

Removal of Carbofuran pesticide from aqueous solution by adsorption onto animal bone meal as new low cost adsorbent

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Abstract

The objective of this study is to investigate the Carbofuran pesticide adsorption from aqueous solution using animal bone meal as an alternative low cost adsorbent. The effects of various experimental factors; adsorbent dose, initial Carbofuran concentration, contact time, solution pH and particle size of adsorbent were studied by using the batch technique. The results showed that Carbofuran adsorption equilibrium was rapidly attained after 70 min of contact time. A maximum of 98.3% removal of the Carbofuran pesticide was observed by 25 mg of Animal Bone Meal (ABM). Langmuir and Freundlich isotherm models were applied for the analysis of equilibrium adsorption data obtained. The maximum monolayer adsorption capacity was 18.5 mg/g. The characteristic results; dimensionless separation factor, R_L , and the adsorption intensity, n , showed that animal bone meal can be employed as an alternative to commercial adsorbents in the removal of Carbofuran pesticide from aqueous solution.

Keywords: Animal Bone Meal, Carbofuran, Adsorption Isotherms, Water treatment.

1. Introduction

Pesticides are widely used in agriculture to control insects, weeds and pathogens; they are vital for efficient production of food, fiber and fuel crops [1]. Due to this extensive use of pesticides, the environment is vastly polluted day by day with pesticides [2]. Besides, toxicity of the parent pesticides and their degradation products is making these chemical substances a potential hazard. When these pesticides are introduced into the environment through spraying on crops, droplets of pesticides fall on soil, plant and water [3].

The presence of pesticides residues in the aqueous environment has raised increasing concerns in recent years due to their recalcitrance, toxicity, mutagenicity, carcinogenicity and tumorigenicity [4-6]. According to the European Union Water Framework Directive and Groundwater Directive, the concentration of pesticides in drinking water and groundwater should not exceed 0,1 µg/L for a single compound, or 0,5 µg/L for the sum of all pesticides [7-8].

In this fact several investigations were conducted and tireless efforts were made to fight against water pollution. In this context we have contributed to this research filed especially the water pollution bay carbofuran pesticide.

Carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl methyl-carbamate) is a broad-spectrum carbamate pesticide and nematicide which has been used against various foliar pests observed in fruit vegetable and forest crops [9-10]. This carbamate pesticide is highly toxic and recognized as an inhibitor of acetylcholinesterase, an enzyme vital of the functioning of the central nervous system [11-12]. It is also highly soluble in water (351 mg/L) [13].

Recent findings reporting the presence of Carbofuran in surface water and groundwater illustrate the fact that carbofuran can enter ground water through leaching and surface water through runoff from applied fields [14-17]. The maximum acceptable concentration for Carbofuran in drinking water is 0,009 mg/L [18].

Several treatments process either independent or in conjunction are in practice for the removal of pesticides from wastewater. These processes include; chemical oxidation with ozone, photo degradation, combined ozone and UV irradiation, Fenton degradation, biological degradation, ozonation, membrane filtration and adsorption [3]. Among treatment technologies, adsorption is rapidly gaining prominence. Activated carbon is the most widely used adsorbent for pesticides removal, but it is too expensive, consequently many studies have been under taken to investigate the use of low cost adsorbent [19].

The aim of the present study was to investigate the feasibility of removal of Carbofuran pesticide from aqueous solutions by using animal bone meal as a new cost adsorbent.

Batch adsorption experiments were achieved out as a function of adsorbent dosage, contact time, initial concentration of Carbofuran, pH and temperature. The thermodynamic parameters were also evaluated from the adsorption measurements. The Langmuir and Freundlich isotherms models, kinetics adsorption are also studied.

2. Materials and Methods

2.1 Adsorbate

Carbofuran (C₁₂H₁₅NO₃) was the pesticide used in this study, which was purchased from Sigma-Aldrich company (Casa, Morocco) and its technical grade was 99,9% purity. The chemical structure of Carbofuran is given in Fig.1. Distilled water was used to prepare all solutions. Adsorption studies for the evaluation of ABM adsorbent for the removal of Carbofuran from aqueous solutions were carried out in duplicate to get concordant results using a batch contact adsorption method.

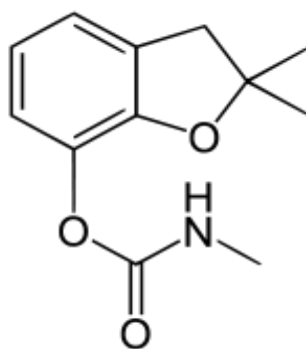


Figure 1. Chemical structure of Carbofuran

2.2 Preparation and characterization of adsorbent

Animal bones were obtained from nearby butcher shops as waste after separating the meat from the bone. The preparation method of the ABM adsorbent is summarized in Fig.2. [20]. The ABM was characterized by X-ray diffraction analysis and with Infrared-spectra. Infrared-spectra were obtained using ATI Mattson Genesis series FTIR_ UNICAM instrument. X-ray diffraction of ABM adsorbent was carried out by using X pert Pro X-ray diffractometer using copper anticathode $\lambda(\text{Cu})=1.5418\text{\AA}$. The surface area of ABM was determined by BET method Using BELSORP-mini (Bell Japan, INC) and the calculated surface area was 85 m²/g.

The point of zero charge (pH_{pzc}) of the ABM adsorbents was carried out by the procedure indicated in Ref. [21]. Initially, 20 mL of 0.05 mol/L NaCl were added to several Erlenmeyer flasks. A range of initial pH (pH_i) values of the NaCl solutions were adjusted to a value between 2 and 12 by adding either 0.1 mol/L of HCl and NaOH. Then the total volume of the solution in each flask was brought to exactly 30 ml by further addition of 0.05 mol/L NaCl solution. The pH_i values of the solutions were then accurately noted and 50 mg of adsorbent was added to each flask, which were securely capped immediately. The suspensions were shaken in a shaker at 25 °C and allowed to equilibrate for two days. The suspensions were then centrifuged at 3600 rpm for 15 min and the final pH (pH_f) values of the supernatant liquid were measured. The pH_{pzc} is defined by the point where the curve of $\Delta\text{pH} (\text{pH}_f - \text{pH}_i)$ versus pH_i crosses the line equal to zero.

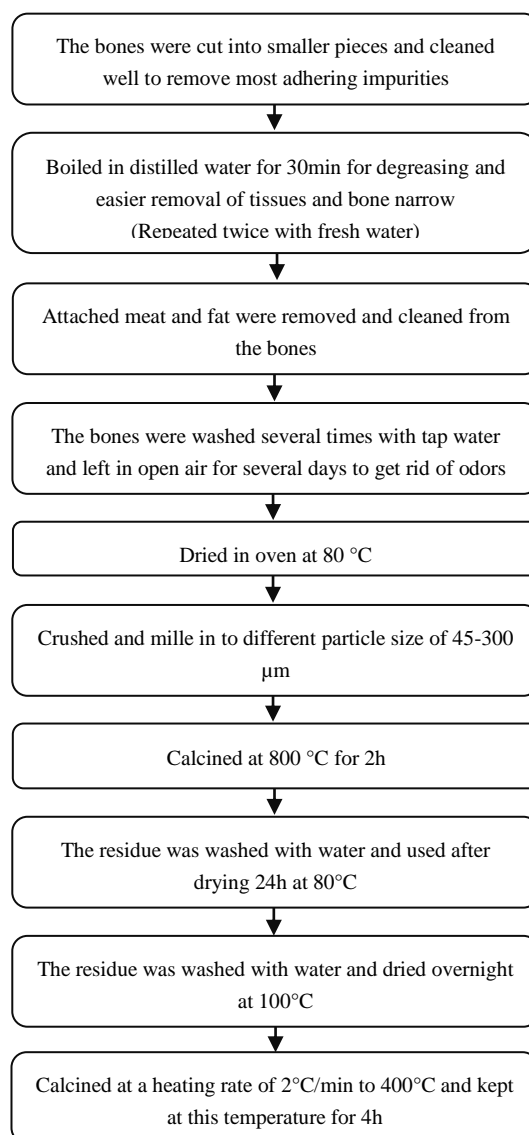


Figure 2. Preparation of ABM

2.3 Batch equilibrium studies

Preliminary experiments shows that the equilibrium was established at 70 min. Adsorption tests were carried out in a set of Erlenmeyer flasks (50 mL) where 25 mL of Carbofuran solutions with initial concentrations of 5, 10, 15 and 20 mg/L were prepared.

An amount of 25 mg of the ABM was added into each flask covered with glass stopper and the flasks were maintained under speed agitation of 120 rpm and under constant temperature 25 °C until to reach equilibrium. All samples were filtered prior to analysis by Millipore membrane type 0.45 μm HA in order to minimize interference of the carbon fines with the analysis. Each batch of the experiment was duplicated under identical conditions.

The concentrations of Carbofuran in the solution before and after adsorption were determined using a liquid chromatography coupled with tandem mass spectrometry LCMSMS (API 3200 System, AB SCIEX /Amérique).

All solvents used for LCMSMS were HPLC grade. For LCMSMS 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 column Gemini-NX C 18 (100 mm x 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 / Phase B: ammonium formate in methanol at 5 mmol / L) as described in table .1. Mass spectra were determined.

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

Identification of Carbofuran was performed using MRM " multiple reaction monitoring " method. The MRM method is a mass spectrometric technique for quantifying one or more target molecules in a complex sample . The mass spectrometer measures the ratio mass/charge (m/z) of ionized molecules . The analytical specificity of the MRM method is afforded by the combination of the value of m/z of the molecule to be assayed (precursor) and the value of m/z of the fragment. Together these two parameters, intended to be specific for the molecule to be assayed, is called a transition. The parameters of the transition of the pesticide studied are presented in Table .2.

Table 2: LCMSMS parameters for Carbofuran

	Q1	Q2	Dwell	DP	EP	CEP	CE	CXP
Carbofuran 1	222.2	123.1	8	35	11	33.7	3	35
Carbofuran 2	222.2	165.2	8	35	11	16.3	4	35

The amount of adsorption at time t, Q_t (mg/g) was calculated using the following formula:

$$Q_t = \frac{C_0 - C_t}{W} V \quad (1)$$

Where C_t (mg/L) is the liquid concentration of Carbofuran at any time, C_0 (mg/L) is the initial concentration of the Carbofuran in solution. V is the volume of the solution (L) and W is the mass of Carbofuran adsorbent (g).

The amount of adsorption at equilibrium, Q_e (mg/g) was calculated using the formula:

$$Q_e = \frac{C_0 - C_e}{W} V \quad (2)$$

Where C_0 and C_e (mg/L) are the liquid concentrations of Carbofuran initially and at equilibrium. The Carbofuran removal percentage can be calculated as follows:

$$\% \text{ of pesticide removal} = \frac{C_0 - C_e}{C_0} 100 \quad (3)$$

Where C_0 and C_e (mg/L) are the initial and equilibrium concentrations of Carbofuran in solution.

2.4 Effect of Carbofuran solution pH

To investigate the effect of initial pH solution on the adsorption capacity of Carbofuran pesticide using ABM adsorbent, we had varied the initial pH of the solutions from pH 2 to 12 using different separate batches of Erlenmeyer flasks (50 mL) simultaneously at the same concentration of the Carbofuran (10 mg/L). The pH was

adjusted using 0.1M sodium hydroxide (NaOH) and/or 0.1M HCl and was measured using pH meter (JENCO Model 6173, USA). The amount of ABM adsorbent was fixed at 1g/L and temperature at 25°C.

2.5 Adsorption isotherm

The equilibrium adsorption isotherm is fundamentally very crucial in designing adsorption systems. In this study, isotherm data was analyzed with Langmuir and Freundlich models. The linear form of the Langmuir [22] model is:

$$\frac{1}{Q_e} = \frac{1}{K_L Q_m} \times \frac{1}{C_e} + \frac{1}{Q_m} \quad (4)$$

Where C_e (mg/L) is the equilibrium concentration of pesticide in solution, Q_e (mg/g) is the amount of pesticide adsorbed per unit weight of adsorbent at equilibrium, Q_m (mg/g) is the monolayer adsorption capacity and K_L (L/mg) is the adsorption equilibrium constant.

Langmuir adsorption model [22] is based on the following hypotheses: uniformly energetic adsorption sites, monolayer coverage and no lateral interaction between adsorbed molecules. Graphically, a plateau characterizes the Langmuir isotherm. Therefore, at equilibrium a saturation point is reached where no further adsorption can occur. A basic assumption is that sorption takes place at specific homogeneous sites within the adsorbent. Once a pesticide molecule occupies a site, no further adsorption can take place at that site.

The Freundlich isotherm [23] endorses the heterogeneity of the surface and assumes that the adsorption occurs at sites with different energy of adsorption. The energy of adsorption varies as a function of surface coverage. The linear form of Freundlich isotherm however is:

$$\ln Q_e = \ln k_f + \frac{1}{n} \ln C_e \quad (5)$$

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.

3. Resultat and discussion

3.1 Characterization of ABM adsorbent

The ABM was identified by X-ray diffraction, IR spectroscopy and chemical analysis. X-ray diffraction was employed to evaluate the phase purity and the crystallographic structural properties of the mineral component of ABM adsorbent. Fig. 3 depicts the X-ray diffraction spectrum of ABM adsorbent. The diffractogram of calcined ABM shows only the characteristic pattern of hydroxyapatite. These results confirm that the amorphous organic component was removed after calcination [24]. For 2θ between 25° and 45°, the main lattice reflections originate peaks at 25, 28.1, 32.8, 33.7, 34.5 and 39.7° being respectively assigned to the (002), (102), (210), (211), (112) and (300) Miller plans of hydroxyapatite [24].

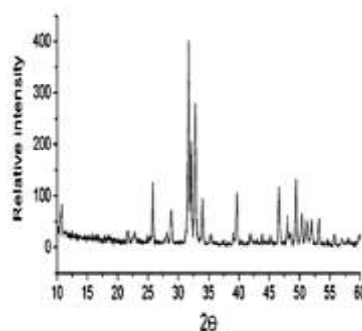


Figure 3. X-ray diffraction of animal bone

Elemental analysis of ABM shows a high yield of Ca (49.62%) and P (42.36%) with a (Ca/P) ratio equal to 1.17. Small amounts of Si (3.88%), Mg (1.32%), Na (0.77%), Al (0.35%), Fe (0.24%), Cl (0.24%), S (0.11%), K (0.07%), Sr (0.03%), Cu (0,03%) and Zn (0.02%) are found.

To obtain FTIR spectra of the ABM prepared, we had encapsulated 0.5 mg of finely powder with 400 mg of KBr to get translucent disk. Fig. 4 shows the FTIR spectra of ABM adsorbent. Carbonate is the most abundant substitution in bone mineral and according to its crystal position, carbonate apatite is designated as type A (OH^-) or type B (PO_4^{3-}), the latter being the most frequent bone [25-26]. It is recognized that hydroxyapatite derived from natural bone [27-28].

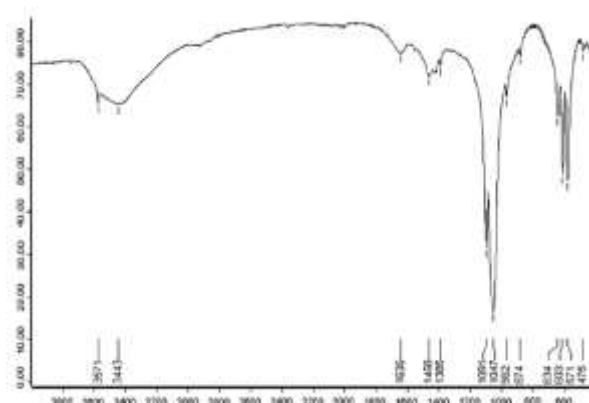


Figure 4. IR Spectra of animal bone

FTIR spectrum of ABM shows the characteristic bands of hydroxyapatite (571, 603, 962 (shoulder), 1047 and 1091 (shoulder) cm^{-1} due to phosphate vibrations and collagen (C=O stretching vibration at 1635 cm^{-1} , N-H in plane bending at 1458 cm^{-1} , C-H and N-H stretching modes in 3000 3571 cm^{-1} region) [29-31]. Additionally, the typical bands of carbonate substituting for phosphate site (type B) in the apatite lattice are also observed: band at 874 cm^{-1} and double bands 1385/ 1445 cm^{-1} [32-33].

3.2 Effect of adsorbent amount

The effect of adsorbent dose on the removal of Carbofuran was studied by contacting different amounts of ABM adsorbent from the range of 0,25 to 3,50g/L with 25 mL of a Carbofuran solutions with initial concentrations fixed at 5 mg/L. The equilibrium experiments were carried out at fixed temperature of 25 $^{\circ}\text{C}$. The agitation was made for 24 h. Fig. 5 describes the variation of percentage of removal of pesticide studied versus adsorbent dose. The percentage of removal of Carbofuran was increased with increasing adsorbent dose. A maximum of 98.3% removal of the Carbofuran was observed by 1 g/L of ABM, as shown in Fig. 5.

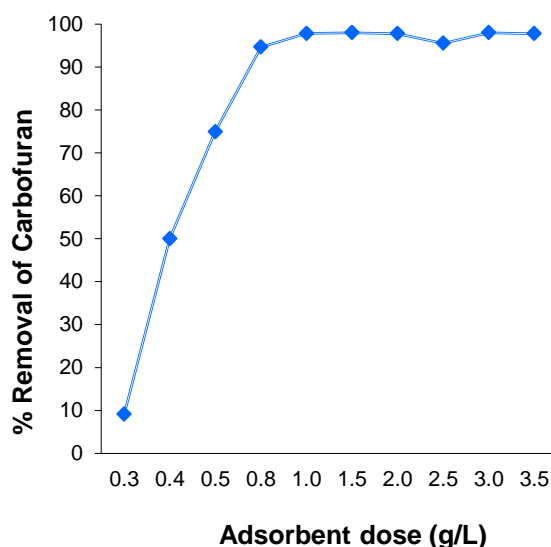


Figure 5. Effect of adsorbent dose on the adsorption of Carbofuran. [Carb]=5 mg/L; contact time =24h

3.3 Effect of contact time and initial concentration of Carbofuran

The effect of contact time and initial Carbofuran concentration on the percentage of removal Carbofuran by ABM was achieved using 1g/L of ABM adsorbent and different concentrations of Carbofuran (5,10,15 and 20 mg/L). Fig.6 depicts these results. It was found that, the adsorption is quite rapid initially, gradually slows down and then reaches a constant value beyond which no more Carbofuran was further removed from the solution. The time of equilibration adsorption was unaffected by initial concentration. Equilibrium was attained at 70 min for ABM-Carbofuran system.

Based on this result, the contact time was fixed at 2h for the rest of the batch experiments to make sure that equilibrium was reached in all cases. Fig.7 represented the LCMSMS chromatogram of one of those adsorption experiments of Carbofuran on ABM studied. It shows a chromatogram of the two MRM transitions obtained by contacting 50 mg of ABM with 50 ml of solution of Carbofuran at initial concentration 5 mg/L. The first chromatogram is the chromatogram of the tow MRM transitions of Carbufuran analyzed after 10 min of agitation, the value obtained was 3010 and 3005 ppb. The second chromatogram is found after 20 min of contact time, it correspond to the values 1798 and 1803 ppb. After 40 min of agitation we had found the values 644 and 635 ppb witch correspond to chromatogram 3. The chromatogram 4, 5 and 6 correspond successively to the chromatogram of the MRM transitions of Carbofuran found after 50, 60 and 70 min and witch correspond to values 357, 349, 204, 199, 98 and 97 ppb.

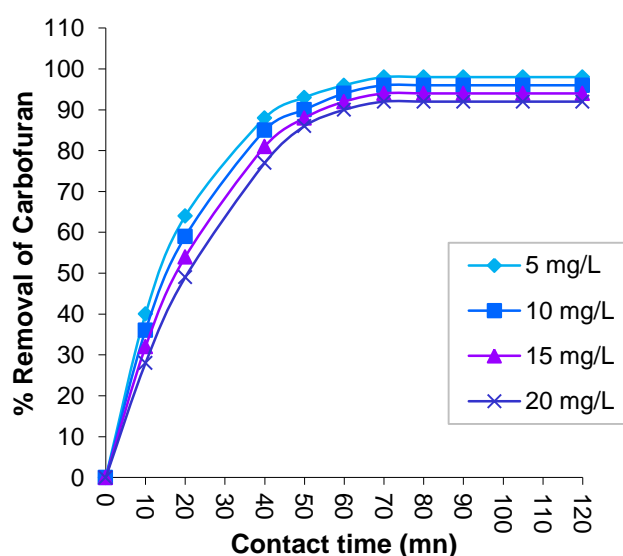


Figure 6. Effect of contact time and pesticide concentration
On the adsorption of Carbofuran. Adsorbent dose: W=50mg and V= 50mL

It was observed from Fig.6 that the removal of Carbofuran pesticide is increased with increasing the contact time at all initial Carbofuran concentrations. Moreover, the % removal pesticide is increased with the decrease in initial pesticide concentration. That can be explained by the fact at lower concentration, 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, the available sites of adsorption at high concentration become fewer and consequently the percentage removal of pesticide depends upon concentration [21].

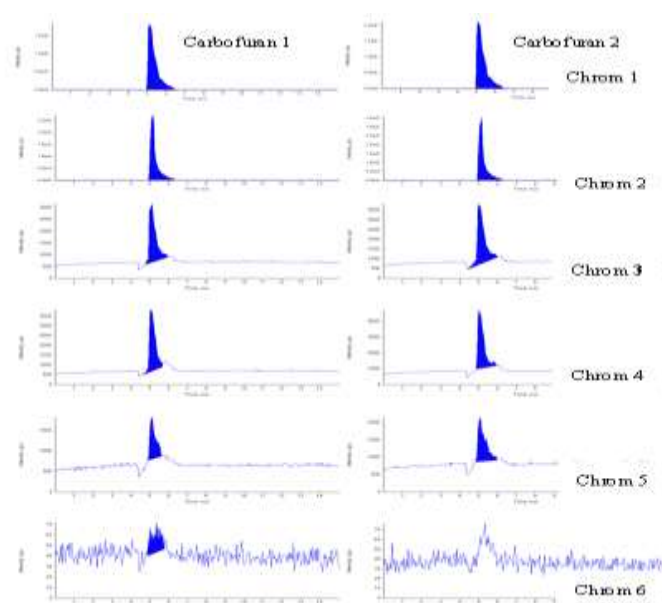


Figure 7. LC-MS/MS chromatogram of Carbofuran adsorption on ABM (initial pesticide concentration 5 mg/L)

The curves obtained were single, smooth and continuous leading to saturation of ABM by carbofuran pesticide. This result suggests the possibility of monolayer coverage pesticide on the surface of ABM adsorbent [34].

3.4 Effect of pH

One of the most important factors in adsorption studies is the effect of the acidity of the medium [35]. It is because both adsorbed molecules and adsorbent particles may have functional groups which are affected by the concentration of hydrogen ions H^+ in the solution and which are involved in the molecular adsorption process at the active sites of adsorbent. In order to investigate the effect of initial pH solution on the adsorption of Carbofuran onto ABM, experiments were performed by varying the pH from 2 to 12 and using 10 mg/L of fixed initial concentration of Carbofuran. The result of this investigation is plotted in Fig.8 which indicate that pH considerably affected Carbofuran adsorption. As it can be seen from this figure, the Carbofuran removal percentage decreases from 88 % to 67 % by increasing pH from 2 to 12.

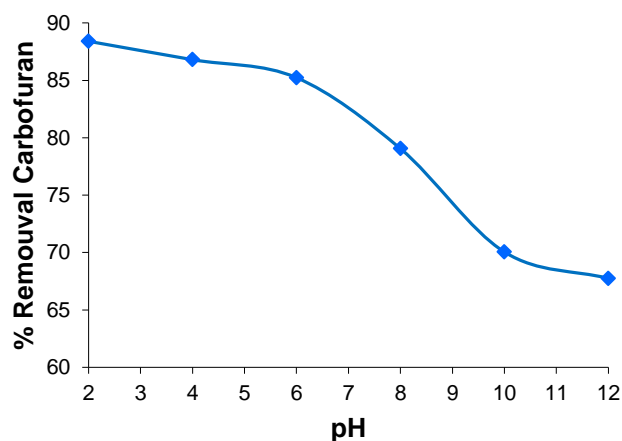


Figure 8. Effect of pH on removal of Carbofuran onto ABM. Initial pesticide concentration 10mg/L. Adsorbent dose 25mg and $V=25\text{mL}$.

To explain the possible pH-mechanism, the determination of pH_{pzc} played an important role because it has been observed that surface functional groups of adsorbate makes adsorption process complex by the type of charge characteristics present at the adsorbent surface [36]. So in order to explain the possible pH-mechanism, we have determined the zero point charge pH of our ABM. Fig. 9 depicts the result of this determination. The pH_{pzc} value for ABM particles was determined and it is above 8.4 which means that the adsorbent's surface was positively charged at pH less than 8.4 and negatively charged at pH values above 8.4.

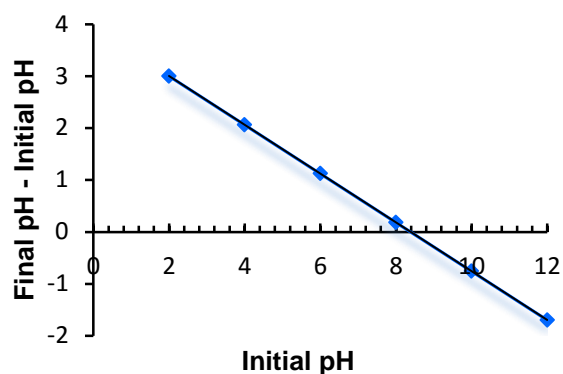


Figure 9. Determination of zero point charge pH

At pH less than 8.4, a significantly high electrostatic attraction phenomenon exists between negatively charged Carbofuran pesticide and the positively charged surface of the ABM. 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 Carbofuran 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 Carbofuran adsorption. The effect of pH on carbofuran adsorption was studied by Gupta et al. [36] and Salman et al. [3] and they reported that when pH was lower, carbofuran adsorption was higher.

3.4 Effect of particle size on adsorption

The effect of particle size on the adsorption of Carbofuran pesticide by animal bone meal was investigated using four particle sizes, < 50 μm , 50–100 μm , 100–200 μm , and 200–300 μm . In each study 25 mg of adsorbent in 25 ml of 10 mg/L of Carbofuran solution was agitated to equilibrium time of 70 min, the adsorbent was separated and the supernatant solution was filtered by Millipore membrane and analyzed for Carbofuran concentration and the values are noted. The result is shown in Fig.10.

The results indicated that the adsorption capacity of animal bone meal increases to some extent with decrease in particle size of the adsorbent. The increase in the uptake by smaller particles was due to the greater accessibility to pores and to the greater surface area for bulk adsorption per unit mass of the adsorbent.

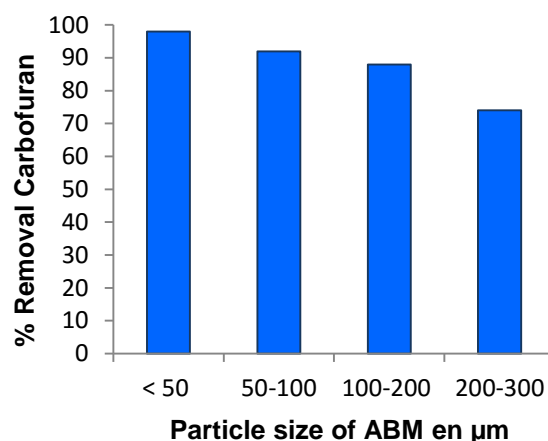


Figure 10: Effect of particle size on removal of Carbofuran onto ABM. Initial pesticide concentration 10mg/L. Adsorbent dose 25mg, $V = 25ml$ and agitation time 70 min.

3.6 Adsorption isotherms

The isotherm is meaningful to the design of adsorption systems, and its shape provides information about the homogeneity or heterogeneity on the adsorbent surface [37]. In the present investigation the equilibrium adsorption isotherm of ABM-Carbofuran system was studied using an initial concentration values of carbofuran pesticide ranged from 5 to 20 mg/L. The experiences were carried out using the same previous conditions and taking into consideration the equilibrium time that is 70 min. Adsorption isotherm of Carbofuran pesticide on ABM adsorbent is plotted in Fig.11.

It is evident from the figure that the adsorption capacity increases with increasing the initial pesticide concentration. This can be due to a high driving force for mass transfer. In fact, high concentration in solution implicates high molecules of pesticide fixed at the surface of the adsorbent. Langmuir and Freundlich isotherm models were applied for the analysis of equilibrium adsorption data obtained and the constants appearing in each equation of those models were determined by nonlinear regression analysis.

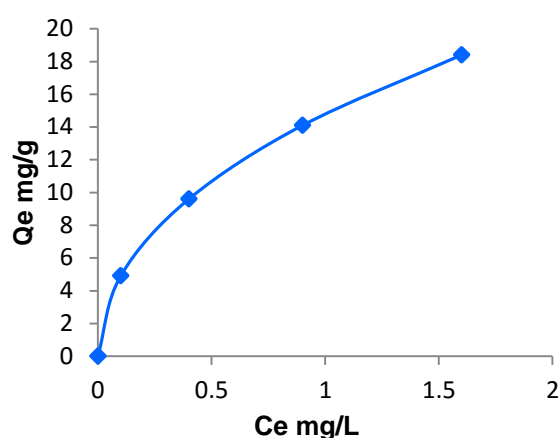


Figure.11. Adsorption isotherm of Carbofuran on ABM.
 Langmuir isotherm model

For Langmuir model the linear plot of the amount of pesticide adsorbed per unit weight ($1/Q_e$) against the equilibrium concentration of pesticide in solution ($1/C_e$) allow to determinate the monolayer adsorption capacity Q_m (mg/g) and the adsorption equilibrium constant K_L which is related with the energy of the adsorption. A linear plot of $\ln Q_e$ versus $\ln C_e$ enables to determine the constant K_f and the adsorption intensity n for Freundlich model (figures not shown). The results of these analyses are tabulated in Table 3. The correlation coefficients R^2 are also shown in this table.

Table 3: Langmuir and Freundlich isotherm model parameters
 For adsorption of Carbofuran on ABM

Langmuir parameters		Freundlich parameters			
K_L	Q_m (mg/g)	R^2	K_f	$1/n$	R^2
3.6	18.5	0.98	14.78	0.477	0.99

For Freundlich model, the $1/n$ value is related to the adsorption intensity. $1/n$ values indicate the type of isotherm to be irreversible ($1/n = 0$), favorable ($0 < 1/n < 1$), unfavorable ($1/n > 1$) [38].

The table indicates that both the isotherms give reasonable fit to experimental data. From this results and basing on the correlation coefficient R^2 , it can be concluded that the adsorption process of Carbofuran on animal bone meal was demonstrated well by both of Langmuir and Freundlich isotherm models. The correlation coefficient, R^2 for both models was $0.98 \leq R^2 \leq 0.99$. Also, it was observed that the maximum adsorption capacity Q_m of ABM for Carbofuran pesticide was found to be 18.5 mg/g.

The essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor called equilibrium parameter, R_L , defined by:

$$R_L = \frac{1}{1 + K_L C_0} \quad (6)$$

Where C_0 is the initial pesticide concentration (mg/L). The R_L parameter values indicated the shape of isotherm as presented in Table .4 [38].

Table 4: 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

Based on the calculated R_L values at different initial pesticide concentration, which were found to be in the range of (0.014- 0.053) at all initial pesticide concentration, it can be concluded that the adsorption process of Carbofuran on animal bone meal was favorable as Langmuir separation factor, R_L was $0 < R_L < 1$ and supported by $1/n$ values of Freundlich which were less than one.

4. Conclusion

In this study, the removal of Carbofuran pesticide from aqueous solution by animal bone meal, as a new low cost adsorbent, was investigated. The percentage of removal of Carbofuran was increased with increasing adsorbent dose. A maximum of 98.3% removal of the Carbofuran was observed by 1 g/L of ABM. The removal of Carbofuran pesticide is increased with increasing the contact time at all initial Carbofuran concentrations. Moreover, the % removal pesticide is increased with the decrease in initial pesticide concentration. The time of equilibration adsorption was unaffected by initial pesticide concentration and the equilibrium was attained at 70 min for ABM-Carbofuran system.

The pH experiments showed that the significant adsorption takes place in acidic range; when pH was taken from 2 to 12 the percentage removal of pesticide onto ABM was decreased from 88% to 67%. The adsorption capacity increases with decrease in particle size of the adsorbent.

The equilibrium data have been analyzed. The results showed that the adsorption process of Carbofuran on animal bone meal was favorable as Langmuir separation factor, R_L was $0 < R_L < 1$ and supported by $1/n$ values of Freundlich which were less than one. The results indicated that animal bone meal is a promising new low cost adsorbent for the removal of Carbofuran from aqueous solution.

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