, and GM3 at 298 K are shown in Figure 7.

The adsorption isotherm is of type L according to Giles classification [53], characteristic of high-affinity systems between adsorbate and adsorbent, and a weak competition between the solvent and the solute molecules.

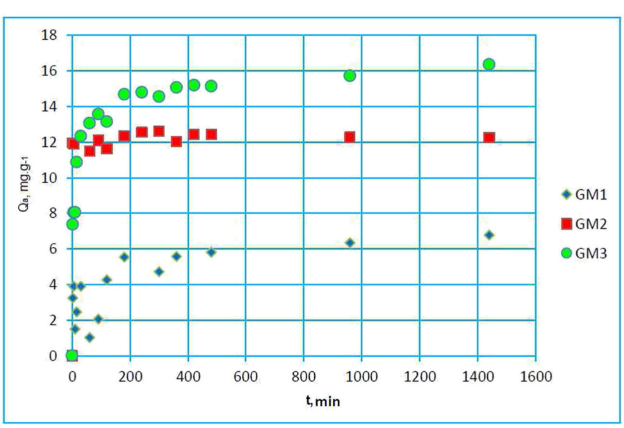


Figure 6: Variation of adsorbed amount as a function of contact time.

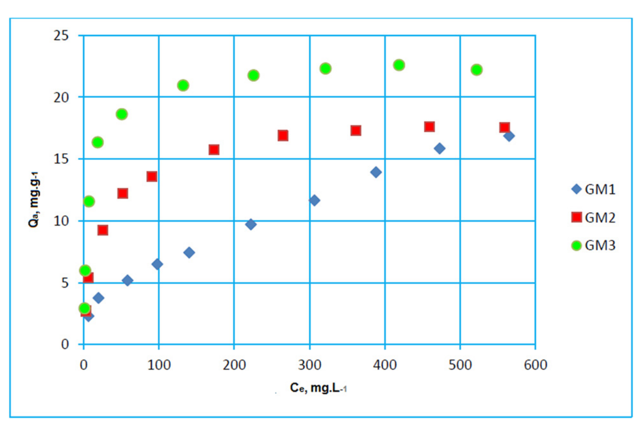


Figure 7: Paracetamol adsorption isotherm on GM1, GM2, and GM3 at 298 K.

3.2.4 Temperature effect

Temperature is one of the parameters that influence adsorption. Figure 8 illustrates the adsorption isotherms at 308 and 318 K.

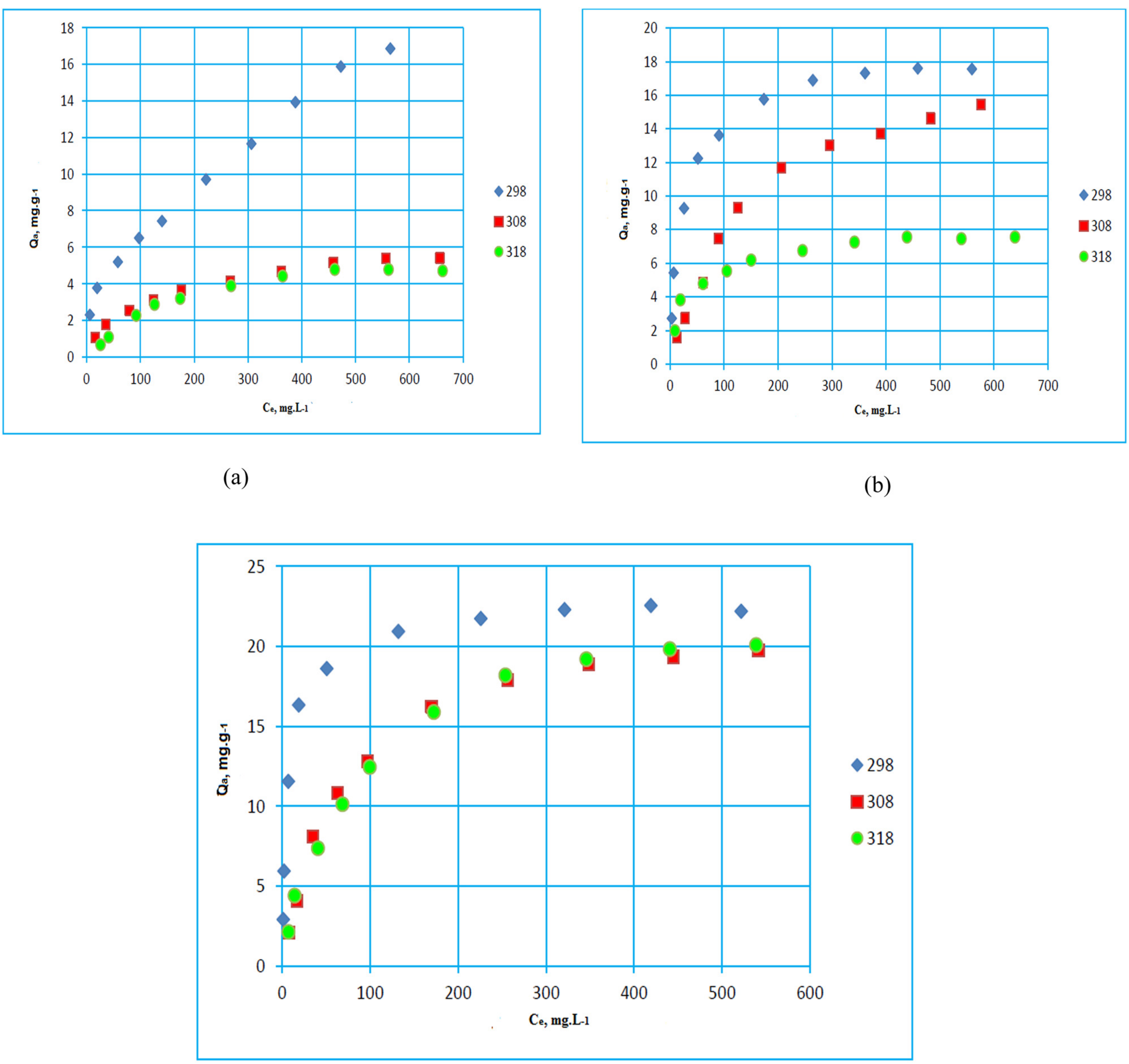
The results reveal the role of temperature (T) on adsorption. Indeed, by increasing T, the adsorbed amount decreases. That breaks the bonds between the adsorbate and the adsorbent.

3.3 The thermodynamic aspect of adsorption

The temperature effect was studied to determine the thermodynamic parameters from the following equation:

$$\ln K_d = \frac{-\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R}$$

where $K_d = q_e/c_e$



(c)

Figure 8: Paracetamol adsorption isotherm on GM1 (a), GM2 (b), and GM3 (c) at different temperatures.

The plot of $\ln K_d$ as a function of $1/T$ (figure not shown) to determine $\Delta H°$, $\Delta S°$, and $\Delta G°$; results are shown in Table 3.

Values of the free enthalpy variations $\Delta G°$ are negative for all geomaterials and indicate the spontaneity of the adsorption.

3.4 pH effect

The pH of the solution is an important parameter that can influence the adsorption and the physicochemical parameters of adsorbates-adsorbents. Figure 9 represents the adsorbed amount as a function of the solution pH.

The paracetamol adsorption on geomaterials is pH-dependent. The adsorbed amount increases until it reaches a maximum at pH 9 and decreases to a higher value. This mechanism is due to the surface load of the geomaterial. Indeed, at acidic pH < pK_a, the ions resulting from the adsorbate were in competition with protons H of the medium. However, groups aluminols and silanols on the surface of GM3 (resulting from the clay) were more protonated [54], and thus less willing to receipt the studied pollutant. This protonation decreases more and more until pH = pK_a. At pH > pK_a very basic, the adsorption was inhibited due to the repulsion of the medium and the geomaterial. At pH = pK_a, the paracetamol is in its molecular form [55]. Hence, the fixation of paracetamol is favored on the sites of GM3.

3.5 Results of error measurement calculation

The result of the uncertainty calculation was represented in Table 4.

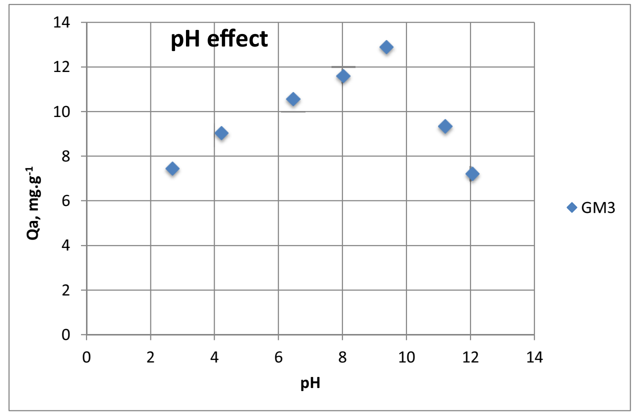


Figure 9: pH effect on paracetamol adsorption onto GM3.

4 Conclusion

The purpose of the present study is, first, to develop composite materials called geomaterials. These materials were based on Algerian clay, activated carbon, cement, and PVA polymer, then these materials were used in the retention of an organic pollutant such as paracetamol. The synthesized geomaterials were characterized by nitrogen adsorption and desorption, X-ray diffraction, and SEM. These methods were performed to investigate their textural properties, their porosities as well as the distribution of the pore size and the different mineral phases that exist in each material. Adsorption experiments were carried out and evaluate the parameters that could affect the paracetamol adsorption on GM1, GM2, and GM3 geomaterials, in particular adsorbent mass, contact time, and temperature. The obtained results showed that:

– The equilibrium is reached after relatively short contact times 180 min for GM1 and 120 min for GM2 and GM3.
– From results, the most suitable geomaterial for paracetamol removal is GM3, due to its physicochemical properties.

Table 3: Thermodynamic parameters of paracetamol adsorption on GM1, GM2, and GM3

Materials	Temperatures (K)	$\Delta H°$ (kJ mol^{-1})	$\Delta S°$ (kJ K^{-1} mol^{-1})	$\Delta G°$ (kJ mol^{-1})
GM1	298	−56.01	−0.218	−8.95
	308			−11.13
	318			−13.31
GM2	298	−38.13	−0.155	−8.06
	308			−9.61
	318			−11.16
GM3	298	−5.30	−0.044	−7.81
	308			−8.25
	318			−8.69

Table 4: Error calculation on paracetamol adsorption study on geomaterials GM1, GM2, and GM3

Geomaterials	GM1	GM2	GM3
Uncertainty on the kinetics of adsorption	6.383 ± 0.195	12.272 ± 0.002	15.900 ± 0.195
Uncertainty on the adsorption isotherm	15.215 ± 0.001 (298 K)	17.2236 ± 0.0004 (298 K)	22.0845 ± 0.0003 (298 K)
(298, 308, 318 K)	5.203 ± 0.001 (308 K)	14.7556 ± 0.0003 (308 K)	19.40236 ± 7 × 10^{-5} (308 K)
	4.792 ± 0.002 (318 K)	7.302 ± 0.001 (318 K)	19.7971 ± 0.0002 (318 K)
Uncertainty on pH			9.77 ± 2.09
Uncertainty on $\Delta H°$ (kJ mol^{-1})	−48.25 ± 2.42	−39.78 ± 1.30	−10.67 ± 7.53
Uncertainty on $\Delta S°$ (kJ mol^{-1} K^{-1})	−0.191 ± 0.008	−0.159 ± 0.0028	−0.06 ± 0.02
Uncertainty on $\Delta G°$ (kJ mol^{-1})	−8.874 ± 0.13 (298 K)	−7.68 ± 0.41 (298 K)	−7.27 ± 0.64 (298 K)
	−10.789 ± 0.15 (308 K)	−9.30 ± 0.42 (308 K)	−7.87 ± 0.43 (308 K)
	−12.912 ± 0.70 (318 K)	−10.88 ± 0.39 (318 K)	−8.47 ± 0.26 (318 K)

- The adsorbed amount decreases by increasing the temperature. This behavior highlighted the exothermic nature of the process.
- The optimum adsorption capacity value was obtained at a basic pH of 9.35, very close to that of the paracetamol acid constant (pK_a).
- The thermodynamic parameter values indicate the process is spontaneous and exothermic process.
- According to the Algerian law of December 12, 2001, relating to the management, control, and elimination of waste, the geomaterial GM3 can be used for containment waste in a landfill and protect the environment.

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Authors' contribution: S. Ait Hamoudi – conceptualization, S. Ait Hamoudi – data curation, J. Arrar – formal analysis, B. Hamdi – funding acquisition, M. Boucha – investigation, S. Ait Hamoudi – methodology, J. Arrar – project administration, B. Hamdi – resources, M. Brahimi – software, S. Ait Hamoudi – supervision, M. Boucha and M. Brahimi – validation, S. Ait Hamoudi – visualization, M. Boucha and M. Brahimi – writing – original draft, S. Ait Hamoudi – writing – review and editing.

Competing interest: There is no competing interest.

Data availability statement: All data generated or analyzed during this study are included in this published article.

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