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Evaluation of performance of calcined bones as a new adsorbent for the removal of carbaryl pesticide from aqueous solutions

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ABSTRACT

In this work, the efficiency of animal bone meal (ABM) as a new low-cost adsorbent for removing a carbaryl pesticide from aqueous solutions has been investigated. Factors affecting the adsorption process: adsorbent amount, contact time, pesticide concentration, solution pH, particle size of adsorbent and temperature were studied by using the batch technique. The results showed that carbaryl adsorption equilibrium was rapidly attained after 50 min of contact time. The isotherms of adsorption data were analyzed by Langmuir and Freundlich adsorption isotherm models. The adsorption capacity, Q_m, obtained from the Langmuir isotherm plots were 24.94, 24.75, 24.63 and 24.27 mg·g^{-1}, respectively, at 303, 313, 323 and 333 K. The rates of adsorption were found to confirm to the pseudo-second-order kinetics with good correlations ($R^2 > 0.99$). The characteristic results namely dimensionless separation factor R_L, the adsorption intensity n and a comparison of maximum adsorption capacity (24.94 mg·g^{-1}) observed in this study with other adsorption capacities as reported in the literature showed that ABM can be employed as a promising alternative to commercial adsorbents in the removal of carbaryl pesticide from aqueous solution.

Keywords: Animal bone meal; Adsorption isotherms; Carbaryl; Removal; Water treatment; Kinetics

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1. Introduction

Developments introduced in agricultural activities during the past four decades have greatly increased the quantity and improved the quality of food for the world's growing population. However, the new technologies rely heavily on the use of pesticides [1]. This extensive use of pesticides in agriculture for controlling pests is vastly polluting the environment day by day [2]. Pesticides are among the most dangerous environmental pollutants because of their stability, mobility, bioaccumulation capability and long-term effects on living organisms. The pesticides contaminate water through agricultural, domestic and industrial activities. When these pesticides are applied to crops, only part of the total amount of pesticide used is bioactive, the rest contaminates the environment. This contamination arises from surface runoff, leaching, wind erosion, deposition from aerial applications, industrial discharges and various other sources [3]. In water, these compounds can undergo transformations leading to the production of substances of even greater toxicity [4].

The harmful influence of pesticides on human health and aqueous environment due to their recalcitrance, toxicity, mutagenicity, carcinogenicity and tumorigenicity has resulted in the imposition of stringent legislation on drinking water quality in many countries [5–8]. Maximum permissible limits of 0.1 μg·L^{-1} for individual pesticides and related products, 0.5 μg·L^{-1} for total pesticides in drinking water

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and 1–3 μg·L^{-1} for surface waters have been recommended [9,10]. Added to this the fact that clean water supply is struggling to meet the ever increasing demands and remains a big challenge. According to World Health Organization, about 780 million people have no access to affordable drinking water [11]. This situation was the cause that various researchers have recognized that wastewater treatment and reuse are the best practices to allay water shortage which induced to make several investigations to fight against water pollution. In this context, we have used animal bone meal (ABM) to remove carbaryl (Car) pesticide from aqueous solution.

Carbaryl (1-naphthalenyl-N-methylcarbamate), a widely used carbamate insecticide, was chosen as the target molecule for the present study. This carbamate pesticide is known to present a wide spectrum of activity and is extensively used for pest control on fruit, vegetables and other crops [12], and it has been detected in the aquatic environment [13]. U.S. Geological Survey National Water-Quality Assessment (NAWQA) Program reported carbaryl as the second most frequently found insecticide in water. At present, there is increased concern about the environmental fate and toxicity of carbaryl because of its high toxicity to both humans and wildlife [14]. This carbamate pesticide inhibits the cholinesterase enzyme, impairing the function of central nervous system and can cause nausea, vomit, bronco-constriction, blurred vision, convulsions, coma and respiratory failure, in addition to its teratogenic characteristics [15]. There are several treatment processes available for pesticides removal from wastewater either independent or in conjunction which includes ozonation, aerobic degradation, electrodialysis membranes, advanced oxidation processes, ultrasound combined with photo-Fenton treatment, photocatalytic degradation and adsorption [16]. Nevertheless, adsorption is the most widespread technology used to deal with purification of water contaminated by pesticides [17]. Various adsorbents are used for the removal of pesticides in water samples including activated carbon which is the most used but very expensive, for that reason many studies have been undertaken to investigate the use of low-cost adsorbent [18–20].

The aim of the present study was to investigate the feasibility of removal of carbaryl pesticide from aqueous solutions by using ABM as a new low-cost adsorbent. The parameters that influence adsorption such as contact time, initial concentration of carbaryl pesticide, adsorbent mass, solution pH and temperature were investigated. The kinetics of adsorption has been studied, and various kinetic models, such as pseudo-first-order and pseudo-second-order models were tested with experimental data for their validity. The Langmuir and Freundlich adsorption isotherm models were used to model the equilibrium adsorption data obtained.

2. Materials and methods

2.1. Absorbate

Technical grade carbaryl ($C_{12}H_{11}NO_2$) of 99.8% purity supplied by Sigma-Aldrich company (Casablanca, Morocco) was used as an adsorbate in this study. The chemical structure of carbaryl is shown in Fig. 1. Distilled water was used to prepare all solutions.

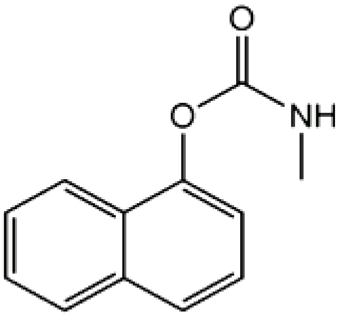

Fig. 1. Chemical structure of carbaryl.

2.2. Preparation and characterization of adsorbent

Animal bones were collected from the nearby butcher shops. All of the attached meat and fat were removed and cleaned from the bones. The fresh bones collected were cut into smaller pieces and cleaned well to remove most adhering meat and fat. The bones were then boiled in distilled water for 30 min for degreasing and easier removal of the residual tissues and bone marrow. This procedure was repeated twice with fresh water. After removing all attached meat and fat from the bones, it was washed several times with tap water and left in open air for several days to get rid of odors. Later, the bones were dried in oven at 80°C then crushed and milled into different particle sizes in the range 45–300 μm then calcined for 2 h at 800°C. The residue was washed with water and after drying at 80°C for 24 h it was washed once more with water and dried overnight at 100°C in a conventional drying oven. The residue was then calcined at a heating rate of 2°C/min to 400°C and in the last step kept at this temperature for 4 h [21]. The surface area of ABM was determined by BET method using BELSORP-mini (Bell Japan, Inc.) and the calculated surface area was 85 m^2/g.

The ABM was characterized by elemental analysis, infrared-spectra which have been obtained using ATI Mattson Genesis series FTIR_UNICAM instrument and with X-ray diffraction analysis which was carried out by using X'pert Pro X-ray diffractometer using copper anticathode λ(Cu) = 1.5418 Å. The morphology of the ABM particles was observed by scanning electron microscopy (SEM), using SUPRA 40 VP COLUMN GEMINI ZEISS, coupled to an analyzer (Oxford Instruments X-Max 20 mm^2) with a detector EDS (Energy dispersive X-ray spectroscopy).

Elemental analysis of ABM shows a high yield of Ca (49.62%) and P (42.36%) compared with small amounts of Si, Mg, Na, Al, Fe, Cl, S, K, Sr, Cu and Zn. While the Fourier transform infrared spectroscopy (FTIR) spectrum of ABM shows band characteristics of hydroxyapatite and more particularly a carbonated fluorapatite type B. X-ray diffraction analysis of calcined ABM confirms the presence of hydroxyapatite which approve that the organic component was removed after calcination [22]. The figures corresponding to the FTIR spectrum and diffractogram of calcined ABM are shown in our previous study [23].

The morphological aspects of the particles of ABM are outlined in Fig. 2. The porosity of the surface is clearly visible. The scanning electron micrograph of ABM shows that its morphology is characterized by the small particles whose average size is between 0.2 and 1 μm, these particles form agglomerates which have a size between 10 and 50 μm.

2.3. Batch equilibrium studies

Adsorption studies for the evaluation of ABM adsorbent for the removal of carbaryl from aqueous solutions were carried out using a batch contact adsorption method. Pesticide solutions were prepared by dissolving requisite quantity of carbaryl in distilled water. Adsorption measurement was determined by batch experiments of known amount of the ABM adsorbent with 50 mL of aqueous pesticide solutions of known concentration in a series of Erlenmeyer flasks. The mixture was shaken at ambient temperature using an incubator shaker at 200 rpm for 120 min. At predetermined time, the bottles were withdrawn from the shaker and the residual pesticide concentration in the reaction mixture was analyzed. An incubator shaker was used for carrying out experiments at 303, 313, 323 and 333 K. Each batch of the experiment was duplicated under identical conditions. Adsorption studies were conducted by varying adsorbent dose, contact time, initial pesticide concentration, initial solution pH and temperature under the aspect of adsorption isotherms.

The determination of carbaryl concentrations in the solution was done by the following method of Fenoll et al. [24]; water samples (10 mL) were added into a centrifuge tube and then extracted with 10 mL of acetonitrile by sonication (15 min at 0.5 cycles and 60% amplitude), followed by a salting-out step with 2 g NaCl. The tube was shaken and centrifuged for 10 min at 3,000×g. Extract was filtered quantitatively through glass funnel containing a filter separation phase paper DP302, 150 mm diameter. The organic phase was concentrated to dryness using rotary vacuum evaporation. The residue was redissolved in 1 mL of acetonitrile, filtered through 0.45 µm filter and analyzed using a liquid chromatography coupled with tandem mass spectrometry LC-MS/MS (API 3200 System, AB SCIEX/Amérique) under conditions described below.

All solvents used for LC-MS/MS were HPLC grade. For LC-MS/MS analysis, the samples were transferred to an HPLC vial after filtration. Samples were kept at 25°C in the autosampler, and 20 µL of subsamples were injected. Analytes were eluted through a colonne Gemini-NX C 18 (100 mm × 2 mm i.d, 3 µm) (Phenomenex, USA) using a gradient elution phase A/phase B (phase A: ammonium formate in ultra pure water at 5 mmol·L^{-1}/phase B: ammonium formate in methanol at 5 mmol·L^{-1}) as described in Table 1. Mass spectra were determined.

Analysis of the carbaryl pesticide was performed in multiple reaction monitoring mode, which is based on MS/MS transitions. This method is a mass spectrometric technique for quantifying one or several molecules in a complex sample by measuring the ratio mass/charge (m/z) of ionized molecules.

The combination of the value of m/z of the precursor and the value of m/z of the fragment is intended to be specific to the molecule to be assayed and is called a transition. The LC-MS/MS parameters of carbaryl pesticide are listed in Table 2.

Eq. (1) was used to calculate Q_t (mg·g^{-1}); the amount of adsorption at time t:

$$Q_t = \frac{C_0 - C_t}{W} V \tag{1}$$

where C_0 (mg·L^{-1}) is the initial concentration of the carbaryl in solution. C_t (mg·L^{-1}) is the concentration of carbaryl at time t, W is the mass of carbaryl adsorbent (g) and V is the volume of the solution (L). The following Eq. (2) was used to calculate Q_e (mg·g^{-1}); the amount of adsorption at equilibrium:

Table 1
Gradient LC using the phase A (5 mM ammonium formate in water) and phase B (5 mM ammonium formate in methanol)

Step	Time (min)	Flow (µL/min)	Phase A (%)	Phase B (%)
0	5	850	70	30
1	5	850	0	100
2	13	850	0	100
3	15	850	70	30

Table 2
LC-MS/MS parameters for carbaryl

	Q1	Q2	Dwell	DP	EP	CE	CXP
Carbaryl 1	202.1	145.3	100	29.5	10	12	5
Carbaryl 2	202.1	127.1	100	31	10	35	5

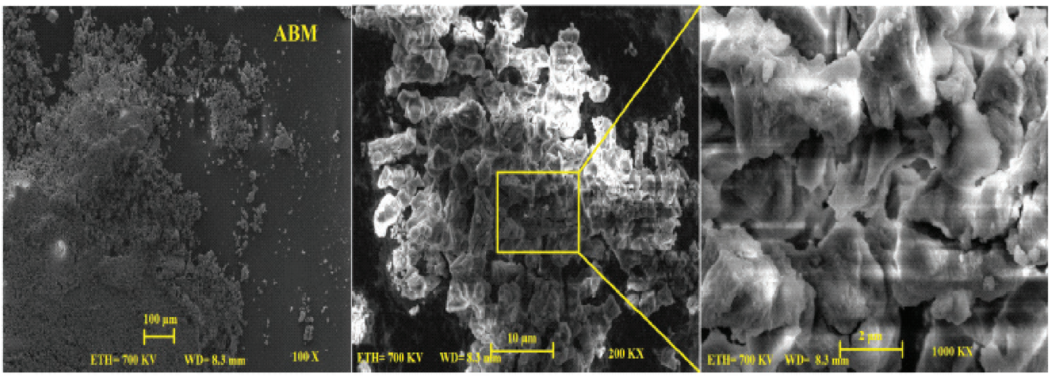

Fig. 2. SEM micrograph of the ABM particles at different magnifications.

$$Q_e = \frac{C_0 - C_e}{W} V \tag{2}$$

where C_0 and C_e (mg·L^{-1}) are the liquid concentrations of pesticide initially and at equilibrium. The following Eq. (3) was used to calculate the carbaryl removal percentage:

$$\%\,\text{of pesticide removal} = \frac{C_0 - C_e}{C_0} 100 \tag{3}$$

where C_0 and C_e (mg·L^{-1}) are the initial and equilibrium concentrations of carbaryl in solution.

2.4. Effect of carbaryl solution pH

To investigate the effect of initial pH of solution on the adsorption capacity of carbaryl pesticide using ABM adsorbent, we had variated the initial pH of the solutions from pH 2 to 12 using different separate batches of Erlenmeyer flasks simultaneously at the same concentration of the carbaryl (15 mg·L^{-1}). A range of pH values of solutions were adjusted from 2 to 12 by using 0.1 M HCl and/or 0.1 M sodium hydroxide (NaOH). pH was measured by a pH meter (JENCO Model 6173, USA). The amount of ABM adsorbent was fixed at 0.8 g·L^{-1}.

2.5. Adsorption isotherm

The adsorption isotherm is the most important information which indicates how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state [25]. For the equilibrium concentration of adsorbate C_e and amount of pesticide adsorbed at equilibrium Q_e, the following linear forms of Langmuir (Eq. (4)) [26] and Freundlich (Eq. (5)) [27] isotherms were studied:

$$\frac{1}{Q_e} = \frac{1}{K_L Q_m} \times \frac{1}{C_e} + \frac{1}{Q_m} \tag{4}$$

$$\log Q_e = \log K_f + \frac{1}{n} \ln C_e \tag{5}$$

where Q_e (mg·g^{-1}) is the amount of pesticide adsorbed per unit weight of adsorbent at equilibrium, Q_m (mg·g^{-1}) is the monolayer adsorption capacity, K_L (L·mg^{-1}) is the adsorption equilibrium constant and C_e (mg·L^{-1}) is the equilibrium concentration of pesticide in solution.

A plot of logQ_e vs. logC_e enables to determine the constant K_f and the adsorption intensity n. K_f represents the quantity of pesticide adsorbed onto adsorbent for an equilibrium concentration; while $1/n$ value is related to the adsorption intensity. The Langmuir isotherm [26] is a model for monolayer localized physical adsorption on homogeneous surface with adsorption sites with uniformness of energy, while Freundlich [27] adsorption model is based upon a heterogeneous surface and on the assumption that the adsorption occurs at sites with different energy of adsorption.

3. Results and discussion

3.1. Effect of ABM adsorbent dose and contact time on the carbaryl removal efficiency

To study the effect of adsorbent dose on the removal of carbaryl pesticide from aqueous solutions, we had agitated various amounts of ABM adsorbent (0.1, 0.2, 0.4, 0.6, 0.8, 1.0 and 1.2 g·L^{-1}) in 50 mL of a carbaryl solutions with initial concentrations fixed at 15 mg·L^{-1}. The equilibrium experiments were carried out at ambient temperature. Fig. 3 depicts the effect of amount of ABM on the carbaryl removal efficiency percentage at different intervals times.

It was found that carbaryl removal percentage increases with increasing time and the response becomes constant for all amounts studied after 50 min of stirring the pesticide solution. Moreover, the removal % increases by increasing the adsorbent amount. After 50 min of stirring the pesticide solution of the appropriate amount of ABM, the carbaryl removal percentage increased from 53.1% for 0.1 g·L^{-1} of ABM to 87.4% for 1.2 g·L^{-1} of ABM. This increase of the elimination percentage of carbaryl can be explained by the fact that if the amount of adsorbent in the solution is increased, the adsorbent surface area and the number of sites available for carbaryl adsorption are also increased. Consequently, the probability of encountering (molecule site) increases as well, leading to a better retention. The optimum adsorbent amount to remove carbaryl pesticide was found to be 0.8 g·L^{-1} for the following studies.

3.2. Effect of initial pesticide concentration and contact time on the carbaryl removal efficiency

In order to achieve accurate effect of contact time and initial carbaryl concentration on the percentage removal of carbaryl by ABM, we have used initially a concentration carbaryl of 15 mg·L^{-1}, 40 mg of ABM adsorbent quantity and 50 mL as solution volume. Fig. 4 depicts these results; it represents the percentage removal of carbaryl vs. different contact times in the range of 10–120 min. It was found that, for the first 30 min, the adsorption uptake was rapid then it proceeds at a slower adsorption rate and finally it attains saturation at 50 min.

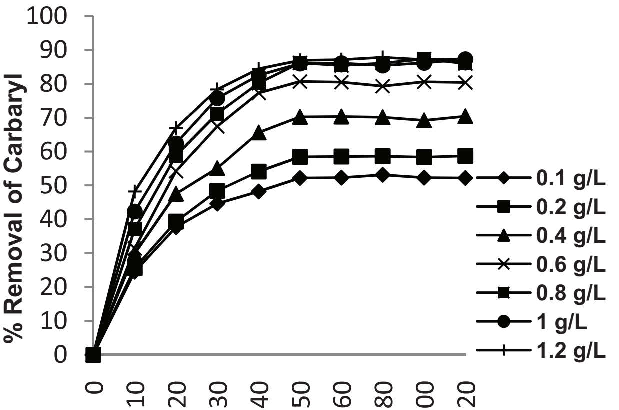

Fig. 3. Effect of adsorbent dose on the adsorption of carbaryl. Ambient temperature; [Car] = 15 mg·L^{-1}; agitation rate = 200 rpm.

Equilibrium was attained at 50 min for ABM–carbaryl system. The curves obtained were single, smooth and continuous leading to saturation of ABM by carbaryl pesticide. This result suggests the possibility of monolayer coverage pesticide on the surface of ABM adsorbent [28]. In the second investigation, the equilibrium adsorption isotherm of ABM–carbaryl system was studied using an initial concentration values of carbaryl pesticide ranging from 5 to 25 mg·L^{-1} and temperature (303, 313, 323 and 333 K).The experiments were carried out using the same previous conditions and taking into consideration the equilibrium time, that is, 50 min. Table 3 depicts the different liquid concentrations of carbaryl at equilibrium C_e (mg·L^{-1}), amount of equilibrium adsorption Q_e (mg·g^{-1}) and percentage of pesticide removal vs. concentration carbaryl and temperature.

At a constant temperature, it was observed from Table 3 that the increasing concentration of carbaryl causes an increase of pesticide concentrations at equilibrium and amount of adsorption at equilibrium. It means that the adsorption is highly dependent on initial concentration of pesticide. The best percentage removal of pesticide was observed at lower concentration of pesticide that can be explained by the fact at lower concentrations, the ratio of the initial number of pesticide molecules to the available surface area is low, subsequently, the fractional adsorption becomes independent of initial concentration. However, at high concentration, the available sites of adsorption become fewer and hence the percentage removal of carbaryl depends upon concentration [29].

At constant concentration of pesticide, the increasing temperature increases the concentration of pesticide at equilibrium and decreases, simultaneously, the amount of equilibrium adsorption and the percentage removal of carbaryl. It is clear from Table 3 that for all of the concentrations studied (5, 10, 15, 20 and 25 mg·L^{-1}) the % pesticide removal decreases by increasing the temperature from 303 to 333 K. This suggests that adsorption is a process of release of activation energy. Generally, when the temperature increases, the pesticide becomes more soluble. As a consequence, it is less retained by the adsorbent [30].

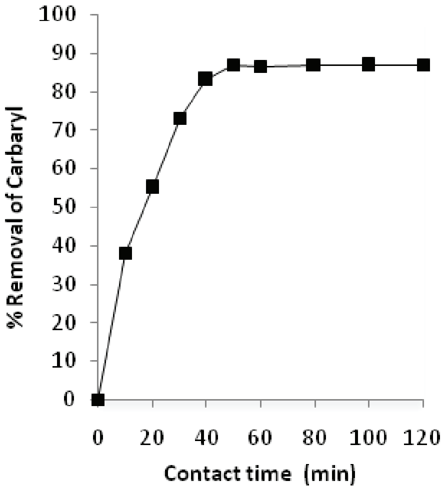

Fig. 4. Effect of contact time on the adsorption of carbaryl onto ABM. [Car] = 15 mg·L^{-1}; W = 40 mg; V = 50 mL; ambient temperature; agitation rate = 200 rpm.

3.3. Effect of pH

The pH is the most important factors affecting the adsorption capacity in wastewater treatment [31]. This is due to the fact that the change in concentration of hydrogen ions H$^+$ in the solution may affect some functional groups of both adsorbed molecules and adsorbent particles which are involved in the molecular adsorption process at the active sites of adsorbent. In order to investigate the effect of initial pH of the solution on the adsorption capacity of carbaryl using ABM adsorbent, experiments were performed within pH range between 2 and 12. The result is plotted in Fig. 5 which indicate that pH considerably affected carbaryl adsorption. As it can be seen from this figure, the carbaryl removal percentage decreases from 89% to 56% by increasing pH between 2 and 12. To explain the possible pH mechanism, the determination of pH$_{pzc}$ played an important role because it has been observed

Table 3
Equilibrium parameters for the adsorption of carbaryl onto ABM adsorbent

	Carbaryl concentration (mg·L^{-1})				
	5	10	15	20	25
C_e (mg·L^{-1})					
303 K	0.29	0.90	1.96	4.11	7.40
313 K	0.34	1.09	2.40	4.80	7.75
323 K	0.51	1.50	3.30	5.40	8.75
333 K	0.71	1.97	3.75	5.88	9.82
Q_e (mg·g^{-1})					
303 K	5.89	11.38	16.30	19.86	22.00
313 K	5.83	11.14	15.75	19.00	21.56
323 K	5.61	10.63	14.63	18.25	20.31
333 K	5.36	10.04	14.06	17.65	18.98
% Removal of carbaryl					
303 K	94.2	91.0	86.9	79.5	70.4
313 K	93.2	89.1	84.0	76.0	69.0
323 K	89.8	85.0	78.0	73.0	65.0
333 K	85.8	80.3	75.0	70.6	60.7

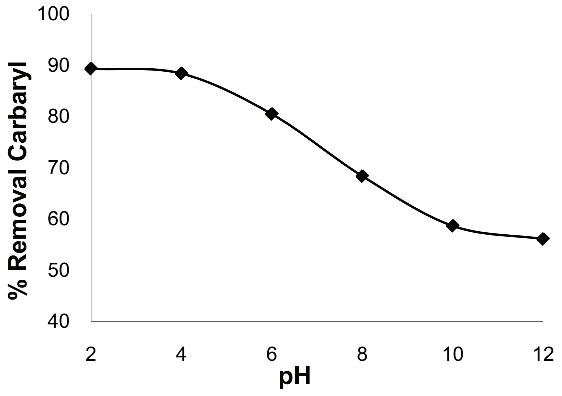

Fig. 5. Effect of pH on removal of carbaryl using ABM. [Car] = 15 mg·L^{-1}; W = 40 mg; V = 50 mL; ambient temperature; contact time = 50 min; agitation rate = 200 rpm.

that surface functional groups of adsorbate makes adsorption process complex by the type of charge characteristics present at the adsorbent surface [32]. In our previous study [23], we have determined the pH_{pzc} of our adsorbent and it was above 8.4, meaning that the adsorbent's surface was positively charged at solution pH below 8.4. This causes better carbaryl adsorption through the aromatic ring of the pesticide and also via a high electrostatic attraction phenomenon that exists between the negative charge associated with the carboxyl group of the pesticide and the positive charge surface of ABM [29]. The lower the pH goes below pH_{pzc}, the greater the density of positive ions on the surface of ABM will be which in turn allows for more adsorption. This is confirmed by high carbaryl removal at a strong acidic pH. When solution pH increases above pH_{pzc}, a negative charge is present on the surface of ABM, which will cause an electrostatic repulsion and, therefore, a reduction of carbaryl adsorption.

3.4. Effect of particle size on adsorption

It is well recognized that particle size of adsorbent is one of the important factors affecting the adsorption process and more workers have reported such results. To study the effect of particle size, adsorbent particles of sizes <50 µm, 50–100 µm, 100–200 µm and 200–300 µm were used. In each study, we had agitated to equilibrium (50 min) 40 mg of adsorbent in 50 mL of the same concentration of the carbaryl (15 $mg \cdot L^{-1}$).

The results are shown in Fig. 6; it was found that the increase in particle size of adsorbent from <50 µm to 200–300 µm decreased the rate of adsorption of carbaryl pesticide from 97.1% to 75.5%. The higher rate of pesticide uptake by smaller particles was due to substantial increase in surface area for bulk adsorption per unit weight of the adsorbent and the greater accessibility of pesticide molecule to the pores of the particles, especially when their sizes are small.

3.5. Adsorption kinetics

The adsorption kinetics of carbaryl onto ABM was investigated with two kinetic models, namely the Lagergren pseudo-first-order and pseudo-second-order model. The Lagergren rate equation is one of the most widely used adsorption rate equations for the adsorption of solute from a liquid solution [33]. The pseudo-first-order kinetic model (Eq. 6) can be expressed by the following equation [34]:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{6}$$

where q_e and q_t (mg/g) are the amounts of carbaryl adsorbed at equilibrium and at any time, t (min), respectively, and k_1 (min^{-1}) is the equilibrium rate constant of pseudo-first-order adsorption.

The pseudo-first-order model parameters are obtained by plotting the curve corresponding to $\log(q_e - q_t)$ vs. t. The slope and intercept are used to determine, respectively, the values of k_1 and q_e (figure not shown). It was found that the correlation coefficient (R^2) had a low value (≤0.98) and that the calculated q_e values deviated from the experimental q_e values at various initial pesticide concentrations for the pseudo-first-order model (Table 4). These results show the inapplicability of the pseudo-first-order model of Lagergren to describe the kinetics of adsorption of carbaryl onto ABM. Similar results were also reported for the adsorption of carbaryl onto treated eggshells [35] and the adsorption of carbaryl onto *Pistia stratiotes* biomass [16].

The linear form of the pseudo-second-order reaction [36] can be given by:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{7}$$

where the equilibrium adsorption capacity (q_e) and the second-order constant k_2 ($g \cdot mg^{-1} \cdot min^{-1}$) can be determined experimentally from the slope and intercept of plot t/q_t vs. t. The curves are shown in Fig. 7 and the corresponding kinetic parameters at various initial pesticide concentrations from both models are listed in Table 4.

The correlation coefficient (R^2) for the pseudo-second-order adsorption model has high values (>0.99) and hence the plots of t/q_t against t at different concentrations showed excellent linearity. The good correlation coefficients and the calculated values of q_e which are in agreement with experimental values for all concentrations (indicated in bold in Table 4.) suggest that the adsorption of carbaryl onto ABM follows the pseudo-second-order kinetic model, which suggested that the adsorption of carbaryl onto ABM was a multistep process involving sorption on the external surface and diffusion into the interior of adsorbent [37,38].

3.6. Adsorption isotherms

The adsorption isotherm is meaningful to the design of adsorption systems, and its shape provides information about the homogeneity or heterogeneity on the adsorbent surface [39]. It indicates how the adsorbate molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state [40].

To optimize the design of an adsorption system for the adsorption of adsorbates, it is important to establish the most appropriate correlation for the equilibrium curves.

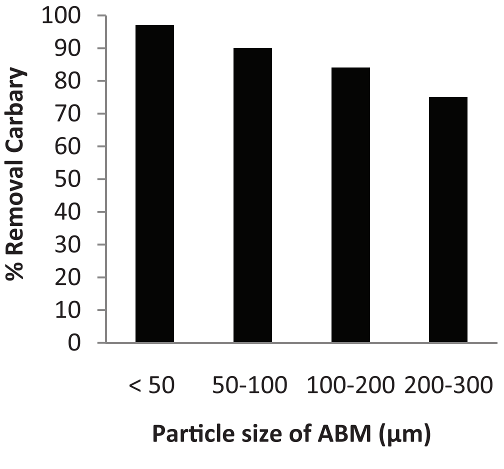

Fig. 6. Effect of particle size of ABM adsorbent on removal efficiency of carbaryl. [Car] = 15 $mg \cdot L^{-1}$; W = 40 mg; V = 50 mL; ambient temperature; contact time = 50 min; agitation rate = 200 rpm.

Table 4
Kinetic parameters for the removal of carbaryl by ABM

Initial concentration (mg·L^{-1})	q_e (exp) (mg·g^{-1})	Pseudo-first-order			Pseudo-second–order		
		$k_1 \times 10^2$ (min^{-1})	q_e (cal) (mg·g^{-1})	R^2	$k_2 \times 10^2$ (min^{-1})	q_e (cal) (mg·g^{-1})	R^2
5	**5.89**	2.51	3.42	0.9609	1.89	**5.74**	0.9996
10	**11.38**	2.51	7.27	0.9820	0.80	**11.24**	0.9998
15	**16.30**	2.46	11.14	0.9826	0.47	**16.26**	0.9995
20	**19.86**	2.40	13.63	0.9744	0.38	**19.72**	0.9999
25	**22.00**	2.40	15.30	0.9718	0.32	**21.93**	0.9998

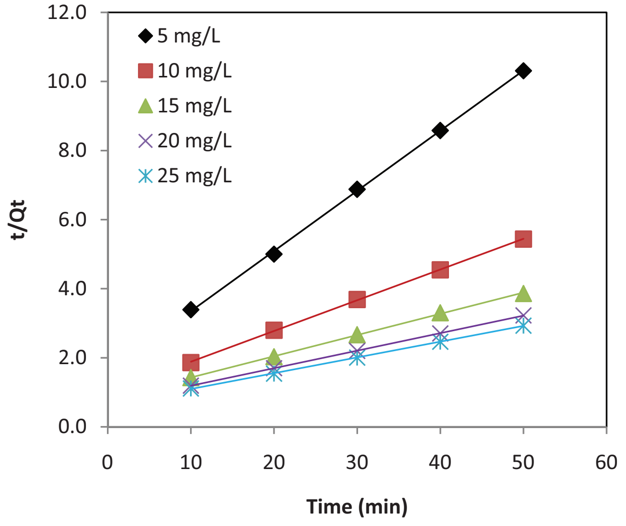

Fig. 7. Pseudo-second-order kinetics for adsorption of carbaryl onto ABM at 30°C.

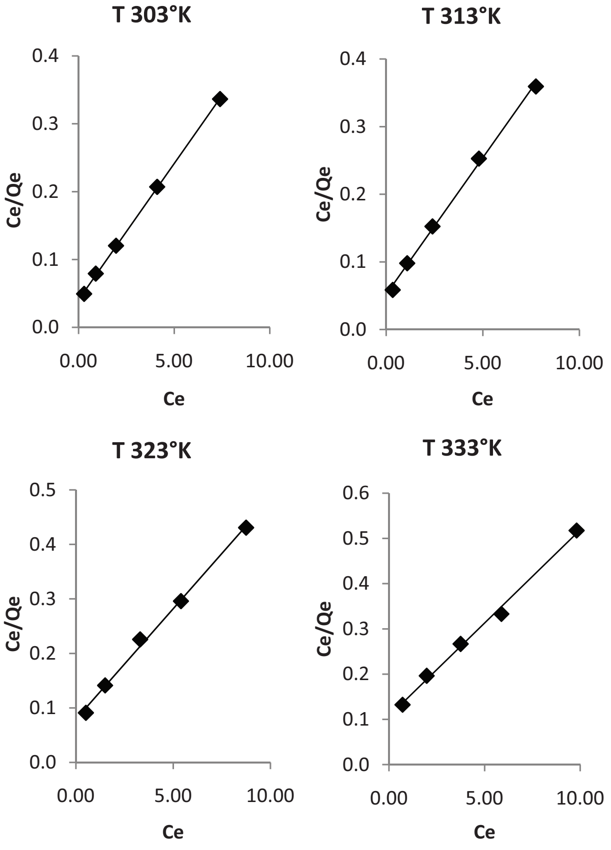

Fig. 8. Linear Langmuir isotherm for the adsorption of carbaryl onto ABM.

Several models have been published to describe the experimental data of adsorption isotherms. Of these models, the Langmuir and Freundlich models are the most frequently employed. Thus, in the present work, the experimental data were analyzed according to linear form of the Langmuir and Freundlich isotherms.

The Langmuir model assumes that adsorption takes place at specific homogeneous sites within the adsorbent by monolayer adsorption without any interaction between adsorbed molecules. Once the adsorbate is attached on the site, no further adsorption can take place at that site, which concluded that the adsorption process is monolayer in nature [41]. The linear form of Langmuir isotherm is expressed as Eq. (8):

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m} \tag{8}$$

where C_e is the equilibrium concentration of carbaryl in solution (mg·L^{-1}), Q_e is the amount of pesticide adsorbed per unit weight of adsorbent at equilibrium (mg·g^{-1}), Q_m is the monolayer adsorption capacity (mg·g^{-1}) and K_L is related with the energies of the adsorption (L·mg^{-1}).

Plots of C_e/Q_e vs. C_e yield a straight line with slope $1/Q_m$ and intercept $1/K_L Q_m$ suggest the applicability of the Langmuir isotherm at different temperatures (Fig. 8). Table 5 lists the maximum adsorption capacity Q_m values for carbaryl adsorption onto ABM at different temperatures.

From the results, it is clear that the value of adsorption efficiency, Q_m, and adsorption energy, K_L, of the ABM decreased when increasing the temperature, suggesting that adsorption is a process of release of activation energy.

The decrease in the amount of carbaryl pesticide removed as the temperature increased may be attributed to the fact that the pesticide becomes more soluble when the temperature increases; as a consequence, it is less retained by the adsorbent [30].

The equilibrium parameter (R_L) also called dimensionless constant separation factor was calculated at different initial concentrations of carbaryl pesticide using Eq. (9) below.

This factor expresses the essential characteristics of the Langmuir isotherm [42,43]:

$$R_L = \frac{1}{1 + K_L C_0} \tag{9}$$

where K_L is the Langmuir constant and C_0 is the highest initial pesticide concentration (mg·L^{-1}). Table 6 presents the relation between the R_L parameter values and the shape of Langmuir isotherm [42,43].

The R_L values depicted in Table 7 range between 0.039 and 0.342 for the range of temperature studied (303, 313, 323 and 333 K) which indicate that the adsorption of carbaryl onto ABM adsorbent is favorable at operation conditions studied.

The Freundlich isotherm is an empirical equation based upon a heterogeneous surface [40]. A linear form of the Freundlich expression can be presented as below:

$$\log Q_e = \log K_f + \frac{1}{n}\ln C_e \tag{10}$$

where K_f is the Freundlich constant and n is the heterogeneity factor. The K_f value is related to the adsorption capacity; while $1/n$ value is related to the adsorption intensity.

A linear plot of logQ_e vs. logC_e enables to determine the constant K_f and the adsorption intensity n for Freundlich model (Fig. 9). K_f represents the quantity of pesticide adsorbed onto adsorbent for an equilibrium concentration. The results of these analyses at different temperatures are tabulated in Table 8. The correlation coefficients R^2 are also shown in this table.

The value $1/n$ for Freundlich model is related to the adsorption intensity. $1/n$ values indicate the type of isotherm to be favorable ($0 < 1/n < 1$), unfavorable ($1/n > 1$), irreversible ($1/n = 0$) [44].

The Freundlich constant, K_f, decreases with increase in temperature. The $1/n$ values depicted in Table 8 ranging between 0.41 and 0.50 for the range of temperature studied (303, 313, 323 and 333 K) indicate that the isotherm adsorption of carbaryl onto ABM adsorbent is favorable ($0 < 1/n < 1$). Examination of the correlation coefficients (R^2) of both Langmuir and Freundlich models reveals that the Langmuir equation provided the best fit to the data.

Table 5
Statistical parameters/constants of Langmuir isotherm results

Langmuir isotherm results			
Temperature	R^2	Q_m (mg·g^{-1})	K_L
303 K	0.999	24.94	0.98
313 K	0.998	24.75	0.78
323 K	0.996	24.63	0.51
333 K	0.995	24.27	0.39

Table 6
Relation between the R_L parameter values and the shape of isotherm

Value of R_L	Type of isotherm
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favorable
$R_L = 0$	Irreversible

Table 7
Dimensionless separation factor R_L

Temperature	Carbaryl concentration (mg·L^{-1})				
	5	10	15	20	25
303 K	0.169	0.093	0.064	0.049	0.039
313 K	0.204	0.114	0.079	0.060	0.049
323 K	0.280	0.163	0.115	0.089	0.072
333 K	0.342	0.206	0.148	0.115	0.094

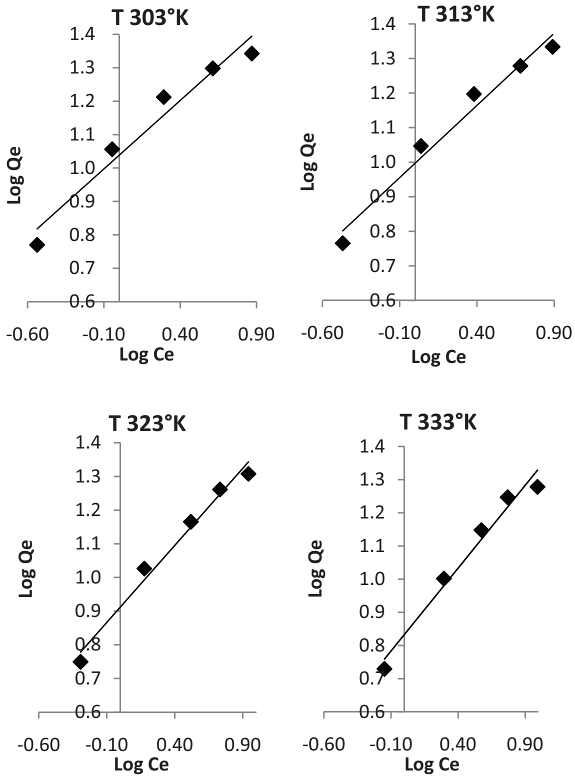

Fig. 9. Linear Freundlich isotherm for the adsorption of carbaryl onto ABM.

Table 8
Statistical parameters/constants of Freundlich isotherm results

Temperature	Freundlich isotherm results			
	R^2	K_f	n	$1/n$
303 K	0.957	10.91	2.44	0.41
313 K	0.974	9.94	2.39	0.42
323 K	0.982	8.16	2.19	0.46
333 K	0.972	6.81	2.00	0.50

Table 9
Adsorption capacity of various adsorbents as reported in literature

Adsorbent	Maximum adsorption capacity ($mg \cdot g^{-1}$)	References
Porogen-treated banana pithcarbon	45.9	Sathishkumar et al. (2008) [29]
Clay	10.75	Ouardi et al. (2013) [30]
Lemna major biomass	6.21	Chattoraj et al. (2014) [14]
Pistia stratiotes biomass	3.1	Chattoraj et al. (2014) [16]
Treated eggshells	13.18	Bakka et al. (2016) [35]
Animal bone meal	24.94	This study

3.7. Comparison of the present study with other adsorbents

To justify its viability as an effective adsorbent for carbaryl removal, the maximum adsorption capacity of ABM on carbaryl was compared with that of other low-cost adsorbents. Table 9 presents a comparison of maximum adsorption capacity (24.94 $mg \cdot g^{-1}$) observed in this study with other adsorption capacities as reported in the literature. This comparative study is presented in terms of carbaryl removal capacity ($mg \cdot g^{-1}$). It is important to note that this comparison has a relative meaning due to different testing conditions (pH, temperature, wastewater composition, type of adsorbent and methods).

It is evident that the use of ABM for carbaryl removal is technically applicable and economically attractive for the treatment of carbaryl-contaminated water. The present study showed that ABM demonstrated good removal capacities for carbaryl (24.94 $mg \cdot g^{-1}$).

4. Conclusion

The ABM examined in this study showed promising properties as low cost and effective adsorbent materials for the removal of carbaryl pesticide from aqueous solution. The effect of different physical and chemical parameters on carbaryl adsorption by this adsorbent was studied. These results revealed that removal of carbaryl pesticide increases with increasing contact time and adsorbent dose, but decreases with increasing initial pesticide concentration, particle size and temperature. The pH experiments showed that significant adsorption takes place in an acidic range. The pseudo-second-order kinetic model fits well with the kinetic data. Adsorption equilibrium data were fitted to Langmuir and Freundlich isotherm models at different temperatures (303, 313, 323 and 333 K) and the results showed that the equilibrium adsorption behavior of carbaryl pesticide onto ABM followed Langmuir isotherm model.

Symbols

C_0 — Initial concentration of adsorbate, $mg \cdot L^{-1}$
C_e — Equilibrium concentration of adsorbate, $mg \cdot L^{-1}$
C_t — Concentration of adsorbate at time t, $mg \cdot L^{-1}$
K_L — Langmuir constant, $L \cdot mg^{-1}$
K_f — Freundlich constant
n — Heterogeneity factor
Q_e — Amount of adsorption at equilibrium, $mg \cdot g^{-1}$
Q_t — Amount of adsorption at time t, $mg \cdot g^{-1}$
Q_m — Monolayer adsorption capacity, $mg \cdot g^{-1}$
R_L — Equilibrium parameter
W — Mass of carbaryl adsorbent, g
V — Volume of the solution, L

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