Original Article

Evaluation of carbaryl sorption in alluvial soil

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Abstract

This study investigated the adsorption potential of carbaryl onto alluvial soil. Parameters that influence the adsorption process such as pH, adsorbent dose, initial carbaryl concentration, stirring rate, particle size, contact time and temperature were studied in a batch process. The carbaryl adsorption capacity was at maximum at pH 6 for an initial concentration of 20 ppm. Adsorption equilibrium time was observed in 180 min. Equilibrium adsorption data was best fitted with Freundlich isotherm and pseudo-first order kinetic model, respectively. The adsorbent was characterized by X-ray diffraction spectrum, Fourier transform infrared spectroscopy and scanning electron microscopy. The experiment performed indicated that the adsorption capacity of carbaryl was significantly correlated with particle size, organic matter and pH of the soil. Therefore, the possibility for carbaryl to contaminate underground water may be greater in the presence of low organic matter content.

Keywords: adsorption, alluvial soil, carbaryl, adsorption isotherms, thermodynamic parameters, adsorption kinetics, ANN

1. Introduction

The use of insecticides is one of the major factors behind the increase in agricultural productivity in the 20th century (Van Emden, 1996). Carbaryl (1-naphthyl methyl carbamate) is a wide-spectrum chemical in the carbamate family used chiefly as an insecticide. Carbaryl disrupts the normal functioning of the insect nervous system and may cause toxicity by contact or ingestion (Tomlin, 2000). Carbaryl kills both targeted (e.g. malaria-carrying mosquitoes) and beneficial insects (e.g. honey bees), as well as crustaceans and earthworms (Gupta and Saxena, 2003). It is a cholinesterase inhibitor, toxic to fish, birds and mammal nervous systems, likely to be human carcinogenic (U.S. Environment Agency, 2003), mutagenic (Delescluse et al., 2001) and reproductive toxic (Xia et al., 2005). Its toxicity to non-target rats and mice was determined to be high. Application of carbaryl is done by foliar spray, through drip irrigation and also by soil drenching around individual vines. Thus, directly or indirectly, the soil system appears as the ultimate sink of carbaryl residues. Once it enters into soil system, it may get partitioned between soil solid and solution phases and maintains dynamic equilibrium. Therefore, the sorption behavior governs the fraction of residues present in soil solution phase, in which it is available for leaching and groundwater contamination. Thus the interaction of carbaryl with the soil thus becomes extremely important. The half-life of carbaryl ranges from four days in aerobic soils (Miller, 1993a) to 72.2 days in anaerobic soils (Miller, 1993b), which may culminate when either during flood or with increased dose. Direct or indirect application of carbaryl in variety of soil textures causing different patterns of adsorption process and affects other related processes such as transport, degradation, volatilization, bioaccumulation, that influence the final fate of carbaryl in the soil environment (Gao et al., 1998)

Hence the extent of surface water and ground water contaminations is there by affected. It is worth-mentioning that various organic and inorganic compounds in varying composition coupled with surface activity are components of soils. They can bind carbaryl and reduce the bioavailability (Torrents and Jayasundra, 2012). Carbaryl adsorption on the soil particles and retention solely depends on the clay
fraction of soil and chemical properties of both soil and carbaryl (USDA, 1998). Previous study shows that the carbaryl sorption on bentonite clay is greater than that on kaolinite (Rajagopal et al., 1984) and the ability of smectite to adsorb organic contaminants and pesticides from aqueous solution is influenced by the exchangeable cations, as well as structural charge and its origin (Haderlein et al., 1996; Boyd et al., 2001). Aly et al. (1980) studied sorption of carbaryl and found that Ca\(^{2+}\)-bentonite exhibited the highest affinity for carbaryl, followed by an alluvial soil, calcareous soil, and calcite. Although carbaryl is subject to alkaline hydrolysis, its degradation by calcite was not noted. Sheng et al. (2001) evaluated the potential contribution of smectite to pesticide retention in soils, and concluded that homoionic K\(^{-}\)-smectite was a more effective sorbent than muck soil for carbaryl. Chatteraj et al. (2013) predicted that carbaryl is moderately adsorbed in alluvial soil.

Artificial neural networks (ANN) are a possible alternative modeling tool for various processes and operations involving nonlinear multivariable relationships. Among several types of ANN architecture multilayer perceptron (MLP) is observed to be most common for chemical processes (Pandharipande et al., 2013). Basically this is a feed forward neural network, has a multilayer structure consisting of one input and output layer and at least one hidden layer in-between. The number of nodes in input and output layers is decided by the number of independent and dependent parameters defining the process whereas the selection of number of hidden layers is dependent on the complexity of the process. The nodes in successive layers are connected with each other through connectionist constants called as weights. The data is transferred in the form of array of matrix from input layer to output layer through hidden layers. The output signal is compared with the target value to generate error signal. By adjusting the weights using appropriated algorithm, training of the network is to be carried out to minimize the error (Rumelhart and McClelland, 1986; Anderson, 1999; Pandharipande 2004).

Various researchers (e.g. Meenakshsipriya et al., 2009) used ANN models to predict adsorption efficiency. In the present work, the sorption behavior of carbaryl in alluvial soil was explored for determining the persistence in the environment. The effects of various experimental parameters such as pH, adsorbent dose, initial carbaryl concentration, stirring rate, particle size, contact time and temperature on adsorption of carbaryl were investigated. Adsorption isotherms and thermodynamic parameters were also evaluated which is finally tested by using ANN Model.

### 2. Materials and Methods

#### 2.1 Chemicals

4-nitrobenzene diazonium fluoborate (Sigma Aldrich) A.R. (99.9% purity) was used as the main reagent and a fresh 0.03% (W/V) methanolic solution was made. An analytical standard pure sample of carbaryl was obtained by the recrystallization of a technical grade sample supplied by Bayer. Extraction solvent was Optima grade methanol. Stock solutions were made in A.R. grade CaCl\(_2\), A.R. grade NaOH and subsequent dilutions were made in methanol. All standard solutions were kept at room temperature of the laboratory.

#### 2.2 Soil

Soil (0-30 cm) used in this study was collected from the banks of river Bhagirathi in West Bengal, India owing to its high alluvial soil content and low permeability. The alluvial soil (inceptisol) sample was not purified prior to usage. The soil sample was air dried for few days and grinded into different particle size using different metal sieves having different mesh size and stored in clean glass jars prior to experiment. The pH values of the soil was measured in a 1/1 ratio (w/v) of soil/water. The physico–chemical characteristics of the soil are listed in Table 1.

#### 2.3 Adsorbent characterization

Adsorbent characterization was performed by means of spectroscopic and quantitative analysis. The surface area of the adsorbent (alluvial soil) was determined by Quanta-chrome surface area analyzer (model NOVA 2200C). The pH of aqueous slurry was determined by soaking 1 g of alluvial soil in 50 ml distilled water, stirred for 24 hrs and filtered and the final pH was measured. The % of clay, silt, and sand was determined by hydrometric method (Saha et al., 2010). The cation exchange capacity (CEC) of the alluvial soil sample was determined by the ammonium acetate method (Rhoades, 1982). The concentrations of sodium and potassium were

### Table 1. Physico-chemical characteristics of soil.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO(_2) (%)</td>
<td>69.0</td>
</tr>
<tr>
<td>Al(_2)O(_3) (%)</td>
<td>3.55</td>
</tr>
<tr>
<td>Fe(_2)O(_3) (%)</td>
<td>2.50</td>
</tr>
<tr>
<td>Mg(_2)O (%)</td>
<td>0.91</td>
</tr>
<tr>
<td>Ca(_{2+}) (mg L(^{-1}))</td>
<td>6.9</td>
</tr>
<tr>
<td>Mg(_{2+}) (mg L(^{-1}))</td>
<td>0.4</td>
</tr>
<tr>
<td>K(_{2+}) (mg L(^{-1}))</td>
<td>16.7</td>
</tr>
<tr>
<td>Na(_{2+}) (mg L(^{-1}))</td>
<td>62.1</td>
</tr>
<tr>
<td>pH</td>
<td>6.2</td>
</tr>
<tr>
<td>Moisture (%)</td>
<td>3.298</td>
</tr>
<tr>
<td>Bulk density (g cm(^{-3}))</td>
<td>1.84</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>40.21</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>1.21</td>
</tr>
<tr>
<td>Particle density (g cm(^{-3}))</td>
<td>2.55</td>
</tr>
<tr>
<td>Clay (%)</td>
<td>3.08</td>
</tr>
<tr>
<td>Sand (%)</td>
<td>81.0</td>
</tr>
<tr>
<td>Organic carbon (%)</td>
<td>1.6</td>
</tr>
<tr>
<td>pH</td>
<td>6.2</td>
</tr>
<tr>
<td>CEC (cmol+ kg(^{-1}))</td>
<td>14.2</td>
</tr>
</tbody>
</table>

...
Determination of point zero charge

The point of zero charge of the adsorbent was determined by the solid addition method (Mondal, 2010). A 50 ml of 0.1 M KNO₃ solution transferred into a series of 100 ml conical flask. The initial pH (pH₀) values of the solution were adjusted from 1.0 to 10.0 by adding either 0.1(N) of HNO₃ or 0.1(N) KOH then 1.5 g of soil was added to each flask which was securely capped immediately. Then the flask were placed into constant temperature water bath shaker and shaken for 24 hrs. The pH values of the supernatant liquid were noted after 24 hrs. The result is presented in Figure 1.

Batch experiments

The batch tests were carried out in 250 mL volumetric flask with 20 mL of working volume stock solution of carbaryl. The stock solution was made in 0.02 (M) CaCl₂ solutions to obtain six different concentrations that were used to the experiment. 2 g air dried alluvial soil sample was added to the solution. The flasks were agitated at a speed of 250 rpm for 120 minutes in a magnetic stirrer (Digital MCO2) at 303±1 K. The influence of pH (range 2.0–12.0), adsorbent dose (ranges 0.5, 1, 1.5, 2, 2.5, 3, 4 g/20 mL) initial carbaryl concentration (0.4, 1, 2, 5, 10, 20, 24 ppm), stirring rate (60, 150, 250, 400, 500, 600 rpm), particle size (50, 100, 150, 250 μm) contact time (ranges 30, 60, 90, 120, 180, 240, 300 min) and temperature (293, 303, 313, 323, 333 K) were evaluated during the present study. Samples were collected from the flasks at pre-determined time intervals for analyzing the residual carbaryl concentration. The residual carbaryl concentration in each flask was determined using the single beam UV-VIS spectrophotometer. The spectrophotometric determination of carbaryl was done by following the method of Sainsbury and Miscus (1964) with some modifications. 5 ml (0.5N) NaOH was added to 5 ml aliquot taken in a 20 ml volumetric flask followed by 5 ml of 0.03% (W/V) methanolic solution of p-nitrobenzene diazonium fluoborate. The mixture was then diluted to 20 ml with methanol and after 20 min absorbance of the greenish–blue color solution was measured at 590 nm using a spectrophotometer (Bausch-Lomb Spectronic 20). The amount of carbaryl adsorbed per unit adsorbent (mg carbaryl per g adsorbent) was calculated according to a mass balance on the carbaryl concentration using the following Equation 1.

\[
q_i = \frac{(C_i - C_{exp}) \times V}{m}
\]

Where \(C_i\) is the initial carbaryl concentration (mgL⁻¹), \(C_{exp}\) is the equilibrium carbaryl concentration in solution (mgL⁻¹), V is the volume of the solution (L) and m is the mass of the soil in g. The (%) adsorption of carbaryl was calculated using the following equation

\[
\% \text{Adsorption} = \frac{(C_i - C_{exp}) \times 100}{C_i}
\]

The soil sorption coefficients \(K_s\) (mLg⁻¹) and \(Koc\) were then calculated as \(K_s = C_i/C_{exp}\) and \(Koc = K_s \times 1000/OC\) where OC is the organic carbon content of the soil (g kg⁻¹) (data not given). Control experiments were performed without the addition of adsorbent confirmed that the sorption of carbaryl on the walls of flasks was negligible.

Statistical analysis

In order to ensure the accuracy, reliability, and reproducibility of the collected data, all adsorption experiments were performed in triplicate, and the mean values were used in data analysis. Relative standard deviations were found to be within ±3%. Microsoft Excel 2007 program was employed for data processing. Non-linear regression analysis using Origin Pro 8.0 software was employed to determine the isotherm parameters and kinetic constants.

Due to the inherent bias resulting from linearization, three different error functions of non-linear regression basin, sum of the square of the errors (SSE), sum of the absolute errors (SAE) and chi-square (\(\chi^2\)), were employed in this study to find out the best-fit isotherm model to the experimental equilibrium data. SSE is given as:

\[
SSE = \sum_{i=1}^{n} \left( q_{exp} - q_{calc} \right)^2
\]

Here, \(q_{exp}\) and \(q_{calc}\) are the calculated and the experimental value of the equilibrium adsorbate solid concentration in the

![Figure 1. pH of zero charge of soil.](image-url)
solid phase (mg/g), respectively, and \( n \) is the number of the data point. SAE is given as:

\[
SAE = \sum_{i=1}^{n} |q_{m,i} - q_{exp,i}|
\]

Chi-square (\( \chi^2 \)) is given as:

\[
\chi^2 = \sum_{i=1}^{n} \left( \frac{(q_{exp,i} - q_{m,i})^2}{q_{m,i}} \right)
\]

The respective values are given in the Table 3. As shown in Table 3, the Freundlich adsorption isotherm model yielded best fit to the experimental equilibrium adsorption data than the Langmuir isotherm model for carbaryl adsorption according to the values of \( R^2 \), \( \chi^2 \), SSE and SAE.

3. Results and Discussion

3.1 Soil characterization

The soil was found to be stable in water, dilute acids and bases. The adsorbent behaves as neutral at pH zero change. To understand the adsorption mechanism, it is necessary to determine the point of zero charge (pHzpc) of the adsorbent. Adsorption of cation is favored at pH>pHzpc, while the adsorption of anion is favoured at pH<pHzpc (Mondal, 2010). The point of zero Charge is 7.2 (Figure 1).

3.2 Adsorbent characterization

3.2.1 FTIR analysis

The FTIR spectral analysis is important to identify the characteristic functional groups on the surface of the adsorbent, which are responsible for adsorption of carbaryl molecule (Sheng, 2004; Ahalya, 2005). The FTIR spectrum of soil was recorded to obtain the information regarding the stretching and bending vibrations of the functional groups which are involved in the adsorption of the adsorbate molecule. The FTIR spectral analysis at before adsorption (Figure 2a) of the soil shows distinct peaks at 4,300, 3,449, 2,365, 2,345, 1,638, 1,408, 1,102, 1,030, 777, 694, 506, 533, 470 cm\(^{-1}\). Among them the strong adsorption band at 3,449 cm\(^{-1}\) indicates the presence of amide group (-NH\(_2\)), the peak at

![Figure 2. (a) FTIR spectra of soil before adsorption of carbaryl. (b) FTIR spectra of soil after adsorption of carbaryl.](image-url)

1,408 is due to aromatic C=C stretching vibration, absorbance at 777 cm\(^{-1}\) and 694 cm\(^{-1}\) is due to aromatic C-H. After carbaryl adsorption the \(-\text{NH}\) group is shifted to lower frequency (3,438 cm\(^{-1}\)) and a strong band at 3,613 cm\(^{-1}\) is appeared, which indicates the presence of \(-\text{OH}\) group. Thus, it can reasonably be concluded that \(-\text{OH}\) and \(-\text{NH}_2\) groups may be the main binding sites for carbaryl adsorption to soil.

### 3.2.2 SEM analysis

SEM analysis is another useful tool for the surface morphology of an adsorbent fundamental physical proportion of the adsorbent (Chadrudee et al., 2011). The porous and irregular surface structure of the adsorbent can be clearly observed in the SEM images shown in Figure 3a. Further the pores on the surface of the adsorbent are highly heterogeneous as shown in Figure 3b. The heterogeneous pores and cavities provided a large exposed surface area for the adsorption of the carbaryl. The size of pores is indicative of the expected adsorption of the carbaryl molecule onto the surface of the soil.

### 3.3 X-ray diffraction analysis

X–ray data is shown in Figure 4. It is clearly revealed that the adsorbent is amorphous and porous in nature.

#### 3.3.1 Effect of pH

pH has been recognized as one of the important factor in carbaryl adsorption (Murthy and Raghu, 1991). The structural stability of the carbaryl molecule is also associated with pH, at alkaline medium carbaryl breaks down into CO\(_2\) and 1-Napthol. Adsorption process is directly related with competition ability of hydrogen ions to active sites on the adsorbent surface. The adsorption of carbaryl by soil was noted to increase with the increase of pH of the carbaryl solution appreciably up to pH 6. A further increase in carbaryl sorption between pH 6.0 to 12.0 adsorption decreases (Figure 5a). So carbaryl binds more readily to acidic soil (Rajagopal et al., 1984). Since the optimum pH for carbaryl adsorption was found to be 6, it was kept constant for further studies.

#### 3.3.2 Effect of adsorbent dose

Adsorbent dose has an influencing power in sorption process since it determines the sorption capacity of an adsorbent for a given initial concentration of the adsorbate at the operation conditions. The adsorption profile of carbaryl versus different concentration of adsorbate (range of 0.5-4 g/20 ml) is shown In Figure 5b. It was observed that the percentage of carbaryl adsorption increased with increase of adsorbent dose. Such a trend is mostly attributed to an increase in the sportive surface area and the availability of more active adsorption sites (Nasuha et al., 2010). Although the percentage adsorption of carbaryl increased with increase of adsorbent dose, the maximum carbaryl adsorption was observed at 3 g and further increase in adsorbent dose did not significantly change the adsorption yield. This is due to the binding of almost all the carbaryl molecule to adsorbent surface and the establishment of the equilibrium between the carbaryl molecule on the adsorbent and in the solution (Akar et al., 2009). Hence in the present study 3 g adsorbent/20 ml carbaryl solution was employed for further experiments.

#### 3.3.3 Effect of initial concentration

The rate of adsorption is a function of the initial concentration of the adsorbate, which makes it an important
Figure 5. (a) Effect of pH on adsorption of carbaryl by soil. Experimental conditions: adsorbent dose 2 g, initial carbaryl concentration 10 ppm, stirring rate 250 rpm, pH 6, temperature 303 K, particle size 100 μm, contact time 120 min.
(b) Effect of adsorbent dose on adsorption of carbaryl by soil. Experimental conditions: adsorbent dose 2 g, stirring rate 250 rpm, initial carbaryl concentration 10 ppm, pH 6, temperature 303 K, particle size 100 μm, contact time 120 min.
(c) Effect of initial carbaryl concentration on adsorption by soil. Experimental conditions: adsorbent dose 3g, stirring rate 250 rpm, pH 6, temperature 303 K, particle size 100 μm, contact time 120 min.
(d) Effect of stirring rate on adsorption of carbaryl by soil. Experimental conditions: adsorbent dose 3 g, pH 6, temperature 303 K, initial carbaryl concentration 20 ppm, particle size 100 μm, contact time 120 min.
(e) Effect of particle size on adsorption of carbaryl by soil. Experimental conditions: adsorbent dose 3 g, pH 6, temperature 303 K, initial carbaryl concentration 20 ppm, contact time 120 min.
(f) Effect of contact time on adsorption of carbaryl by soil. Experimental conditions: adsorbent dose 3 g, stirring rate 400 rpm, pH 6, temperature 303 K, initial carbaryl concentration 20 ppm, particle size 50 μm.
(g) Effect of temperature on adsorption of carbaryl by soil. Experimental conditions: adsorbent dose 3 g, stirring rate 400 rpm, pH 6, initial carbaryl concentration 20 ppm, contact time 180 min, particle size 50 μm.
factor to be considered for effective adsorption. The effect of different initial carbaryl concentration on the adsorption of carbaryl onto soil is shown on Figure 7. It is evident from the Figure 5c that the percentage adsorption of carbaryl increased with increase in initial concentration of carbaryl (Chattoraj et al., 2013). After certain concentration (20 ppm) there is no significant change in the adsorption yield. This can be explained that all adsorbents have a limited number of active sites, which become saturated at a certain concentration (Akar et al., 2009).

3.3.4 Effect of stirring rate

Studies on the effect of stirring rate were conducted by varying speed from (60-600 rpm) at pH 6 with adsorbent dose 3 g/20 ml and contact time 120 min. The influence of stirring rate on the extent of adsorption is shown in Figure 5d. It is revealed from the above figure that the carbaryl adsorption is a function of stirring rate. Carbaryl adsorption increases with the increase of stirring rate (Jana and Das, 1997). The percentage adsorption is less at lower stirring rate and increases with stirring rate up to 400 rpm and there after it remains more or less constant (Figure 5d). The x-shaped curve indicates multilayer adsorption and the carbaryl molecule binds the soil surface with availability of new sites to the solvent as adsorption takes place (Giles et al., 1960). The reason for the increase in efficiency is that at higher speeds better contact between the adsorbent and adsorbate is possible (Tembhurkar and Dongre, 2006). The adsorption extent for stirring rate after 400 rpm does not show any significant increase and hence stirring rate 400 rpm was considered for further studies.

3.3.5 Effect of particle size

Studies on the effect of particle size were conducted by varying particle size (50-250 µm) at a speed of 400 rpm, pH 6 with adsorbent dose 3 g/20 ml, contact time 120 min and 20 ppm initial concentration of carbaryl. The influence of particle size on the extent of adsorption is shown in Figure 5e. Data obtained from the experiments are clearly indicated that carbaryl adsorption decreased with increase particle size. The observed decrease in the adsorption capacity with increase of particle size from (50-250 µm) indicates that low particle size favors the carbaryl adsorption process on to soil. These results indicate that as contact area increases adsorption of carbaryl process also increases with a maximum at 50 µm.

3.3.6 Effect of contact time

It is essential to evaluate the effect of contact time required to reach equilibrium for designing batch adsorption experiments. Therefore the effect of contact time on adsorption of carbaryl was also investigated. The uptake of carbaryl as a function of contact time is shown in Figure 5f. It shows that adsorption of carbaryl increased with rise in contact time up to 180 min. Further increase in contact time did not enhance the carbaryl adsorption process. Slow increase of adsorption at initial stage indicates that interaction between carbaryl and soil was not by an ion exchange (Bunzl et al., 1976) and the equilibrium is reached within 240 minutes. Similar observation is shown by Jana and Das (1997).

3.3.7 Effect of temperature

Temperature is also an additional factor which has an influencing power in any adsorption process. So batch adsorption experiments were carried out at different temperature ranging from 293K to 333 K. Data obtained from the experiments are clearly indicate that carbaryl adsorption decreased with increase in temperature. The observed decrease in the adsorption capacity with increase of temperature indicates (Figure 5g) that indicates that low temperature favors the carbaryl adsorption process onto soil (Aly et al., 1980).

3.4 Adsorption isotherm

The Langmuir and Freundlich models were used to describe the equilibrium adsorption data at different temperatures. The linearized form of isotherms (Babu and Gupta, 2008) and their constants are given in Table 3. The experimental data obtained at equilibrium was fitted satisfactorily with Freundlich isotherm and is shown in Figure 6. The Freundlich isotherm reveals the multilayer adsorption. Similar observations have been shown by Joseph et al. (1974) and Jana and Das. (1997).

3.5 Adsorption kinetics

Two kinds of models were used to study the reaction pathways and potential rate limiting steps of the adsorption of carbaryl on to soil. The linearized form of adsorption kinetics (Guo et al., 2002) and their constants are presented in Table 3. From the table, it is confirmed that the adsorption of carbaryl onto alluvial soil followed the pseudo-First order reaction and is shown in Figure 7.

3.6 Activation energy and thermodynamics parameter

From the pseudo second order rate constant k2 was determined (Table 3). The activation energy E1 for the adsorption of carbaryl on soil was determined using the Arrhenius equation. By plotting ln k2 versus 1/T, E1 was obtained from the slope of the linear plot (figure not shown). The value of E1 for adsorption carbaryl on soil was 8.56 kJmol⁻¹. The magnitude of activation energy may give an idea about the type of sorption. There are two main types of adsorption: physical and chemical. The activation energy for physical adsorption is usually less than 40 kJ mol⁻¹, since the forces involved in physical adsorption are weak. Higher
Table 2. Adsorption isotherm constants for adsorption of carbaryl by soil at different temperatures.

<table>
<thead>
<tr>
<th>Isotherm model</th>
<th>Equation</th>
<th>Parameter</th>
<th>Temperature</th>
<th></th>
<th></th>
<th></th>
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<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>293K</td>
<td>303K</td>
<td>313K</td>
<td>323K</td>
<td>333K</td>
</tr>
<tr>
<td>Langmuir isotherm</td>
<td>( \frac{C_I}{q_s} = \frac{C_I}{q_m} + \frac{1}{k_cq_m} )</td>
<td>( q_m ) (µg·g(^{-1}))</td>
<td>91</td>
<td>88</td>
<td>82</td>
<td>67</td>
<td>56</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( K_c ) (L·mg(^{-1}))</td>
<td>0.114</td>
<td>0.092</td>
<td>0.071</td>
<td>0.043</td>
<td>0.022</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( R^2 )</td>
<td>0.9710</td>
<td>0.9434</td>
<td>0.9558</td>
<td>0.9653</td>
<td>0.9741</td>
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<tr>
<td></td>
<td></td>
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<td>293K</td>
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<td>313K</td>
<td>323K</td>
<td>333K</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \log q_s = \log k_f + \left( \frac{1}{n} \right) \log c_f )</td>
<td>( k_f ) (L·mg(^{-1}))</td>
<td>2.75</td>
<td>2.63</td>
<td>2.23</td>
<td>2.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \frac{1}{n} )</td>
<td>1.427</td>
<td>1.411</td>
<td>1.023</td>
<td>1.007</td>
<td>1.004</td>
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<tr>
<td></td>
<td></td>
<td>( R^2 )</td>
<td>0.9940</td>
<td>0.9982</td>
<td>0.9991</td>
<td>0.9984</td>
<td>0.9975</td>
</tr>
</tbody>
</table>

\( q_s \) (µg·g\(^{-1}\)) and \( q_e \) (µg·L\(^{-1}\)) are the solid phase concentration and the liquid phase concentration of adsorbate at equilibrium respectively, \( q_m \) (µg·g\(^{-1}\)) is the maximum adsorption capacity and \( k_c \) (L·mg\(^{-1}\)) and \( K_c \) (mg·g\(^{-1}\)) (L·mg\(^{-1}\)) and is the adsorption equilibrium constant. 
\( n \) is the heterogeneity factor.

Table 3. Kinetic parameters for adsorption of carbaryl by soil.

<table>
<thead>
<tr>
<th>Kinetic model</th>
<th>Equation</th>
<th>Parameter</th>
<th>Temperature</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Pseudo-first order</td>
<td>( \ln(q_e - q_t) = \ln q_e - K_1 t )</td>
<td>( q_{exp} ) (µg·g(^{-1}))</td>
<td>80</td>
<td>78</td>
<td>65</td>
<td>55</td>
<td>47</td>
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<tr>
<td>kinetics model</td>
<td></td>
<td>( q_{cal} ) (µg·g(^{-1}))</td>
<td>81.2</td>
<td>77.6</td>
<td>64.5</td>
<td>54.5</td>
<td>46.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( K_1 ) (min(^{-1}))</td>
<td>0.02763</td>
<td>0.2553</td>
<td>0.02303</td>
<td>0.02072</td>
<td>0.01876</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( R^2 )</td>
<td>0.9980</td>
<td>0.9991</td>
<td>0.9998</td>
<td>0.9979</td>
<td>0.9991</td>
</tr>
<tr>
<td>Pseudo-second order</td>
<td>( t = \frac{1}{k_2 q_e} + \frac{t}{q_e} )</td>
<td>( q_{cal} ) (µg·g(^{-1}))</td>
<td>76.3</td>
<td>69.7</td>
<td>60.1</td>
<td>46.5</td>
<td>36.9</td>
</tr>
<tr>
<td>kinetics model</td>
<td></td>
<td>( K_2 ) (g·mg(^{-1})·min(^{-1}))</td>
<td>0.04926</td>
<td>0.04212</td>
<td>0.03125</td>
<td>0.02514</td>
<td>0.02112</td>
</tr>
<tr>
<td></td>
<td></td>
<td>( R^2 )</td>
<td>0.941</td>
<td>0.936</td>
<td>0.928</td>
<td>0.933</td>
<td>0.956</td>
</tr>
</tbody>
</table>

\( q_s \) and \( q_e \) are the amount of Carbaryl adsorbed (µg·g\(^{-1}\)) at time \( t \) and at equilibrium and \( K_1 \) (min\(^{-1}\)) is the Lagergren rate constant of first order adsorption and \( k_2 \) (g·mg\(^{-1}\)·min\(^{-1}\)) is the second order adsorption rate constant.

Figure 6. Comparison of the experimental data with the Langmuir and Freundlich isotherms for the adsorption of carbaryl on to soil.

Values represent chemical reaction process as chemical adsorption is specific and involves forces much stronger than in physical adsorption. According to literature, the adsorption process of carbaryl onto soil may be physisorption (\( E \approx 8 \) kJ·mol\(^{-1}\)) (Bansal, 2004; Anirudhan and Radhakrishnan, 2008). The standard Gibb free energy (\( \Delta G^0 \)) for the adsorption of carbaryl onto soil at all temperatures was calculated obtained using the Equation 3.
The values of enthalpy ($\Delta H^0$) and entropy ($\Delta S^0$) were determined from the slope and intercept of the plot of $\Delta G^0$ vs. $T$ (figure not shown) and are listed in Table 4. A negative value of free energy change shows that adsorption phenomenon is spontaneous in nature. Increase in value of $\Delta G^0$ with increase in temperature indicates that lower temp makes the adsorption easier. The negative value of $\Delta H^0$ suggests that adsorption process is exothermic. The negative value of $\Delta S^0$ indicates that adsorption complex of carbaryl with soil were stable (Bansal, 2004).

### 3.7 Soil organic carbon partition coefficient and groundwater ubiquity score

Other parameters for the adsorption process soil organic carbon partition coefficient ($K_{oc}$), and groundwater ubiquity score (GUS) have been calculated by using Equations 6 and 7, respectively (Banerjee et al., 2008) as follows

$$K_{oc} = K_s \times \frac{100}{\% oc}$$

$$GUS = \log t_{1/2} \left[ 4 - \log (k_{oc}) \right]$$

The GUS score is used to study the leaching behavior of pesticides which can be classified as leacher (GUS>2.8), transition (2.8>GUS>1.8) and non-leacher (GUS<1.8) (Papa et al., 2004). Under aerobic condition half life of carbaryl is found to be seven days. The calculated $K_{oc}$ and $t_{1/2}$ values were put in the Equation 12 and the GUS was found to be 1.94. Hence, carbaryl is considered to be a chemical belonging to medium leaching potential category.

### 3.8 Artificial neural network approach

A Neural Network Toolbox Neuro Solution 5® mathematical software was used to determine carbaryl adsorption efficiency. Figure 8a shows the ANN Model used in the study. In this investigation 31 set of experimental data is used to estimate the percentage adsorption of carbaryl onto soil with using pH of the solution, initial carbaryl concentration, adsorption dose, contact time, stirring rate, and temperature. There is just one neuron in output layer which is the amount of adsorption predicted by ANN versus amount of adsorption obtained from experiments, during the training process. The plot of amount of adsorption predicted by ANN versus amount of adsorption obtained from experiments is shown in Figure 8b. The slope line 1.006 and amount $R^2=0.953$ show good training of the network.

### 4. Conclusions

In the present study carbaryl adsorption onto alluvial soil was investigated in a batch process. The adsorption studies were carried out as a function of pH, adsorbent dose, initial carbaryl concentration, stirring rate, particle size, contact time and temperature. The carbaryl adsorption capacity of the soil was found to be moderate and strongly dependent on its pH, particle size and organic matter contents. Therefore, application of carbaryl to strongly acidic soils with high organic matter contents may reduce its efficacy in controlling target organisms, at the same time, reducing the potential of ground water pollution through leaching. Further research on the fate of carbaryl in different soils would be very valuable in predicting ground water pollution resulting from carbaryl application.

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**Nomenclature**

- $A$: Arrhenius constant
- $C_a$: equilibrium Carbaryl concentration on the soil (mgL$^{-1}$)
- $C_f$: equilibrium Carbaryl concentration in solution (mgL$^{-1}$)
- $C_i$: initial Carbaryl concentration(mgL$^{-1}$)
- $E_a$: activation energy (kJ mol$^{-1}$)
- $\Delta G^0$: Gibb’s free energy (kJ mol$^{-1}$)
- $\Delta H^0$: enthalpy of reaction (kJ mol$^{-1}$)
- $H$: initial adsorption rate (mg g$^{-1}$ min$^{-1}$)
- $K_d$: distribution coefficient for adsorption
- $K_F$: Freundlich constant (mgg$^{-1}$(Lmg$^{-1}$)$^{-n}$)
- $K_L$: Langmuir constant (Lmg$^{-1}$)
- $K_1$: pseudo first order rate constant
- $K_2$: pseudo second order rate constant
- $m$: weight of the adsorbent (g)
- $n$: Freundlich adsorption isotherm constant
- $q_e$: equilibrium Carbaryl concentration on the soil (mgg$^{-1}$)
- $q_m$: maximum adsorption capacity (mgg$^{-1}$)
- $R$: universal gas constant (8.314 jmol$^{-1}$ K$^{-1}$)
- $R^2$: correlation coefficient
- $\Delta S^0$: entropy of reaction (j mol$^{-1}$k$^{-1}$)
- $T$: temperature (K)
- $V$: volume (L)