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Adsorption of Paraquat onto Activated Bleaching Earth

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There have been many authenticated cases of the detection of pesticide residues (e.g. paraquat) in water sources and factory effluent. Also, regulatory frameworks for pesticides in drinking water and effluent have been developed to protect the health of humans and the environment. Paraquat, also known as methyl viologen, is frequently used as a quaternary ammonium herbicide due to its excellent action within plant cells. In addition, it is known that this compound is one of the most toxic poisons if deliberately or accidentally ingested. (WHO 1984). Since paraquat is the most widely used pesticide in Taiwan, the maximum contaminant level (MCL) is set at 0.01 mg/L according to the Drinking Water Standard.

There are two principal treatment processes for removal of paraquat in water and wastewater: destructive processes such as destructive oxidation (Andreozzi et al. 1993), and recuperative processes such as adsorption into porous solids (Tanada et al. 1994, Nakamura et al. 1999). For virtually all pesticides, granular activated carbon (GAC) filter has been considered as a best available technology. However, an important feature of cationic paraquat is to adsorb strongly on clay minerals, and somewhat less on activated carbon due to its highly polar nature for an expanding lattice clay, like montmorillonite (de Keizer 1990). Retention by adsorption at a solid/liquid interface depends on the natures of both paraquat and clay and on the medium conditions (Draoui et al. 1999). Clays are the main components of the mineral fraction of soils. They are effective natural adsorbents due to their particle size (lower than 2 μm), lamellar structures and negatively charged surfaces, which make them good adsorbents by ion exchange. Thus, treatment of paraquat detoxification is directed toward the contact with clay or earth (i.e., Fuller's earth or bentonite) (WHO 1984). The aim of the present work is to study the sorption of paraquat on activated bleaching earth. The adsorption capacities were determined through the adsorption isotherms. The influence of salts and pH was also analyzed.

MATERIALS AND METHODS

Activated bleaching earth (ABE), which consists essentially of acid-activated clay minerals of the montmorillonite group, was obtained from an edible oil workshop (Taiwan Sugar Co., Kaohsiung, Taiwan) (Werner 1994). The clay is a

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mesoporous adsorbent having a mean pore diameter of around 53.5 Å, determined by the Barrett-Joyner-Halenda (BJH) method in the nitrogen adsorption/ desorption isotherms (Gregg & Sing 1982). The cation exchange capacity for Na^+ is 42.3 meq/100g, determined in the column mode by the sodium acetate method (U.S. EPA Method 9081A). Its BET surface area is 268 m^2/g. Analyzed by an inductively coupled plasma- atomic emission spectrometer, the main components are SiO_2, Al_2O_3 and Fe_2O_3 having 72.9 %, 3.49 % and 1.37 %, respectively. The adsorbate used in the adsorption experiments is paraquat, which was purchased from Sigma Chemical Co. with purity of min. 99%.

Adsorption capacities of paraquat were determined by using the standard method of ASTM-D 3860 (ASTM 1996). In each experiment, 0.1 g of fine sample was used after degassing at 105 ℃ for 24 hr in the oven. Adsorption was carried out by shaking (at 110 rpm) with fixed value (i.e., 0.050 L) of paraquat solutions at different initial concentration in a thermostatted shaker bath at 25 ± 0.1 ℃ for all experiments. The paraquat solutions were contacted for at least 20 hr, which had been shown previously and was well in excess of the 2 hr contact time requirement established to reach equilibrium in the standard method (i.e. ASTM-D 3860). The aqueous solutions of paraquat varied in concentrations up to about 30 mg L^{-1}. Concentration analysis of the solutions after centrifuge filtration was carried out by spectrophotometer (Shimadzu UV-1201) at λ_{max} of 394 nm. The amount of paraquat adsorbed was determined by the difference of the initial and equilibrium liquid-phase concentration. In order to study the effects of common salts on the adsorption capacity of the clay adsorbent, the sample was used to investigate the adsorption capacities at the NaCl, KCl and LiCl concentrations of 2.5 M, and at the NaCl concentrations of 0, 0.5 and 2.5 M. Further, the effect of pH on the adsorption capacity was proceeded under the pH values of 3, 4, 5, 6, 7 and 8, adjusted by adding HCl or NaOH.

RESULTS AND DISCUSSION

The adsorption isotherms of paraquat on activated bleaching earth (i.e., ABE) at three NaCl concentrations are given in Figure 1. Typical high-affinity isotherms (i.e., Type-H isotherms) were obtained at 0 ~ 2.5 M NaCl. This means that the observed high-affinity is probably the consequence of adsorption in the interlayer between the clay platelets (de Keizer 1990). This observation is similarly consistent to those of paraquat/soil adsorption systems (Wang 1997). It is also noted that the effect of electrolyte concentration on adsorption is significant. The amount adsorbed is great in 2.5 M of NaCl concentration. It has been reported that the adsorption capacity increased in a normal saline solution by using activated carbon (Nakamura et al. 1989), and chitosan (Tanada et al. 1994). Figure 2 shows the relationship between the amounts of paraquat adsorbed and 2.5 M concentration of chloride salts (i.e., LiCl, NaCl, KCl). As seen from Figure 2, chloride salt had little effect on the adsorption capacities of paraquat. It should be noted that NaCl seems to be more effective in adsorbing paraquat than in those

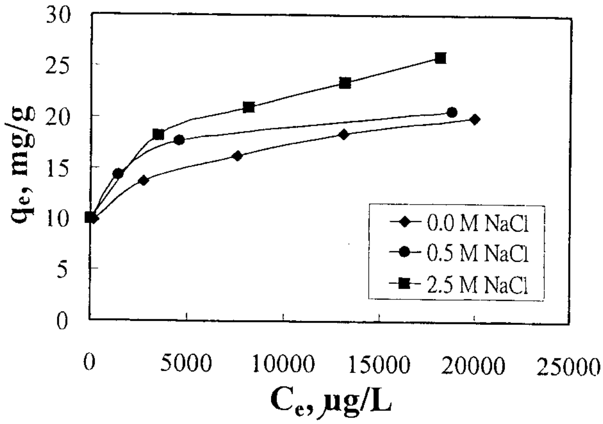

Figure 1. Adsorption isotherms of paraquat onto adsorbent ABE under 0, 0.5, and 2.5 M NaCl.

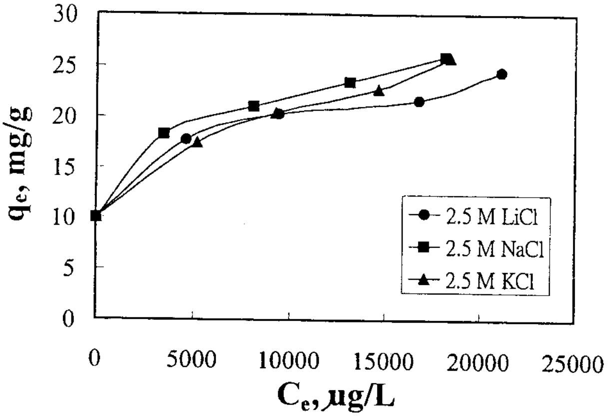

Figure 2. Adsorption isotherms of paraquat onto adsorbent ABE under 2.5 M chloride salts.

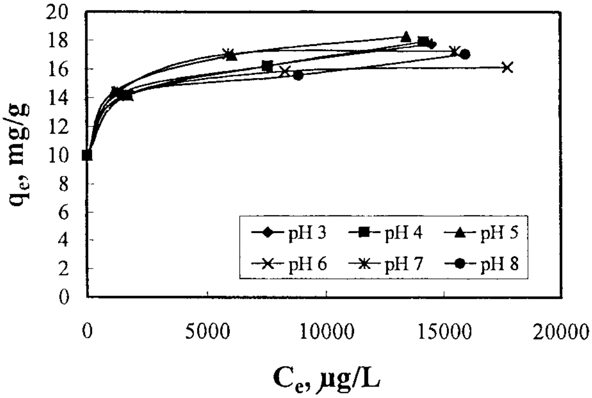

Figure 3. Adsorption isotherms of paraquat onto adsorbent ABE under the pH of 3 ~ 8.

cases of LiCl and KCl in the present study. The adsorption isotherms in Figure 3 also show the presence of a strong adsorption capacity for paraquat on the montmorillonite-type adsorbent at pH ranges of 3 ~ 8. At these levels the effect of pH can be considered to be negligible.

Nakamura et al. (1999) reported the efficacy of microporous activated carbon as adsorbent in removing paraquat from aqueous solution. Although the surface area (i.e. 268 m^2/g) of activated bleaching earth is lower than that (i.e. 1080 m^2/g) of activated carbon, the activated bleaching earth adsorbs more paraquat in the present work. It is recognized that the adsorption mode of paraquat onto hydrophobic carbon adsorbent is mainly physical adsorption, whereas the high affinity of paraquat for the clay mineral is related to its characteristics of polar surface nature and expanding lattice (de Keizer 1990).

A variety of models have been developed to characterize the relationship in the adsorption isotherms. To facilitate the estimation of adsorption capacities at various liquid-phase concentrations in the paraquat/clay (i.e. activated bleaching earth) system, the two most used adsorption isotherm models, Langmuir and Freundlich, were employed in the present study. Applicability of the isotherm equations is compared by calculating a correlation coefficient, R^2. The Langmuir equation is the widely used two-parameter equation, commonly expressed as

$$C_e/q_e = 1/(K_L q_m) + (1/q_m)\, C_e \qquad (1)$$

where q_e and C_e are defined as the amount of paraquat adsorbed (mg g^{-1}) and equilibrium liquid-phase concentration (μg L^{-1}), respectively. K_L is a direct measure of the intensity of the sorption (L μ g^{-1}), and q_m a constant related to the area occupied by a monolayer of adsorbate, reflecting the adsorption capacity (mg g^{-1}). From the data of C_e/q_e vs. C_e, q_m and K_L can be determined from its slope and intercept. The Freundlich isotherm, an empirical equation, has been shown to be satisfactory for low adsorbate concentration (Noll et al. 1992). The equation is commonly given by

$$q_e = K_F\, C_e^{1/n} \qquad (2)$$

where K_F, related to the bonding energy, is a constant for the system. K_F can be defined as adsorption or distribution coefficient and represents the amount of adsorbate adsorbed onto adsorbent for a unit equilibrium concentration (i.e., $C_e = 1$ mg L^{-1}). The slope 1/n, ranging between 0 and 1, is a measure of the adsorption intensity or surface heterogeneity. A plot of ln q_e vs. C_e enables the empirical constants K_F and 1/n to be determined from the intercept and slope of the linear regression.

Table 1 presents the results of the two isotherm fits of paraquat to the measured adsorption capacity data for the clay adsorbent. The two models appear to fit the data reasonably well, reflecting with correlation coefficients (R^2) in the ranges of

Table 1. Effects of chloride salts on parameters in Langmuir and Freundlich adsorption isotherm models of paraquat onto adsorbent ABE at 25 ℃.

Salts	Concentration (M)	Langmuir			Freundlich		
		q_m (mg g^{-1})	K_L (L μg^{-1})	R^2	K_F [mg g^{-1}(L μg^{-1})$^{1/n}$]	1/n (-)	R^2
NaCl	0	20.41	0.0007	0.9370	2.92	0.1942	0.9951
NaCl	0.5	20.88	0.0015	0.9848	5.23	0.1410	0.9754
NaCl	2.5	26.74	0.0006	0.9107	9.80	0.0891	0.9582
KCl	2.5	29.15	0.0003	0.9484	9.79	0.0846	0.9196
LiCl	2.5	25.32	0.0005	0.9105	9.84	0.0812	0.9575

0.911 ~ 0.995. Obviously, it can be seen that the Freundlich model yields a somewhat better fit than the Langmuir model when comparing the R^2 values in Table 1. Table 1 indicates the q_m and K_F increase with increasing NaCl concentration as expected. As also shown in Table 1, the values of 1/n in the range of 0.081 ~ 0.194 indicated the highly favorable adsorption for paraquat-clay adsorbent system. On the other hand, the values of 1/n decrease with increasing NaCl concentration as also showed in Figure 1. The results of the two isotherm fits at the pH of 3 ~ 8 are given in Table 2. As expected, the effect of pH on adsorption capacity is negligible.

Table 2. Effects of pH on parameters in Langmuir and Freundlich adsorption isotherm models of paraquat onto adsorbent ABE at 25 ℃.

pH	Langmuir			Freundlich		
	q_m (mg g^{-1})	K_L (L μg^{-1})	R^2	K_F [mg g^{-1}(L μg^{-1})$^{1/n}$]	1/n (-)	R^2
3	17.54	0.0031	0.9113	9.89	0.0566	0.9802
4	17.83	0.0022	0.9172	9.86	0.0567	0.9649
5	18.28	0.0032	0.9680	7.82	0.0886	0.9988
6	16.37	0.0037	1.0000	9.97	0.0494	0.9952
7	17.73	0.0033	0.9930	9.93	0.0576	0.9815
8	16.72	0.0034	0.8471	9.93	0.0518	0.9839

In viewing emergency treatment, the activated bleaching earth can be used as an excellent oral adsorbent for the acute paraquat poisoning. Also, the amount of paraquat adsorbed increased in the presence of chloride salts, like sodium chloride. Therefore, it is stipulated that a mixture of the detoxifying adsorbent and physiological saline solution is desirable to heighten the removal effect for paraquat.

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