

Removal of herbicide paraquat from an aqueous solution by adsorption onto spent and treated diatomaceous earth

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Abstract

A spent diatomaceous earth from the beer brewery has been tentatively activated by sodium hydroxide at about 100 °C. The resulting product was used as a novel adsorbent for the adsorption of herbicide paraquat from an aqueous solution in a continuously stirred adsorber and batch flasks, respectively. The results showed that the adsorption process could be well described by the pseudo-second-order reaction model. From the view of the negatively charged surface of diatomaceous earth and cationic property of paraquat, the results were also reasonable to be explained by physical adsorption in the ion-exchange process under the effects of pH and temperature. Further, it was found that the Freundlich model appeared to fit the isotherm data better than the Langmuir model.

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1. Introduction

Diatomaceous earth or diatomite is a naturally occurring, white-colored, sedimentary mineral or clay composed of the hydrosilica microfossils of single-cell diatoms. Its porous structure, low density and fine particle size (typically 10–200 µm) result in industrial applications as filtration media (filter aid) for various beverage and inorganic/organic chemicals, fillers or extenders, catalyst carriers, biofilm/biomass supports, packed materials for chromatography separation, anti-caking agents, natural insecticides, fertilizer conditioners, thermal insulators as well as absorbents for pet litter and oil spills (Engl, 1993; Lemonas, 1997). In Taiwan, spent diatomaceous earth is an agro-industrial waste, mainly generated from the food processing, alco-

hol and wine brewing industries. It has been estimated that the annual production of spent diatomaceous earth is approximately 5000 metric tons (Hsien, 2003). In the past decades, the agro-industrial waste was commonly discarded in the field, or simply disposed of in a landfill. It is obvious that these approaches are not desirable practices in view of the odour from biological degradation. Alternatively, most of the mineral waste is currently reused as filter-aid for dewatering activated sludge in the wastewater treatment plants, and fertilizer source and soil conditioner due to the integrated and preventive approach stipulated for industrial waste management in Taiwanese government policies in recent years (Tsai and Chou, 2004).

Although many treatment processes have been proposed for the removal of environmental contaminants from an aqueous solution, adsorption is considered to be a particularly important purification and separation process on an industrial scale (Al Duri, 1996). Among these adsorbents, activated carbons are the most widely

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used adsorbents in environmental protection systems due to their excellent adsorption properties. However, the use of activated carbon is not suitable due to its high cost and cost of treatment/disposal of spent carbon. In recent years, there have been considered interest in the use of alternative low-cost materials as potential adsorbents (Pollard et al., 1992; Allen, 1996; Bailey et al., 1999). Based on the effective utilization of mineral resource, the reuses of spent diatomaceous earth as adsorbents are scarce in the literature. Li et al. (2002) reported that wine processing waste sludge containing diatomaceous earth was reused as an adsorbent for the removal of heavy metal Pb(II) from an aqueous solution. The isotherm models (i.e., the Langmuir and Freundlich) and adsorption kinetics models (e.g. pseudo-second-order) were used for simulating the adsorption system in the batch experiments under controlled conditions, such as pH value of solution, sludge particle size and initial Pb(II) concentration.

The main objectives of this work were to examine the feasibility of using spent and treated diatomaceous earth as an adsorbent for the removal of herbicide paraquat (1,1'-dimethyl-4,4'-dipyridinium chloride or methyl viologen), which is one of the most widely used pesticides in Taiwan, from an aqueous solution. The waste had been treated by using alkaline activation at the boiling condition, which involved the etching process of the precursor mainly containing silica in the presence of sodium hydroxide (i.e., NaOH), followed by deionized water-cleaning of the resulting base-activated clay. Thus, this work examined the effects of factors such as pH and temperature on adsorption rate of paraquat, and evaluating the usefulness of pseudo-second-order model for analyzing the adsorption system. In addition, this paper further evaluated the applicability of common isotherm models (i.e., the Langmuir and the Freundlich) and differences in using spent diatomaceous earth and base-activated adsorbent from the waste for the adsorption of paraquat from an aqueous system at 25 °C.

2. Methods

2.1. Materials

Spent diatomaceous earth, a waste generated from the production of beer, was supplied by Shan-Hua Factory of Taiwan Tobacco & Liquor Co. (Tainan, Taiwan) with proximate analysis shown in Table 1. The median particle size and median pore size of diatomaceous earth (product grade: 577) from the manufacturer (Celite Co., USA) were 14.6 and 2.5 μm , respectively. In addition, the main components of the fresh material were approximately 91.5% SiO_2 , 4.0% Al_2O_3 and 1.1% Fe_2O_3 . The adsorbate used in the kinetic experiments was paraquat ($\text{C}_{12}\text{H}_{14}\text{Cl}_2\text{N}_2$, FW = 257.2) with a purity of min. 99%,

Table 1
Proximate analysis of spent diatomaceous earth^a

Moisture	Ash	Volatile organics	Fixed carbon
$0.017 \pm 0.002\%$ ^b	$99.90 \pm 0.01\%$	$0.077 \pm 0.007\%$	$0.006 \pm 0.003\%$

^a wt.% as dry basis (i.e., the sample was first dried at 105 °C for 48 h, and then cooled and stored in the desiccator.)

^b Denote the mean \pm standard deviation for three determinations.

which was purchased from Sigma Chemical Co. (USA). H_2SO_4 and NaOH with purity of min. 96% and 99%, respectively, used for adjusting the initial pH value of aqueous solution and base-activation, were purchased from Merck Co. (Germany).

2.2. Base-activated treatment of spent diatomaceous earth

Based on the etching reaction between silica (i.e., SiO_2) and strong base (e.g., NaOH), spent diatomaceous earth was preliminarily treated with sodium hydroxide in the present study. Five grams of the sludge waste were mixed with 100 ml of the NaOH solution of 2.5 M concentration. Impregnation was carried out at boiling condition ($\approx 100 \pm 5$ °C) on a stirrer/hot plate with boiler-reflux condenser for 2 h. Then, the sample solution was filtered in a vacuum filter flask and washed sequentially with deionized water five times to remove the salt ions and other residues. The resulting solid was finally dried at 105 °C for 24 h, and stored in a desiccator after drying.

The pore structures of spent diatomaceous earth and base-activated product relating to surface area and pore volume were obtained by measuring their nitrogen adsorption-desorption isotherms at -196 °C in an ASAP 2010 apparatus (Micromeritics Co., USA). Brunauer-Emmet-Teller (BET) surface area (S_{BET}) was calculated using the adsorption data in a relative pressure range from 0.05 to 0.20 (Gregg and Sing, 1982). The total pore volume (V_t) was assessed by converting the amount of nitrogen gas adsorbed (expressed in cm^3/g at STP) at a relative pressure of 0.97 to the volume of liquid adsorbate. The true densities of these samples were measured by a helium displacement method with an AccuPyc 1330 pycnometer (Micromeritics Co., USA) (Lowell and Shields, 1991). From the data of V_t and ρ_s , particle density (ρ_p) and porosity (ϵ_p) can be further obtained (Smith, 1981). The characteristics of these two samples used as adsorbents in the present study are listed in Table 2.

2.3. Adsorption kinetics

The apparatus and experimental methods of adsorption kinetic system employed in the present work were similar to those for adsorption of paraquat onto activated bleaching earth reported previously (Tsai et al.,

Table 2
Main physical properties of spent and treated diatomaceous earths used as adsorbents

Sample	$S_{\text{BET}}^{\text{a}}$ (m^2/g)	V_{t}^{b} (cm^3/g)	$\rho_{\text{s}}^{\text{c}}$ (g/cm^3)	$\rho_{\text{p}}^{\text{d}}$ (g/cm^3)	$\varepsilon_{\text{p}}^{\text{e}}$ (-)
Spent diatomaceous earth	$0.29 \pm 0.13^{\text{f}}$	0.0029 ± 0.0014	2.436 ± 0.033	2.419	0.014
Treated diatomaceous earth	96.4 ± 2.4	0.279 ± 0.03	2.663 ± 0.096	1.528	0.426

^a Denoted as BET surface area.

^b Denoted as total pore volume.

^c Denoted as true density.

^d Denoted as particle density, which is calculated from V_{t} and ρ_{s} , i.e., $\rho_{\text{p}} = 1/[V_{\text{t}} + (1/\rho_{\text{s}})]$.

^e Denoted as particle porosity, which is computed from ρ_{s} and ρ_{p} , i.e., $\varepsilon_{\text{p}} = 1 - \rho_{\text{p}}/\rho_{\text{s}}$.

^f Denote the mean \pm standard deviation for two determinations.

2003a,b). All adsorption kinetics experiments were set as follows: initial paraquat concentration = 30 mg/L, adsorbent dosage = 1.0 g/2 L, and agitation speed = 400 rpm. The adsorber was immersed in a refrigerated circulating-water bath to maintain isothermal conditions prior to the experiment. Preliminary investigations on the adsorption rate by using the clay adsorbent have indicated that the process occurred rapidly. After the period of 60–120 min, a gradual approach to the adsorption capacity was observed. Also, the effect of agitation speed ranging from 200 to 600 rpm on paraquat adsorption seemed to be negligible. Thus, each sample of the solution ($\approx 15 \text{ cm}^3$) was withdrawn from the adsorber by using a 20 mL syringe at intervals of 0.5, 1.0, 2.0, 5.0, 10.0, 30.0, 60.0, and 120.0 min. It was then filtered with fiber membrane (Cat. No.: A045A025A; ADVANTEC MFS, Inc., USA). The paraquat concentration of the filtrate was immediately analyzed after adding sodium dithionite, with a 1.0 cm light path quartz cells using a spectrophotometer (Hitachi UV-1500A) at λ_{max} of 600 nm (AOAC, 2000). The amount of paraquat adsorbed was determined by the difference between initial and liquid-phase concentrations of paraquat solution. The effects of initial pH (i.e., 3.0, 5.0, 7.0, 9.0 and 11.0) and temperature (i.e., 25, 30, 40 and 50 °C) on the adsorption kinetics were investigated in the present study. In each experiment, the adsorption was carried out under conditions where one parameter was changed at a time while the other parameters were held constant.

2.4. Adsorption isotherm

In order to establish the adsorption isotherms of spent diatomaceous earth and the resulting clay adsorbent prepared from the waste, adsorption capacities of paraquat were determined as reported earlier (Tsai et al., 2002, 2003a). In each experiment, about 0.1 g of the above-mentioned adsorbent was poured into a thermostatted shaker bath at 25 ± 0.1 °C and initial pH of 11.0 for all experiments. Isotherm experiments were carried out by shaking (at 110 rpm) with fixed value (i.e., 0.050 L) of paraquat solutions at different initial concentration for a specified contact time (24 h). The concen-

tration of paraquat was analyzed at the end of each contact period.

3. Results and discussion

3.1. Adsorption kinetics

Due to the rapid decrease in residual paraquat concentration at a short time scale, implying an ion-exchange interaction between the negatively charged surface and paraquat cation, a simple kinetic analysis of adsorption, pseudo-second-order equation, was thus used to fit experimental data in the present work as reported previously (Tsai et al., 2003a,b):

$$dq_{\text{t}}/dt = k(q_{\text{e}} - q_{\text{t}})^2 \quad (1)$$

where k is the rate constant of pseudo-second-order adsorption (g/mgmin), q_{e} and q_{t} are the amount (mg/g) of paraquat adsorbed at equilibrium and time t , respectively. Integrating Eq. (1) for the boundary conditions $t = 0$ to $t = t$ and $q_{\text{t}} = 0$ to $q_{\text{t}} = q_{\text{t}}$, gives:

$$1/(q_{\text{e}} - q_{\text{t}}) = 1/q_{\text{e}} + k \cdot t \quad (2)$$

Eq. (2) can be rearranged to obtain a linear form:

$$t/q_{\text{t}} = 1/(k \cdot q_{\text{e}}^2) + (1/q_{\text{e}}) \cdot t \quad (3)$$

Rate parameters, k and q_{e} can be directly obtained from the intercept and slope of the plot of (t/q_{t}) against t . The equilibrium concentration (i.e., C_{e}) can be further calculated as the value of q_{e} has been obtained from the fitting of Eq. (3).

3.1.1. Effect of pH

Prior to the investigation of the effect of pH on the paraquat adsorption, zeta potential of spent and treated diatomaceous earths in the absence of paraquat was determined by a Zeta Meter System 3.0 (ZETEMETER Inc., USA). From the data of zeta potential vs. pH (Fig. 1), it is clear that the isoelectric point or pH of point of zero charge (i.e., pH_{pzc}) of the diatomaceous earth–water system was thus determined to be approximately 1.5. Thus, the surface of these diatomaceous earths at the experimental conditions (i.e.,

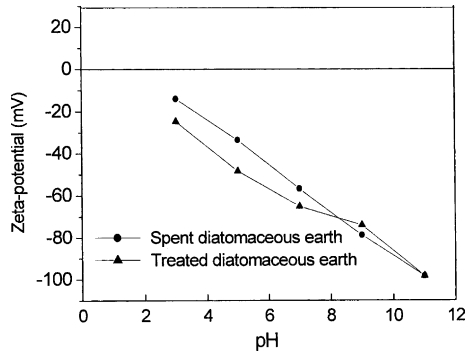


Fig. 1. Effect of pH on the ζ -potential of spent and treated diatomaceous earths (each point is the average of 5–10 readings).

pH > 3.0) should exhibit negative charges mainly due to the variable charge from pH dependent surface hydroxyl sites (Sparks, 1995). It is noted that with the increase of pH the adsorbed amount of cationic paraquat increased in response to the increasing number of negatively charged sites that are available due to the loss of H^+ from the surface (Sparks, 1995). From the results in Fig. 1, this behavior was also demonstrated by pH_{pzc} (≈ 1.5) of the clay–water system determined in the electrokinetic experiment.

These negative charges increase with increasing pH, which is consistent with the results of the increased amounts adsorbed onto treated diatomaceous earth with pH under the initial concentration of paraquat at 30 mg/L and 25 °C as shown in Fig. 2. From Fig. 2, it is evident that the rate of adsorption decreased with time until it gradually approached a plateau because the equilibrium concentration was approached in an aqueous solution. Also, the paraquat adsorption by the base-activated diatomaceous earth was evidently affected over the pH ranges of 3–5. The kinetic data obtained from

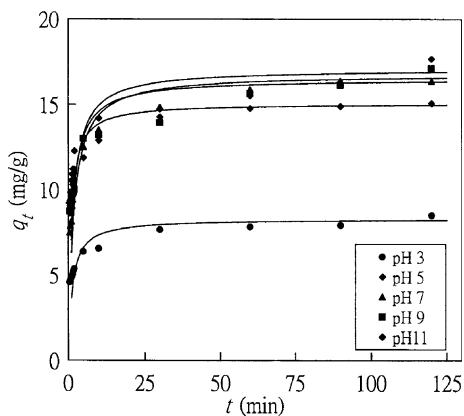


Fig. 2. Plots of adsorbed paraquat amount vs. time for various initial pH (initial concentration = 30 mg/L, treated diatomaceous earth dosage = 1.0 g/2 L, agitation speed = 400 rpm, and temperature = 25 °C; symbols: experimental data, full lines: calculated from Eq. (3) and Table 3).

Table 3

Kinetic parameters for adsorption of paraquat onto treated diatomaceous earth at various initial pH^a

Initial pH	k (g/mg min)	q_e (mg/g)	Correlation coefficient	C_e (mg/L)
3.0	0.094	8.28	0.998	25.86
5.0	0.078	15.06	1.000	22.47
7.0	0.047	16.47	1.000	21.77
9.0	0.036	16.75	0.997	21.63
11.0	0.041	17.06	0.996	21.47

^a Adsorption conditions: initial concentration = 30 mg/L, adsorbent dosage = 1.0 g/2 L, agitation speed = 400 rpm, and temperature = 25 °C.

batch studies have been analyzed by using the pseudo-second-order adsorption model. Values of k , q_e , correlation coefficient (R^2) and C_e for the paraquat adsorption system, computed from Eq. (3), are listed in Table 3, from which it will be seen that the kinetics of paraquat adsorption on the treated diatomaceous earth follow this model with regression coefficients of higher than 0.99 for all the systems in this study.

3.1.2. Effect of temperature

The plots of q_t vs. t at various temperatures of paraquat solution under the initial paraquat concentration of 30 mg/L and pH of 11.0 are shown in Fig. 3. The adsorption process still confirms to fit the pseudo-second-order model with high correlation coefficient (>0.99). Values of model parameters (i.e., k and q_e) and C_e for different temperatures have been calculated from Eq. (3) and the results are given in Table 4. It is clear that fitted adsorption capacity at equilibrium (i.e., q_e) for each temperature decreased with increasing temperature. For example, values of q_e decreased from 16.13 mg/g at 30 °C to 11.70 mg/g at 50 °C. Based on mass law concept, values of C_e increased with increasing

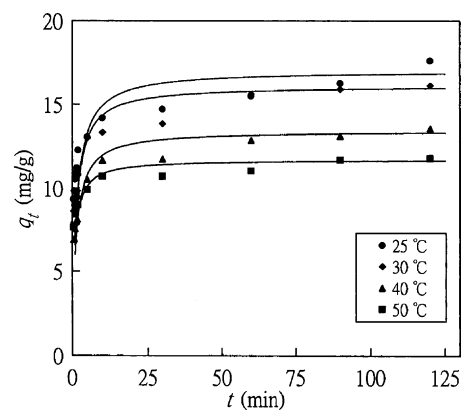


Fig. 3. Plots of adsorbed paraquat amount vs. time for various temperatures (initial concentration = 30 mg/L, treated diatomaceous earth dosage = 1.0 g/2 L, initial pH = 11.0, and agitation speed = 400 rpm; symbols: experimental data, full lines: calculated from Eq. (3) and Table 4).

Table 4
Kinetic parameters for adsorption of paraquat onto treated diatomaceous earth at various temperatures^a

Temperature (°C)	<i>k</i> (g/mg min)	<i>q_e</i> (mg/g)	Correlation coefficient	<i>C_e</i> (mg/L)
25	0.041	17.06	0.996	21.47
30	0.050	16.13	0.999	21.94
40	0.060	13.42	0.999	23.29
50	0.108	11.70	0.999	24.15

^a Adsorption conditions: initial concentration = 30 mg/L, adsorbent dosage = 1.0 g/2 L, initial pH = 11.0, agitation speed = 400 rpm.

temperature. Values of rate constant (i.e., *k*), on the other hand, showed an increasing trend with increasing temperature. The experimental results described above were consistent with that of Nakamura et al. (1999) where adsorption capacity of paraquat was also found to decrease with increasing temperature in the adsorption removal of the adsorbate onto activated carbon. Based on the results of the effect of temperature on the adsorption capacity, the main mode for the adsorption of paraquat onto treated diatomaceous earth should be physical adsorption, which is an exothermic process and the amount of adsorbate adsorbed onto adsorbent increases with the lowering of adsorption temperature.

3.2. Adsorption isotherm

In order to design an optimal adsorption system to remove environmental contaminants, the study of adsorption isotherms is helpful in determining the adsorption capacity of an adsorbent at specific temperatures. Two common isotherm equations (the Langmuir and Freundlich models) were applied to the adsorption equilibrium at all temperatures studied in the present study. Applicability of the isotherm equations was compared by using the correlation coefficients, *R*².

3.2.1. Langmuir model

The Langmuir equation is the most widely used two-parameter equation, commonly expressed as

$$1/q_e = 1/(K_L \cdot q_m) \cdot 1/C_e + (1/q_m) \quad (4)$$

In Eq. (4), *C_e* and *q_e* are as defined in Eq. (1), *K_L* is a direct measure for the intensity of the adsorption process (L/mg), and *q_m* is a constant related to the area

occupied by a monolayer of adsorbate, reflecting the adsorption capacity (mg/g). From a plot of $1/q_e$ vs. $1/C_e$, *q_m* and *K_L* can be determined from its slope and intercept. Table 5 presents the results of the Langmuir isotherm fits of paraquat to the measured adsorption capacity data for spent and treated diatomaceous earths at 25 °C. The Langmuir isotherm appears to fit the data slightly well, as reflected with correlation coefficients (*R*²) of 0.84 and 0.86 for spent diatomaceous earth and treated diatomaceous earth, respectively. It is noted that the monolayer adsorption capacity (i.e., *q_m*) and Langmuir constant (i.e., *K_L*), of treated diatomaceous earth are significantly larger than those of spent diatomaceous earth. This tendency is reasonable since the adsorption affinity and monolayer adsorption capacity will be enhanced by the increase in surface area observed between these two adsorbents (Table 2). Therefore, the monolayer adsorption capacities of adsorbents are mainly dependent upon physical properties such as BET surface area.

3.2.2. Freundlich model

The Freundlich isotherm is an empirical equation and shown to be satisfactory for low concentrations. The equation is commonly given by

$$q_e = K_F \cdot C_e^{1/n} \quad (5)$$

where *K_F* is a constant for the system, related to the bonding energy. *K_F* can be defined as adsorption or distribution coefficient and represents the quantity of adsorbate adsorbed onto adsorbents for a unit equilibrium concentration (i.e., *C_e* = 1 mg/L). The slope $1/n$, ranging between 0 and 1, is a measure for the adsorption intensity or surface heterogeneity, becoming more heterogeneous as its values gets closer to zero (Haghseresht and Lu, 1998). A value for $1/n$ below one indicates a Langmuir-type isotherm because it becomes more and more difficult to adsorb additional adsorbate molecules at higher and higher adsorbate concentrations (Fytianos et al., 2000). A plot of $\ln q_e$ vs. $\ln C_e$ enables the empirical constants *K_F* and $1/n$ to be determined from the intercept and slope of the linear regression. Table 5 also presents the results of the Freundlich model, indicating the satisfactorily good correlation between the model predictions and the experimental data. Obviously, it can be seen that the Freundlich model yields a

Table 5
Parameters in Langmuir and Freundlich adsorption isotherm models of paraquat onto spent and treated diatomaceous earths at 25 °C^a

Sample	Langmuir			Freundlich		
	<i>q_m</i> (mg/g)	<i>K_L</i> (L/mg)	<i>R</i> ²	<i>K_F</i> (mg/g(L/mg) ^{1/n})	$1/n$ (–)	<i>R</i> ²
Spent diatomaceous earth	3.46	0.04	0.835	3.37	1.89	0.932
Treated diatomaceous earth	17.54	1.72	0.859	12.80	13.51	0.949

^a Batch adsorption conditions: initial concentration = 15–200 mg/L, adsorbent dosage = 0.1 g/0.05 L, agitation speed = 110 rpm, initial pH = 11.0, and temperature = 25 °C.

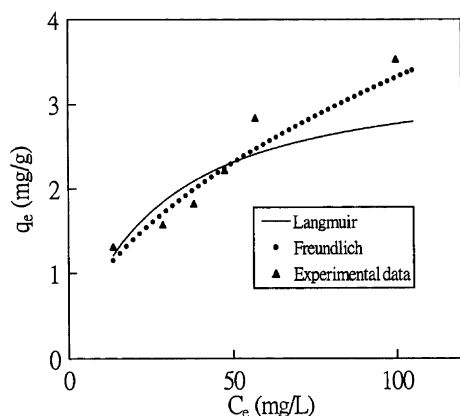


Fig. 4. Isothermal adsorption of paraquat in aqueous solution onto spent diatomaceous earth at 25 °C; (▲): experimental data, (●): simulation of Freundlich model, (—): simulation of Langmuir model.

somewhat better fit than the Langmuir model as shown in Figs. 4 and 5 for spent diatomaceous earth and treated diatomaceous earth, respectively. It is also seen from Tables 2 and 5 that the values of K_F increased with surface area of diatomaceous earth adsorbents at the same temperature, because the magnitude of K_F indicates a measure of the adsorption capacity. As also illustrated in Table 5, the values of $1/n$ are below unity, which indicate favorable adsorption. The Freundlich model for paraquat adsorption onto diatomaceous earth also provides insight that the adsorbate was partitioned between the aqueous solution and the solid adsorbent. The treated diatomaceous earth is more favorable for paraquat adsorption than the spent diatomaceous earth, which is consistent with the values of q_m and K_L for which the former adsorbent has larger values of q_m and K_L determined from the Langmuir model. This also indicates that the effect of surface heterogeneity is more pronounced, for treated diatomaceous earth, when a stronger adsorbate–adsorbent interaction is formed.

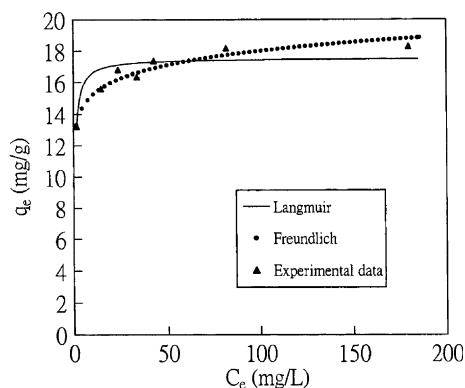


Fig. 5. Isothermal adsorption of paraquat in aqueous solution onto treated diatomaceous earth at 25 °C; (▲): experimental data, (●): simulation of Freundlich model, (—): simulation of Langmuir model.

4. Conclusions

This study indicated that spent diatomaceous earth from wine processing could be used as a precursor for the preparation of porous clay adsorbent. The results showed that the novel adsorbent (base-activated clay mineral from spent diatomaceous earth) had a larger adsorption capacity at a higher pH value over the range of 3–11 and at lower temperature. The adsorption kinetics were well described by the pseudo-second-order model equation. Furthermore, the Freundlich model appeared to fit the data better than the Langmuir model for describing the adsorption behavior of paraquat from an aqueous solution on spent diatomaceous earth and its activated product.

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