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Methomyl adsorption onto Cotton Stalks Activated Carbon (CSAC): equilibrium and process design

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Abstract

Equilibrium studies were carried out for adsorption of an insecticide (Methomyl) from aqueous solutions onto a prepared cotton stalk activated carbon (CTAC) in a batch adsorption system. Parameters affecting adsorption capacity including contact time, adsorbent size ($d_p = 355:800 \mu\text{m}$) and temperature ($T = 25:60 \text{ }^\circ\text{C}$) were investigated. Three mathematical models, Langmuir, Freundlich and Redlich-Peterson were employed for fitting the equilibrium data. Linear regression was used to determine the best fit and was found that the equilibrium data are best represented by Langmuir model thus suggesting the monolayer sorption of methomyl. The Langmuir constants ($q_{\text{max}} = K_L/a_L$) decreases with the increasing of temperature as well as decreasing the particle size of adsorbent. The adsorption capacity was found 72.85 mg/g at 25°C and decreased to 47.36 mg/g when temperature increased to 60 °C . The value of enthalpy change was calculated ($\Delta H = -2.35 \text{ kJ/mol}$) indicating that the removal process was exothermic and physical in nature. A single stage batch adsorber was designed for the adsorption of methomyl onto CSAC based on the optimum isotherm.

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Keywords: adsorption, equilibrium isotherm, activated carbon, insecticide

1. Introduction

Water is a basic need of life and is used in many ways to cater the needs of daily life, so the control of water pollution is one of today's major scientific activities. Indiscriminate use of pesticides leads to the contamination of soils, surface and ground waters. Numerous cases of pesticide residue have been reported in the literature [1]. Pesticides, which indeed seem indispensable for the nutrition of mankind, take a special place among the environmentally problematic substances. Small quantities of pesticides

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may enter the water environment through drift, leaching and run-off from nearby applications. Also, pesticides can enter water through spills, leaks and back-siphoning from nearby mixing, loading, storage, equipment cleanup sites and improper disposal of pesticides. Natural water, viz. lakes, rivers, streams and oceans have been reported to be contaminated with residue of various pesticides [2&3]. The ground water contamination due to pesticides has also been reported [4].

The insecticide (methomyl), $C_5H_{10}O_2N_2S$, is a broad spectrum insecticide which belongs to the carbamate family of pesticides. It is used for foliar treatment of vegetable, fruit and field crops, cotton, commercial ornamentals, and in an around poultry houses and dairies [5]. According to [6], it is a very toxic and hazardous compound and a pollutant causing environmental concerns because of its high solubility in water (57.9 g/L at 25 °C). Since sorption affinity of methomyl to soils is rather low, it can easily cause contamination of both ground and surface water resources. In addition, various amounts of methomyl have been detected in surface and ground waters not only during actual insecticide application but also after a long period of use [7].

Most of the past works have focused on the removal of pesticides from water by the more traditional and expensive methods, such as, cation exchange [8] and dialysis [9]. Advanced oxidation processes using hydrogen peroxides are, often ineffective because carbonate and bicarbonate ions, which are abundant in all natural water, react as strong free radical scavengers. Pesticides are not completely degraded into inorganic compounds such as CO_2 by ozonation [10]. These findings suggest that the breakdown products of pesticides remain in water after treatment, need complementary operations and are not economical. The use of enzymes to detoxify wastewater failed to attract much attention due to the high cost of enzyme-based systems [11]. Filtration through membranes needs another method, such as oxidation reaction catalyzed by enzyme to transform the pesticide into an insoluble product; so, this method is highly expensive [12]. Compared to the above methods, adsorption of different pesticides onto activated carbon and clay minerals has demonstrated efficiency and economic feasibility and gained high favorability for removing pesticides that are chemically and biologically stable [13].

For preliminary design of adsorption technologies, the adsorption capacity of an adsorbent for special adsorbate must be estimated. As in any separation process, adsorption efficiency is a complex attribute dependent on the kinetic and equilibrium properties of the adsorbate/adsorbent system. The aim of this work is to develop activated carbon from cotton stalks and evaluate its capability to remove the methomyl from aqueous solutions. The adsorption equilibrium was determined at different system variables. The isotherm data were analyzed using three models, viz. the Langmuir, Freundlich and Redlich-Peterson. A single-stage batch adsorber has been designed for the removal of methomyl using the prepared activated carbon based on the equilibrium data obtained.

2. Materials and methods

2.1. Adsorbate and solutions

The adsorbate used in this study was insecticide and methomyl (S-methyl N-[(methylcarbamoyl)oxy]thioacetimidate) supplied by Egyptian Company for commerce and agriculture, Egypt. The physicochemical properties of the methomyl are shown in Table 1. The concentrations of methomyl solutions were measured by a UV- Spectrophotometer (Shimadzu, Inc. kyoto Japan model U.V-1601). All measurements were made at the wavelength corresponding to maximum absorbance, λ_{max} , which is 233 nm for methomyl. Synthetic stock solutions were prepared by dissolving accurately weighed amounts methomyl in 1 L of distilled water. The desirable experimental concentrations of solutions were prepared by diluting the stock solution with distilled water when necessary.

Table 1. Physicochemical properties of methomyl*.

Property	Parameter value
Chemical structure	$ \begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3-\text{C}=\text{N}-\text{O}-\text{C}-\text{N} \\ \qquad \qquad \qquad / \quad \backslash \\ \text{S}-\text{CH}_3 \qquad \qquad \text{H} \quad \text{CH}_3 \end{array} $
CAS number	16752 - 77 - 5
Chemical formula	C ₅ H ₁₀ N ₂ O ₂ S
Molecular weight	162.21 g/mol
Molecular volume	179.9 cm ³ /mol
Colure	White crystalline solid
Sp.gr at 298.15 K, (-)	1.29
Solubility in water at 298.15 K	58,000 mg/L
Log octanol/water partition coefficient, log <i>K_{ow}</i>	0.60
Log soil organic carbon-water partitioning coefficient	2.6
Melting point, K	351.15 - 316.15
Vapor pressure at 298.15 K, mm Hg	5.4(10 ⁻⁶)

* Resource: Hazardous Substances Data Bank (HSDB), <http://toxnet.nlm.nih.gov/>.

2.2. Adsorbent and its preparation

A locally activated carbon was prepared in our laboratories from cotton stalks which collected from El- Minia governorate, Egypt. The sun-dried cotton stalks was crushed and sieved onto three ranges of particle sizes, (0.6:1mm), (1:2mm) and (2:4mm). The raw material (40 g) were impregnated with concentrated solution of ortho-phosphoric acid (0.2 L) of pre-adjusted concentrations, this amount of acid solution was found to be sufficient to cover the whole mass and to give a paste of soft consistency of (2PA:1CS). The carbonization and activation were completed by heating the mixture for 12hs in an air oven until complete evaporation of the excess water and to facilitate the absorption of phosphoric acid by the raw material. The resulting material was heated in tubular furnace at 7°C/min with a constant flow of nitrogen up to 500°C at which, it was left for 2 hours, then it was allowed to cool to a room temperature in nitrogen atmosphere. The resulting carbon was washed with distilled water till a constant pH of the slurry was reached then deride at 100°C overnight in an air oven [14]. The dried carbon was then ground and sieved to get three different particle size ranges, (355-500), (500-630) and (630-800) μm. Phosphoric-acid treated cotton stalk carbon (CSAC) is characterized and presented in Table 2. The pH value (pH=5.4) of CSAC indicates that this carbon has a predominance of acid functional groups on its surface.

Table 2. Characteristics of cotton stalks activated carbon (CSAC).

Surface and physical properties	Parameter value
Bulk density, ρ _b , (g/cm ³)	0.0958 ± 0.03
Particle density, ρ _p , (g/cm ³)	0.11 ± 0.04
Solid-phase density, ρ _s , (g/cm ³)	0.126 ± 0.04
Porosity (ε _p)	0.13 ± 0.01
Surface area, (m ² /g)	1600 ± 2%
pH (-)	5.4 ± 0.3
Moisture content (%)	7.1 ± 0.3

2.3. Batch equilibrium studies

Experiments of equilibrium have been undertaken to assess the efficiency of prepared CSAC to remove methomyl from solutions and also finding isotherm constants. Batch experiments were performed in a set of 250 ml stoppered that contain a definite volume (50 ml) of fixed initial concentrations of methomyl solution where a certain amount of CSAC|carbon was added for each one. The flasks were kept in a thermostated water bath shaker at a constant speed of 150 rpm. After shaking, the supernatant solution was separated from adsorbent by centrifugation at 400 rpm for 15 min and the remaining concentrations were determined. Duplicate experiments were carried out for all the operating variables studied and only the average values were taken into consideration. These average data were used to calculate the adsorbent phase concentrations, q_e , of methomyl according to the following equation:

$$q_e = V(C_0 - C_e)/m \quad (1)$$

where C_0 and C_e are the initial and equilibrium concentrations of methomyl (mg/l), respectively, V is the volume of the solution (l), and m is the mass of adsorbent (g). Finally, the solid phase concentration, q_e , was plotted against the equilibrium concentration, C_e to give the equilibrium isotherm. The experiments were conducted for three particle size ranges, 355-500, 500-630 and 630-800 μm , and three different temperatures, 25, 40 and 60 °C.

3. Results and Discussion

3.1. Equilibrium time

Equilibrium time is one of the most important parameters in the design of economical wastewater treatment systems. The adsorption of methomyl onto CSAC at two different initial concentrations, 43.7 and 125.1 mg/l, was studied as a function of contact time in order to determine the time necessary for adsorption to reach equilibrium, and for experimental purposes, each system was given a contact time in excess of this period. It is evident from experimental data that, the removal of methomyl increases with time and attains equilibrium in 2.5 h at 25±1° C for both concentrations. The removal of methomyl onto CSAC was rapid in the initial stages of contact and gradually decreases with lapse of time until saturation and the removal was reached 87.9% for 125.1 mg/l initial concentration. The plot of the solid phase concentration of methomyl, q_t , versus time, figure not present, depicted is smooth and continuous, indicating mono layer coverage of adsorbate on the surface of the adsorbent [15].

3.2. Equilibrium isotherms

The most common representation of the adsorbate concentration and quantity of material adsorbed is the adsorption isotherm. The equilibrium adsorption isotherm is fundamental in describing the interactive behavior between solute and adsorbent, and is important for the design of adsorption system. Figures 1 and 2 show the adsorption isotherms of methomyl onto CSAC for different particle size ranges and temperature respectively. As it is clear from Figs 1 and 2, the shape of the isotherm indicated L-behavior according to Giles classification [16]. Effect of particle size on adsorption isotherm represented in Fig. 1 shows adsorption capacity increases with decreasing particle size rang this may be attributed to the large surface area when small particle size are used. This is in agreement with the statement that if the mechanism of uptake is simply one of adsorption on a specific external site, then the rate should vary reciprocally with the first power of the diameter, whereas, in intraparticle diffusion, the rate should vary with the reciprocal of the square of the diameter [17].

Figure 2 represents the adsorption isotherm at three different temperatures (25, 40 and 60°C). It can be seen that there is a slight decrease from 64.5 to 42.2 mg/g with an increase in temperature from 25 to 60°C, indicating the exothermic nature of the adsorption process. The reason may be that the physical bonding between methomyl molecules and the active sites of the adsorbent weakened as temperature increased, whereas, the solubility of methomyl increased thus enhancing the interaction forces between the solute and the solvent. In the present case the solubility of methomyl increases with temperature and chemical potential will also increase, i.e., both the normal temperature effects act in the same direction and, thus, the decrease in the amount of uptake (which is borne out by the present results) is expected.

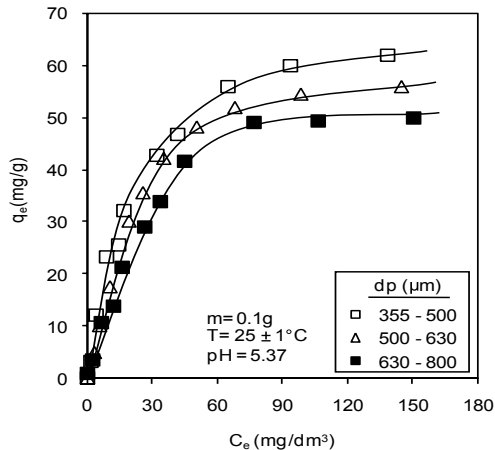


Fig. 1. Adsorption isotherms for methomyl onto cotton stalk activated carbon (CSAC) at different particle size ranges.

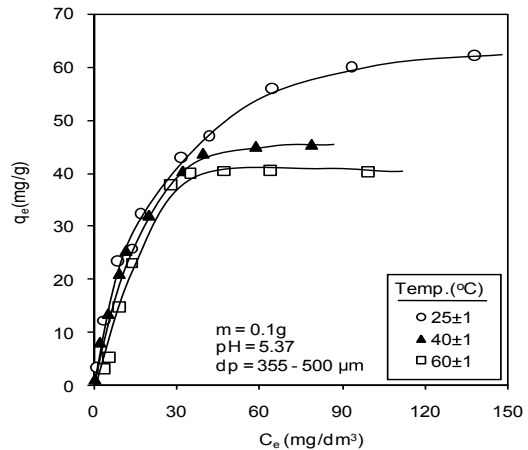


Fig. 2. Adsorption isotherms for methomyl onto cotton stalk activated carbon (CSAC) at different temperatures.

3.3. Isotherms modeling

Equilibrium data, commonly known as adsorption isotherms, describe how the adsorbate interacts with adsorbents, and give a comprehensive understanding of the nature of interaction. It is basically important to optimize the design of an adsorption system. The parameters obtained from the different models provide important information on the surface properties of the adsorbent and its affinity to the adsorbate. Three important isotherms, Langmuir, Freundlich and Redlich-Peterson isotherms are applied in this study. Analysis of such isotherm data is important in order to develop a model which both accurately represents the experimental adsorption results and could be used for design purposes.

The Langmuir isotherm is based on the assumption that the adsorption process takes place at specific homogeneous sites within the adsorbent surface and that once a methomyl molecule occupies a site, no further adsorption can take place at that site, which concluded that the adsorption process is monolayer in nature [18]. The equation of Langmuir isotherm is represented as follows:

$$q_e = (K_L.C_e)/(1 + a_L.C_e) \quad (2)$$

where C_e is the equilibrium concentration (mg/l), q_e is the amount of adsorbate adsorbed per unit mass of adsorbent at equilibrium (mg/g), K_L is the Langmuir isotherm constant related to the energy of adsorption (l/mg). A well-known linear expression for the Langmuir isotherm is represented as:

$$C_e/q_e = (1/K_L) + (a_L/K_L) C_e \tag{3}$$

Figures 3 and 4 show the Langmuir plot (C_e/q_e vs. C_e) at different particle size ranges and different temperatures respectively. Linear plots with extremely high correlation coefficients suggest the applicability of the Langmuir isotherm for the present system. Values of K_L and a_L and the correlation coefficients have been calculated at different system variables and are tabulated in Table 3. The values of the constant, K_L/a_L , correspond to the theoretical maximum adsorption capacity (q_{max}) of CSAC for methomyl. The values of q_m decrease with temperature increase, thereby confirming that the process is exothermic. The Langmuir constant, K_L when temperature varied can be used to determine the enthalpy change (ΔH) during the adsorption process using the Clausius-Clapeyron equation, Eq. (4).

$$K_L = A_c \cdot \exp(-\Delta H / RT) \tag{4}$$

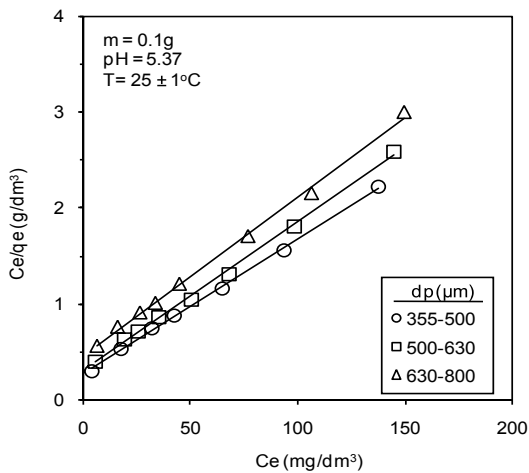


Fig. 3. Lagmuire plots for the adsorption of methomyl onto (CSAC) at different particle size ranges.

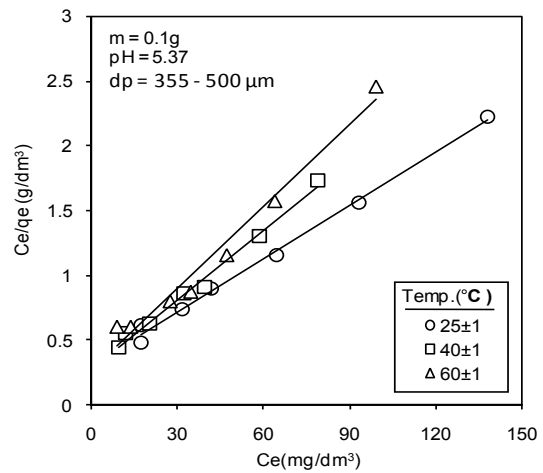


Fig. 4. Lagmuire plots for the adsorption of methomyl onto (CSAC) at different temperatures.

Table 3. Predicted parameters of Langmuir and Redlich-Peterson models for adsorption of methomyl onto CSAC.

Conditions	Langmuir parameters				Redlich-Peterson parameters			
	K_L (dm^3/g)	a_L (dm^3/mg)	q_{max} (mg/g)	C.F. (-)	K_{RP} (dm^3/g)	a_{RP} (dm^3/g) ^{1/β}	β (-)	C.F. (-)
<u>dp(μm)</u>								
355-500	3.321	0.046	72.85	0.997	3.321	0.064	0.896	0.86
500-630	2.657	0.039	68.01	0.992	2.657	0.093	0.776	0.95
630-800	2.036	0.032	63.09	0.983	2.036	0.070	0.799	0.90
<u>Temp.(°C)</u>								
25±1	3.321	0.046	72.85	0.997	3.321	0.064	0.896	0.86
40±1	3.592	0.064	56.13	0.989	0.807	0.083	0.973	0.95
60±1	3.836	0.081	47.36	0.978	0.346	0.081	0.532	0.71

The plot of $\log K_L$ versus $1/T$ produces a straight line with the gradient $(-\Delta H/2.303R)$ from which (ΔH) may be calculated using the least-squares method and correspond to (-2.35 kJ/mol) which conform the exothermic nature of the process.

The Freundlich isotherm is an empirical equation assuming that the adsorption process takes place on a heterogeneous surface through a multilayer adsorption mechanism. The Freundlich equation predicts that the methomyl concentrations on the adsorbent will increase so long as there is an increase in the methomyl concentration in the aqueous solution [19]. The Freundlich equation is given as:

$$q_e = K_F \cdot C_e^{1/n} \tag{5}$$

where K_F is the Freundlich adsorption constant related to adsorption capacity of the adsorbent $((\text{mg/g})(\text{l/mg})^{1/n})$ and $1/n$ is the adsorption intensity. To determine exponent, n , and the constant, K_F , the equation linearized as follow:

$$\log q_e = \log K_F + (1/n) \log C_e \tag{6}$$

The values of K_F and $1/n$ were calculated from the intercept and slope of the plot of $\log q_e$ versus $\log C_e$. Inspection of the results derived from the Freundlich analysis and depicted by Eq. (6) shows that a plot of $\log q_e$ versus $\log C_e$ exhibits some curvature. Indeed, the results may be better represented by more than one straight line. A general equation for the entire concentration range may be expressed as:

$$q_e = K_{F,i} C_e^{1/m_i} \tag{7}$$

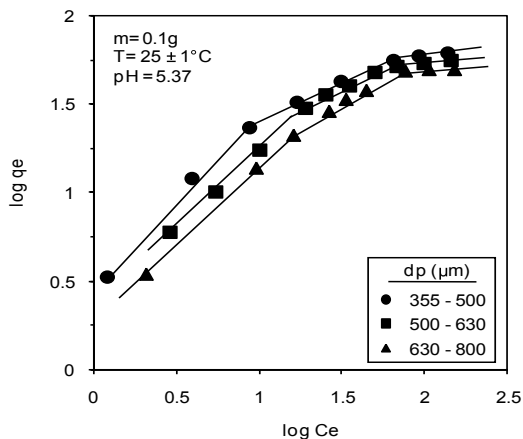


Fig. 5 Freundlich plots for the adsorption of methomyl onto (CSAC) at different particle size ranges.

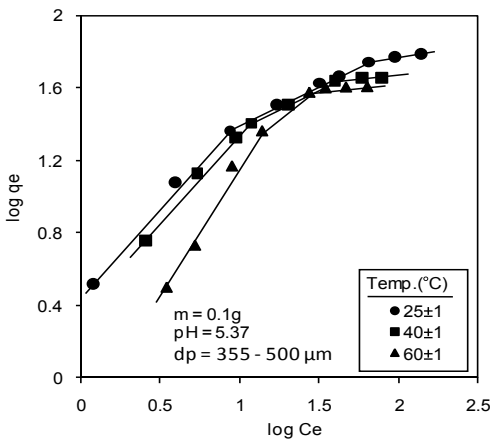


Fig. 6. Freundlich plots for the adsorption of methomyl onto (CSAC) at different temperatures.

The Freundlich parameters have been calculated using the least-squares method applied to the straight lines shown in Figs. 5 & 6 and are listed in Table 4 together with the appropriate concentration ranges and the correlation factors. The magnitude of exponent, n , gives an indication of the favorability and capacity of the adsorbent-adsorbate system, values of $n > 1$ represent favorable adsorption [20]. In this work, the values of n are greater than one which indicates a favorable adsorption by CSAC.

Table 4. Freundlich isotherm parameters for adsorption of methomyl onto CSAC at different system variables.

Conditions	First section of plot				Second section of plot				Third section of plot			
	K_f (dm^3/g)	n (-)	C.R. (mg/g)	C.F. (-)	K_f (dm^3/g)	n (-)	C.R. (mg/g)	C.F. (-)	K_f (dm^3/g)	n (-)	C.R. (mg/g)	C.F. (-)
<u>dp(μm)</u>												
355-500	2.86	1.01	1.2:12.1	2.86	9.27	2.3	14.1-55.3	0.99	31.62	7.23	64.6-138.1	0.97
500-630	6.23	2.10	2.9:11.6	6.23	7.82	2.15	25.2-50.5	0.95	30.24	2.29	68.0-144.9	0.96
630-800	44.4	15.7	2.1:13.7	44.4	34.9	10.5	16.1-44.7	0.89	32.60	6.22	76.9-150.2	0.96
<u>Temp.($^{\circ}C$)</u>												
25 \pm 1	2.86	1.01	1.2:12.1	2.86	9.27	2.3	14.1-55.3	0.99	31.62	7.23	64.6-138.1	0.97
40 \pm 1	2.46	1.04	2.4:11.8	2.46	8.36	2.23	13.2-39.7	0.99	35.85	18.3	39.6-78.9	0.96
60 \pm 1	0.49	0.67	2.3:13.9	0.49	4.59	1.61	25.6-30.8	0.97	36.44	37.7	34.9-63.9	0.94

The Redlich-Peterson isotherm model combines elements from both the Langmuir and Freundlich equations and the mechanism of adsorption is a hybrid one and does not follow ideal monolayer adsorption. The Redlich-Peterson isotherm represented by the Eq. (8):

$$q_e = (K_{RP} \cdot C_e) / (1 + a_{RP} \cdot C_e^\beta) \tag{8}$$

For $\beta=1$, the above equation converts to the Langmuir isotherm; and for $1 \ll a_{RP} \cdot C_e^\beta$ it is identical with the Freundlich isotherm. The parameters of Eq. (8) were determined by minimizing the distance between the experimental data points and the theoretical model predictions using an iterative computer program for data fitting. The estimated parameters of Redlich-Peterson model are tabulated in Table 3 for different operating parameters. Figures 7 and 8 show plots of Redlich-Peterson model in linear form represented in Eq. (9).

$$\log \{ [K_{RP} \cdot C_e / q_e] - 1 \} = \log a_{RP} + \beta \log C_e \tag{9}$$

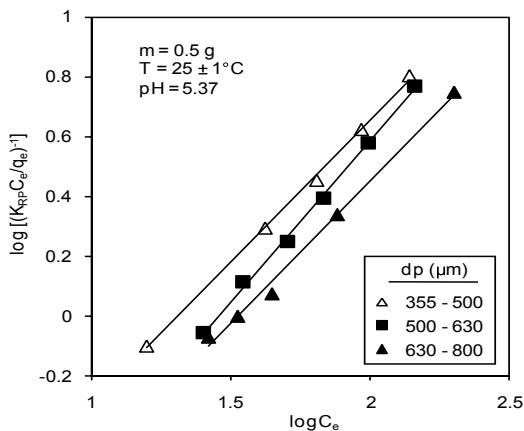


Fig. 7 Redlich-Peterson plots for the adsorption of methomyl onto (CSAC) at different particle size ranges.

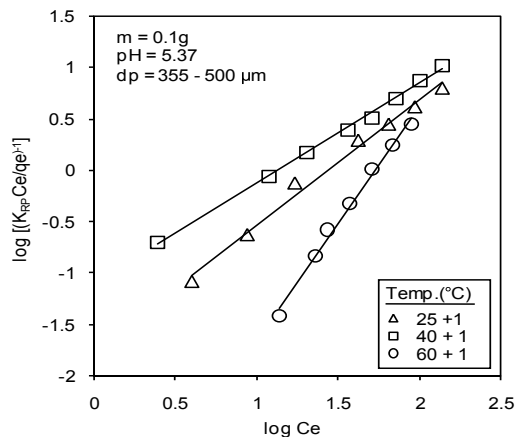


Fig. 8. Redlich-Peterson plots for the adsorption of methomyl onto (CSAC) at different temperatures.

Results in Tables 3&4 show that, the Langmuir model fits the experimental data significantly better than other models. This conclusion was supported by comparing correlation coefficients generated by linear plots of models, where it approximately higher overall (i.e. closer to 1) for the Langmuir plots.

3.4. Process design

Based on the best fit isotherm, a single stage adsorber, as shown in Fig.9, was designed for different solution volumes V from an initial concentration C_0 to C_1 . The amount of adsorbent is M and the solute loading on the adsorbent changes from q_0 to q_1 . At time $t = 0$, $q_0 = 0$ and, as time proceeds, the mass balance equated the methomyl removal from the liquid to that picked up by the solid [21].

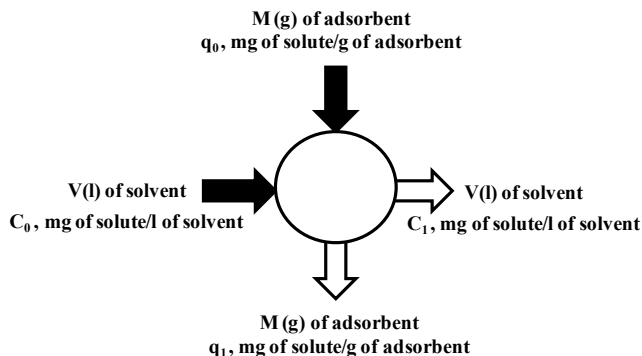


Fig. 9. A single-stage batch adsorber

The mass balance equation for the adsorption system in Fig.9 can be written as:

$$V(C_0 - C_1) = M(q_1 - q_0) = Mq_1 \tag{10}$$

At equilibrium conditions, $C_1 \rightarrow C_e$ and $q_1 \rightarrow q_e$

Since the equilibrium studies confirm that the equilibrium data for methomyl-CSAC follows a Langmuir isotherm equation, it was used for batch adsorber design. The Eq. (10) can be rearranged as,

$$M/V = (C_0 - C_e)/q_e = (C_0 - C_e)/[K_L C_e/(1 + a_L C_e)] \tag{11}$$

Except for 100% removal conditions, Eq. (11) can be used to calculate the dose required for specified percentage removal for different C_0 , (Fig. 10a), or specified C_0 for different percent removal (Fig. 10b).

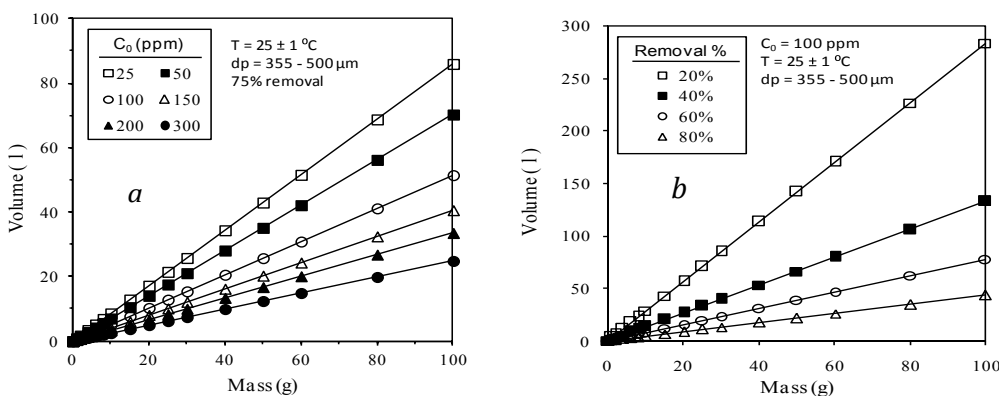


Fig. 10. Design plot generated using Langmuir isotherm (a) 75% removal, (b) initial methomyl concentration, $C_0 = 100$ ppm.

4. Conclusions

The present study showed that activated carbon prepared from chemically treated cotton stalks can be used as an effective adsorbent for removal of an insecticide methomyl from aqueous solution. The surface area of the prepared activated carbon by phosphoric acid-activation was relatively high (1600 m²/g). The equilibrium adsorption is practically achieved in 2.5h. The adsorption capacity was found to increase with increase methomyl concentration and contact time and found to decrease with increase temperature. The activation energy, ΔH , of adsorption was found to be -2.35 kJ/mol indicating that the adsorption process is exothermic with a physical nature. Adsorption parameters for the Langmuir, Freundlich and Redlich-Peterson isotherms were determined. The Langmuir model is the best one to simulate the experimental data, which confirm that the adsorption process is limited with the monolayer coverage and the surface is relatively homogenous in terms of functional groups and there is no significant interaction among the methomyl molecules. The present study concludes that the activated carbons prepared from cotton stalks could be employed as low-cost adsorbents as alternatives to commercial activated carbon for the removal of methomyl from aqueous solutions.

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