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Investigation and Comparison of Experimental Data of Ethylene Dichloride Adsorption by Bagasse with Adsorption Isotherm Models

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ABSTRACT

Due to the fact that the concentration of ethylene dichloride in the effluent of Alkali Petrochemical chlorine unit is often less than 500 ppm. Therefore, this method can be used to reduce the amount of ethylene dichloride in wastewater. Using bagasse as a carbon adsorbent to remove EDC from aquatic environments can be more cost-effective than commercial activated carbon, as well as a new approach. This could be because ethylene dichloride does not ionize easily. The adsorbent value. Also Freundlich isotherm model, the mean constant value of proportion K_f = 1.1 mg/g and the adsorption size intensity 1/n = 0.16 and the Langmuir model mean constant values were a = 0.1 and b = 2.6. Since ethylene dichloride is not easily ionized, the changes in soluble pH and the type of bagasse pre-treated with acid, base and distilled water have little effect on the adsorption rate.

1. Introduction

Effluent contains nutrients that can stimulate the growth of aquatic plants and may contain toxic kinetics, therefore, the reasons for the rapid and trouble-free transfer of effluent from production sources and then its treatment and disposal are not only desirable but essential in industrial societies [1].

hlorine is an important chemical element in water treatment, disinfectants and bleach and in mustard gas. Chlorine is also used in making a wide range of everyday items. Also, used to kill bacteria and other germs in drinking water supplies. Today, chlorine is always added to small reserves of water. Chemical 1, 2 D-chloroethane, commonly known by its old name ethylene dichloride is a chlorinated hydrocarbon and mainly used to produce vinyl chloride monomer (VCM, chloroethane) which is the main constituent for PVC production [2]. That is a colorless liquid with a smell similar to chloroform. 1, 2 D-Chloroethane is also used as intermediate for the production of other chemical compounds and as a solvent [3, 4].

If untreated effluent accumulates, decomposition of its organic matter may result in the production of large quantities of odorous gases. In addition, untreated effluent usually contains many pathogenic microorganisms that live in the human gastrointestinal tract or are present in some industrial wastes [5].

Effluent treatment is usually performed in three stages:

- The initial stage refers to the physical unit operations
- The secondary stage refers to the chemical and biological processes
- The advanced stage is a combination of all three types of processes [6, 7].

2. Bagasse and its Characteristics

Bagasse is one of the sugarcane by-products that make up about 20-30% of its weight. This product is a residual fibrous residue after extraction of sugar which is in the form of chipboard chips in yellow [8]. The overall composition of bagasse is fiber, moisture and soluble solids (mainly sugar). Bagasse fiber is a water-insoluble compound consisting mostly of cellulose (pentosane) and lignin. Cellulose is a polysaccharide with a chemical formula $(C_6H_{10}O_5)_n$ that forms the major part of the plant tissue [9]. It is less pure in nature and is often combined with substances such as lignin, pentosane, gums, adhesives, tannins, fats and dyes. Pure cellulose is present in plant tissues and consists of long chains. The

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variety of cellulose polymers gives rise to a variety of different compounds. Bagasse has active sites with negative charge [10, 11].

2.1. Materials

In this part of Bagasse, which is prepared from Shushtar Sugar and Sugar Factory, after screening in three stages, very small and large bagasse are separated and the size that is appropriate and considered in this design is selected and pre-treatment operation by water. Distilled, nitric acid and sodium hydroxide on it should be done as follows:

First, pour 33 grams of bagasse into a 2.5 liter man and add about 2 liters of distilled water to it and heat it for about 6 hours at 100 C C, while during this time the magnetic stirrer with the right speed that the bagasse in the solution as It is used evenly distributed. After this time, the bagasse is separated from the water by filtration and dried in the oven for 4 hours at 110-105 - 10 C. To repeat the experiments, a large amount of bagasse is prepared in the same way in the next time and stored at room temperature in a suitable container.

About 11 grams of Bagasse, which has been pre-treated with distilled water and 2 liters of normal nitric acid per liter in humans, is 2.5 liters, and after 24 hours, filter the solution and wash the purified Bagas several times with distilled water. The oven is dried at 105 ° C to 105. C and stored in a suitable container at room temperature.

About 11 grams of pre-treated Bagasse distilled water, as in the previous method, except that it is purified and prepared with normal sodium hydroxide 2. 5-2 Preparation of ethylene di chloride solution

Pour a small amount of distilled water into a 200 cc Erlenmeyer flask and add about 0.2 g of ethylene dichloride (99.99%) to it using a four-digit digital scale, then pour the solution into a one-liter balloon and infuse. By distilled water to one liter and thus 200 ppm ethylene dichloride solution is prepared in distilled water. The same procedure was used to prepare the solution at different concentrations, with the difference that the amount of ethylene di chloride was changed.

3. Testing steps

3.1. Preparation of ethylene dichloride solution

Pour a little distilled water into a 200 cc Erlenmeyer flask and add about 0.1 gr of ethylene dichloride (99.99%) by a digital scale of four decimals then pour this solution into a 1-liter balloon and bring its volume to 1-liter by distilled water, thus, 100 ppm ethylene dichloride solution will be prepared in distilled water. The same procedure will be used to prepare the solution at different concentrations but the amount of ethylene dichloride will be changed. For example, 0.2 gr of ethylene dichloride (EDC) is added to prepare 200 ppm solution.

3.2. Materials and equipment required for testing

Graduated cylinder, 1-liter balloon, funnel, filter paper, magnetic stirrer 3 pieces, 2.5-liter beaker, 1-liter beaker, 200 cc Erlenmeyer flask 5 pieces, thermometer, oven, digital scale, pipette, pH meter, CG device
Nitric acid, sodium hydroxide, distilled water, bagasse, pure ethylene dichloride.

3.3. Batch test instructions

Batch experiments are performed to calculate the EDC adsorption potential by bagasse, study the adsorption kinetics and determination of the equilibrium parameters. All experiments are performed at ambient temperature and stirred by a magnetic stirrer at 1000 rpm. Changes in pH, initial EDC concentration and the amount of adsorbent to investigate their effect on EDC adsorption are tested. Since ethylene dichloride is a volatile compound, the increasing temperature has caused it to evaporate and this causes the adsorption process to be affected by evaporation and steam generation at the surface of the test vessel and the results are not accurate, so temperature changes and their effects have not been studied. After preparing the initial solution, pour about 100 cc of this solution into a 200 cc Erlenmeyer flask and add 3 gr of refined bagasse with distilled water and dried after that stir on the shaker for 5 hours then filter and pour about 50 cc of the isolated solution into a sample vessel to measure the concentration of ethylene dichloride. Each refined bagasse that gives better results will be used to monitor the rate of absorption with the same state and this time change the pH of ethylene dichloride solution to 3, 5, 7.5, 9, 10.5 then conduct the test in these pHs after that measure the results and investigate the adsorption rate on acidic, base and neutral pHs and choose the better state. The pH values are determined by the digital pH meter [12].

4. Investigation the effect of important parameters

4.1. Effect of pH and type of refined bagasse

Removal of contamination from aqueous environment by the adsorbent is directly dependent on the pH of the solution which affects the adsorbent surface electric charge and the degree of adsorption ionization. The effect of soluble pH and the type of charged bagasse (electric charge) on the absorption rate is shown in Figures (1) and (2). Since ethylene dichloride is a non-polar material and does not readily ionize, pH changes and the type of refined bagasse (electric charge on the adsorbent surface) have no effect on the adsorption rate.

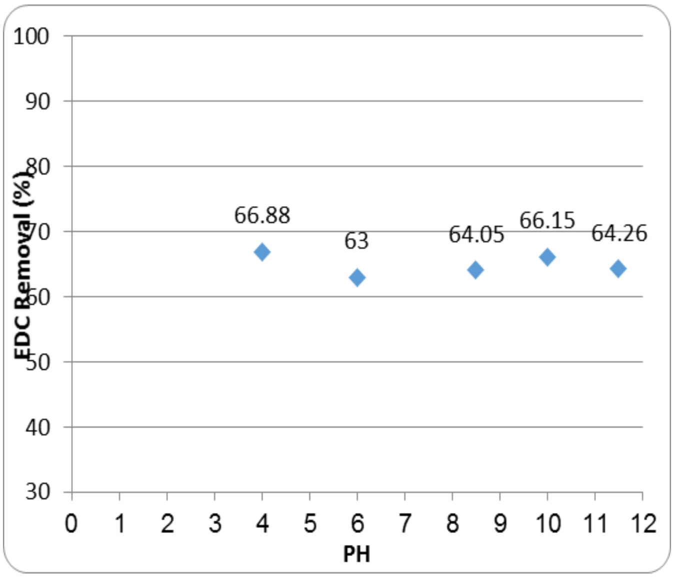

Figure 1. Effect of solution pH on EDC adsorption rate (Absorbent-EDC, initial absorbent concentration: 102 mg/L, stirring speed: 1000 rpm, test temperature: 26 ± 1 °C and bagasse adsorbent: 30 g/L

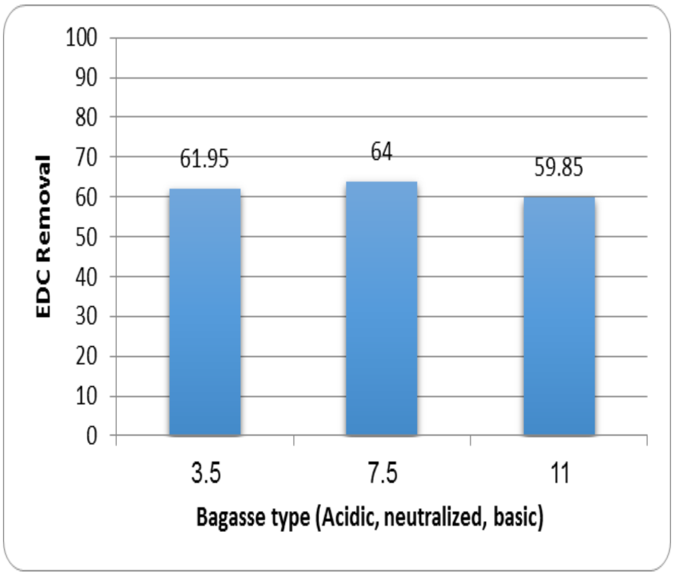

Figure 2. Influence of bagasse adsorbent pre-treated with distilled water, acid or base on EDC adsorption rate (initial absorbent concentration: 102 mg/L, pH: 7.5 (distilled water), stirring speed: 1000 rpm, test temperature: 26 ± 1 °C and bagasse adsorbent: 30 g/L)

4.2. Investigation of isotherms and adsorption equilibrium

After selecting the appropriate pH of the solution, change the adsorbent rate by weight (5, 10, 15, 20 and 30 g/L) and check for different bagasse levels and select the optimum state and check the subsequent parameters. After this step, change the initial solution concentration and do this for the initial solutions concentrations of 52, 76, 102, 148, 197 and 301 mg/L and each one has a better absorption rate is selected for further experiments. Based on the equilibrium contact times that has been obtained from adsorption kinetics studies, these experiments are performed at the appropriate time (5 h). Due to the difficulty of measuring the amount of ethylene dichloride in the effluent and the limitations, it is attempted to consider at least one sample for EDC measurement and if there is no limit, experiments can also be investigated at different pH, different initial solution concentrations, different stirring times and to ensure the accuracy of the experiments, we can repeat one experiment at least three times. Meanwhile, the adsorbent particle size can also be studied.

4.3. Adsorption isotherms

Laboratory isotherms are very useful for describing the adsorption ability of an adsorbent. However, the isotherm plays a vital role in analyzing and designing the adsorption systems as well as it does for a predicted model. The surface absorption rate and the resulting equilibrium relationships are correlated with Freundlich empirical relationships and Langmuir's theoretical relation. In scientific applications, Freundlich isotherm correlation is usually appropriate. Both Freundlich and Langmuir models are plotted for the isotherm sample results and by comparing them in Figures (9-8) and (10-8), it is known that the Freundlich isotherm model is better for expressing the data.

5. Discussion

Laboratory isotherms are very useful for describing the adsorption capacity of an adsorbent. However, the isotherm plays a vital role in the analysis and design of gaming systems as well as it does for a predicted model. The incidence of superficial adsorption and equilibrium equilibrium has been correlated with Frondelich's experimental relationships and Langmir's theoretical relationship. In scientific applications, the correlation of Freundlich's isotherm is usually appropriate.

5.1. Freundlich Isotherm

$$\frac{X}{M} = C_e^{\frac{1}{n}} K_f \qquad (1)$$

Where X, the mass of the adsorbed material (mg), M the adsorbent mass used, K_f a proportional constant, 1/n the size of the absorption intensity, meanwhile n and K_f , are the constants that depends on temperature, adsorbent and the material to be absorbed and C_e equilibrium adsorbent concentration in the solution after adsorption (mg/L). Freundlich isotherm constants can be determined by plotting $(\frac{X}{M})$ in terms of C_e by using equation (1) which is linearized as follows.

$$\log\left(\frac{X}{M}\right) = \log K_f + \frac{1}{n}\log C_e \qquad (2)$$

The Freundlich constants of several primary pollutants are shown in Table (2).

Table 1. Summary of Freundlich parameters at neutral pH at 30˚C and activated carbon adsorbent

Compound	K_f, mg/g	1/n
Hexa Chloro butadiene	360	0.63
Anethole	300	0.42
Phenyl mercuric acetate	270	0.44
ρ-Nonylphenol	250	0.37
Acridine yellow	230	0.12
Benzidine dihydrochloride	220	0.37
n-Butylphthalate	220	0.45
N-Nitrosodiphenylamine	220	0.37
Dimethylphenylcarbinol	210	0.33
Bromoform	200	0.83
β-Naphthol	100	0.26
Acridine orange	180	0.29
α-Naphthol	180	0.31
α-Naphthylamine	160	0.34
Pentachlorophenol	150	0.42
ρ-Nitroaniline	140	0.27
1-Chloro-2- nitrobenzene	130	0.46
Benzothiazole	120	0.27
Diphenylamine	120	0.31
Guanine	120	0.40
Styrene	120	0.56
Dimethyl phthalate	97	0.41
Chlorobenzene	93	0.98
Hydroquinone	90	0.25
ρ-Xylene	85	0.16
Acetophenone	74	0.44
1,2,3,4-Tetrahydronaphthalene	74	0.81
Adenine	71	0.38
Nitrobenzene	68	0.43
Dibromochloromethane	63	0.93

The Langmuir adsorption isotherm is written based on the equilibrium between a density and evaporation of the adsorbed molecules by considering a single molecular adsorption layer:

$$\frac{X}{M} = \frac{abC_e}{(1+aC_e)} \quad (3)$$

The above relationship is linearized as follows:

$$\frac{1}{X/M} = \frac{1}{b} + \frac{1}{ab}\frac{1}{C_e} \quad (4)$$

Where $\frac{X}{M}$ the amount of material absorbed per unit weight of absorptive (mg/g)

C_e , Equilibrium concentration of adsorbent in solution after adsorption (mg/L)

b is the amount of adsorption needed to form a complete single and a constant layer that increases with increasing molecule size.

Since most efflunt contains more than one absorbent element, the Langmuir equation cannot be applied directly. Weber-Morris developed a relation based on the Langmuir equation for the competitive adsorption of two substances:

$$\frac{X_A}{M} = \frac{a_A b_A C_A}{1+a_A C_A + a_B C_B} \quad (5)$$

$$\frac{X_B}{M} = \frac{a_B b_B C_B}{1+a_A C_A + a_B C_B} \quad (6)$$

For multi-blend mixtures can be developed more complex relations. It should be noted that although the equilibrium capacity of any single material absorbed in the mixture is lower than that substance itself, the absorption is greater than the substance itself. In industrial applications, the call time is usually less than 1 hour. Because the absorption rate increases with increasing the amount of carbon, it is possible to reach equilibrium if high amounts of carbon are used. The Langmuir adsorption isotherm is obtained by assuming that:

- The absorptive has a fixed number of locations accessible which all of them have equal energy.
- Adsorption is reversible.

The equilibrium is created when the adsorption rate of the molecules to the surface is equal to the repulsion rate of the molecules from the surface. So the adsorption rate is proportional to the thrust force which is equal to the difference between the amount absorbed at a particular concentration and absorbable amount at the same concentration that at equilibrium concentration, this difference is equal to zero.

Matching the experimental data with the Langmuir equation does not mean that the assumptions expressed in the system under study are true because deviations from these assumptions may have a negative effect. The Langmuir isotherm constants can be determined by drawing $\frac{1}{(\frac{X}{M})}$ in term of $\frac{1}{C_e}$. The Freundlich and Langmuir isotherm models has been plotted separately for the variable adsorbent state and same initial adsorbent concentration also for the same adsorbent value and the variable initial adsorbent concentration and the combination of both diagrams. The results of the adsorption equilibrium isotherm experiments have been presented in Table (3). The values of K_f and 1/n for the Freundlich model and the values of and b for the Langmuir model have been written in all three different states in Table (4). The higher K_f , the amount of adsorbent better and more useful.

Table 2. Results of adsorption isotherm experiments

dose (g/L)	M (g)	Ci (mg/L)	Ce (mg/L)	X/M (mg/g)	Ln (Ce)	Ln (X/M)	Removal (%)	1/Ce	1/(x/m)
30	3	52	7	1.5	1.95	0.405	90.82	0.143	0.67
30	3	76	22	1.8	3.09	0.588	74.55	0.045	0.56
30	3	110	40	2.07	3.69	0.726	63.84	0.025	0.48
30	3	148	81	2.23	4.39	0.803	47.56	0.012	0.45
30	3	220	129	2.27	4.86	0.818	36.22	0.008	0.44
30	3	301	222	2.63	5.40	0.968	27.50	0.0045	0.38
5	0.5	110	90	2.40	4.50	0.875	12.39	0.011	0.42
10	1	110	79	2.30	4.37	0.833	23.62	0.013	0.43
15	1.5	110	68	2.27	4.22	0.818	34.96	0.015	0.44
20	2	110	58	2.20	4.06	0.788	45.25	0.017	0.45

Table 3. Adsorption constants for the Freundlich and Langmuir model

b	a	K_f	1/n	Absorbent amount (g / L)	Initial concentration (mg / L)
2.68	0.083	1.078	0.175	variable	110 mg / L identical
2.56	0.11	1.122	0.154	Equivalent to 33 g / L	variable
2.58	0.10	1.123	0.159	Combining the first and second modes	Combining the first and second modes

The Freundlich and Langmuir isotherm diagrams for the initial constant concentration and different amounts of adsorbent are shown in Figures (3) and (4).

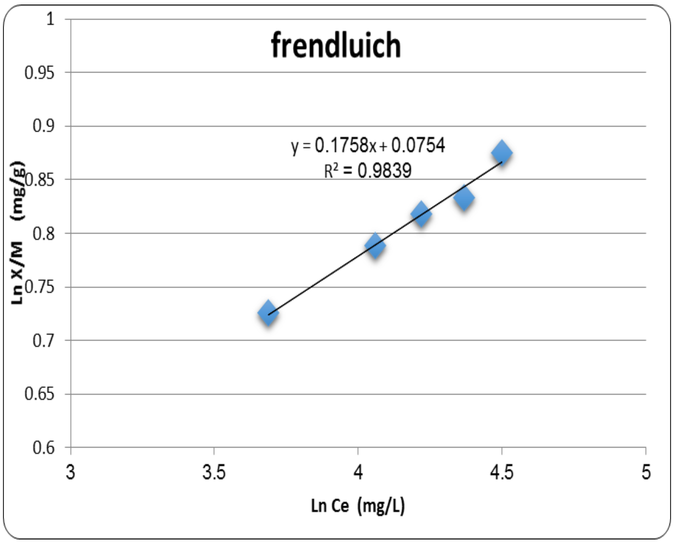

Figure 3. Freundlich isotherm for constant adsorbent concentration (EDC) and change in adsorbent concentration (initial adsorbent concentration: 102 mg/L, pH = 7.5 (distilled water), stirring speed: 1000 rpm, test temperature: 26 ± 1 °C)

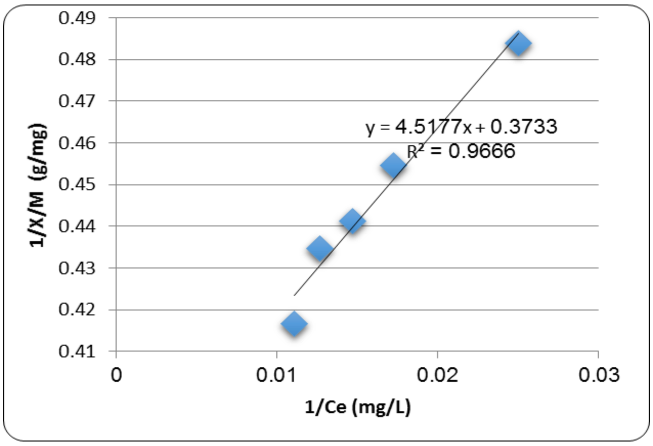

Figure 4. Langmuir isotherm for constant adsorbent concentration (EDC) and change in adsorbent concentration (initial adsorbent concentration: 102 mg/L, pH = 7.5 (distilled water), stirring speed: 1000 rpm, test temperature: 26 ± 1 °C)

Also different initial concentrations and equal bagasse value of 30 g/L have been considered for the adsorption isotherms investigation and necessary experiments have been performed and the diagrams of Freundlich and Langmuir isotherms have been plotted according to Figures (5) and (6).

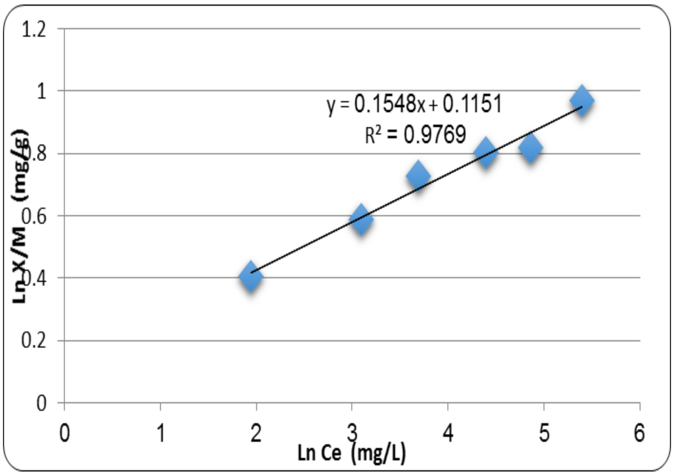

Figure 5. Freundlich isotherm for when the initial adsorbent concentration (EDC) is changed and the adsorbent value should be constant (pH = 7.5 (distilled water), stirring speed: 1000 rpm, test temperature: 26 ± 1 °C and bagasse adsorbent: 30 g/L)

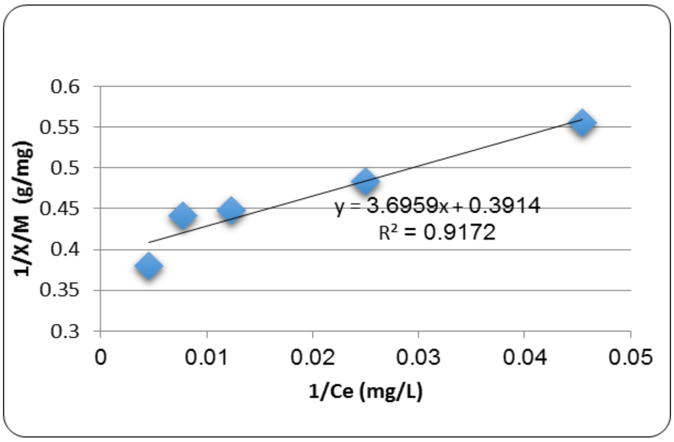

Figure 6. Langmuir isotherm for when the initial adsorbent concentration (EDC) is changed and the adsorbent value should be constant (pH = 7.5 (distilled water), stirring speed: 1000 rpm, test temperature: 26 ± 1 °C and bagasse adsorbent: 30 g/L)

Freundlich and Langmuir isotherms diagrams for two different states (1- the initial adsorbent concentration is constant and the amount of adsorbent change and 2- the amount of adsorbent is the same and change the initial concentration) are combined and in accordance with Figures (7) and (8) are drawn and the values of K_f and 1/n are obtained for the Freundlich isotherm and a and b values for the Langmuir isotherm.

6. Conclusion

This study looked at ways to remove chlorine organic compounds, especially ethylene dichloride (EDC) from industrial effluents. Surface adsorption process is one of the effective processes of advanced wastewater treatment for industrial pollution treatment including toxic substances in low concentrations. Due to the fact that the concentration of ethylene dichloride in the effluent of Alkali Petrochemical chlorine unit is often less than 500 ppm.

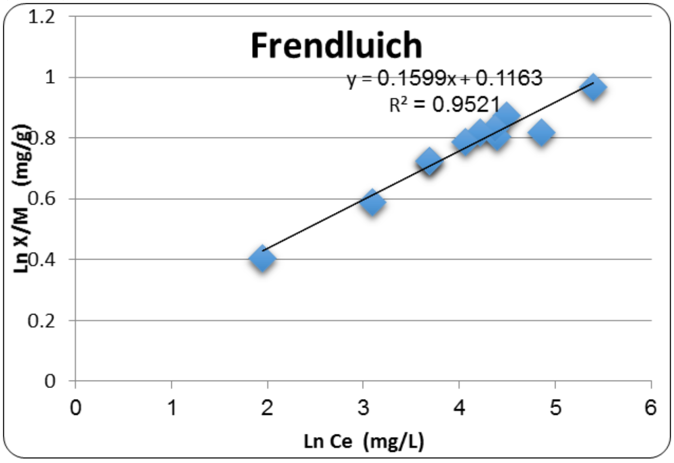

Figure 7. Freundlich isotherm for integrating two constant concentration diagrams: 102 mg/L, the variable adsorbent value, and the constant adsorbent value: 30 g/L and adsorbent initial concentration of variable EDC, (pH= 7.5, stirring speed: 1000 rpm, test temperature: 26 ± 1 °C)

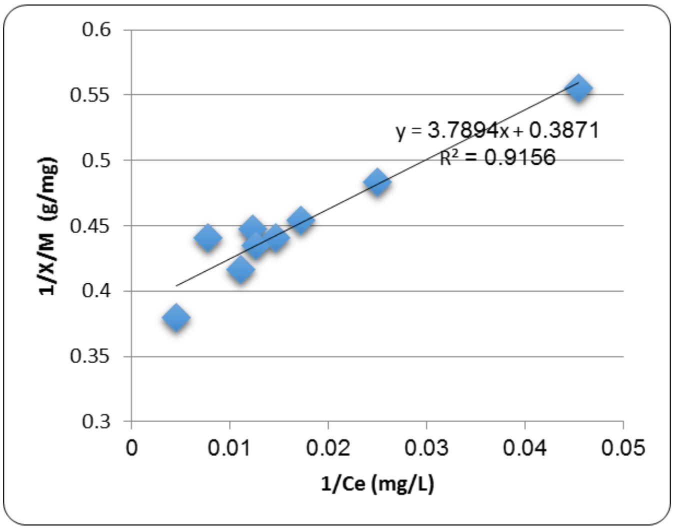

Figure 8. Langmuir isotherm for integrating two constant concentration diagrams: 102 mg/L, the variable adsorbent value and the constant adsorbent value: 30 g/L and adsorbent initial concentration of variable EDC, (pH= 7.5, stirring speed: 1000 rpm, test temperature: 26 ± 1 °C)

Therefore, this method can be used to reduce the amount of ethylene dichloride in wastewater. Using bagasse as a carbon adsorbent to remove EDC from aquatic environments can be more cost-effective than commercial activated carbon, as well as a new approach. This could be because ethylene dichloride does not ionize easily.

- Using bagasse can be more cost-effective and newer method than commercial carbon as a carbon adsorbent to remove EDC from aquatic environments.
- Changes in residual adsorbent concentration decrease with time and in equilibrium state the adsorbent concentration in the solution remains constant in other words, the concentration changes to zero. This is due to a decrease in the concentration gradient (the

adsorbent concentration in the solution and on the adsorbent surface). The absorption process has two fast and slow zones. The initial hour of absorption is fast and from that time until the equilibrium is slow absorption and in the first hour of adsorption, the adsorption value is more than 50% of the total adsorption until equilibrium time which varied for different experimental conditions, initial concentrations and the adsorbent value.

- Freundlich and Langmuir isotherms models has been investigated in equilibrium conditions for EDC adsorption by Bagasse that the results show that the equilibrium data follow the Freundlich model. For the Freundlich isotherm model, the mean constant value of proportion K_f = 1.1 mg/g and the adsorption size intensity 1/n = 0.16 and the Langmuir model mean constant values were a = 0.1 and b = 2.6.
- Since ethylene dichloride is not easily ionized, the changes in soluble pH and also the type of bagasse pre-treated with acid, base and distilled water have little effect on the adsorption rate.

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