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SHORT COMMUNICATION

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Very fast sorbent for organic dyes and pollutants

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Abstract The increasing use of organic compounds endangering the environment encourages search for more efficient sorbents. While crude clay minerals are effective for the adsorption of cations, modified organoclays may adsorb negative and hydrophobic molecules. In this short communication, we present a very fast adsorbing organoclay based on montmorillonite with crystal violet pre-adsorbed up to neutralization of the negative charges. Sorption of erythrosin-B and 2,4,5-trichlorophenol to such organoclay reaches equilibrium in less than a minute, whereas with activated carbon, it took tens of minutes. The pseudo second-order kinetic coefficient for the process was at least two orders of magnitude smaller for the organoclay. Because sorption kinetics is an important factor in water purification, such fast sorbent might have broad environmental applications.

Keywords Organoclays · Sorption kinetics · Montmorillonite · Crystal violet · Erythrosine-B · 2,4,5-trichlorophenol

Abbreviations *AC*: High quality powdered activated carbon · *CEC*: Cation exchange capacity · *CV*: Crystal violet · *EB*: Erythrosin-B, 2′,4′,5′,7′-Tetraiodofluorescein disodium salt · *M100*: Motmorillonite SWy-1 with CV adsorbed up to 100% of the CEC · *TCP*: 2,4,5-trichlorophenol

Introduction

The increasing use of organic compounds endangering the environment encourages the search for better and more efficient sorbents to remove such contaminants from water.

Crude clay minerals are usually negatively charged as a result of isomorphous substitution in the crystal lattice [1], therefore efficient in the adsorption of cations and polar molecules but quite ineffective in sorbing non-ionic organic pollutants from water solutions. Sorptive properties to nonpolar or anionic molecules can be modified by exchanging the inorganic exchangeable cations with large organic cations or surface active agents [2, 3]. Such nanoparticles form a stable complex referred as an organoclay [4].

Most organoclays are based on smectites with an organic layer comprised of quarternary alkyl-ammonium cations exchanged on the surface [5]. The exchange process usually causes a swelling of the basal plane that can be measured by X-ray diffraction measurements [6]. In the increased interlammelar space that is formed, aromatic molecules may intercalate increasing further the basal spacing [7]. Dékány et al. [8] showed that the amounts of benzene sorbed increased with the chain length of the cation used to modify the clay, whereas the amounts of methanol adsorbed were not influenced. Farkas and Dekany [7] demonstrated that adsorption of pollutants such as nitrobenzene is more strongly encouraged on hexadecyl-pyridinium montmorillonite as compared to the one measured on Ca-montmorillonite, and this is reflected also on the basal spacing which remains unchanged for the latter [9]. Borisover et al. [10] showed that organoclays based on the cationic dyes crystal violet (CV) and rhodamine-B might be effective for the removal of atrazine,

phenol, and naphthalene from aqueous solution. In this study, we used an organoclay based on montmorillonite and CV added so that it neutralizes all the cation exchange capacity (CEC) of the clay. In preliminary experiments, it was observed that the sorption kinetics of several organic phenolic derivatives is considerably faster than the observed using other sorbents such as powdered or granular activated carbon. In all cases, sorption to the organoclay reached equilibrium in less than the time needed to separate the supernatant from the sorbent (less than 30 s), with almost complete removal of the pollutants. The results appeared to be considerably faster than those presented in previous studies for hexadecyltrimethyl ammonium organoclay, in which it took at least tens of minutes to reach equilibrium for the sorption of phenol and aniline [11]. Studies recently performed with sorption of 2,4-dichlorophenol (DCP) on an organoclay based on montmorillonite with dodecyltrimethylammonium [12] presented fast kinetics (1–2 min), but the efficiency of the sorption was relatively low. Moreover, in a sorbent concentration of 1 g l^{-1} and an initial concentration of DCP of about 0.07 g l^{-1}, only 35% of the pollutant was adsorbed at equilibrium.

To quantify the effect observed on CV-montmorillonite organoclay, adsorption experiments of the anionic dye erythrosine-B (EB) and the pollutant 2,4,5-trichlorophenol (TCP) to organo-montmorillonite with CV neutralizing all the charged sites (M100) were performed and compared to the adsorption to high-quality powdered activated carbon (AC). Previous studies on the adsorption of EB on M100 [13] revealed H-type isotherms indicating high affinity between sorbent and the organoclay with complete removal of the dye at low concentrations. The use of EB as sorbent allowed fast and accurate measurements of relatively low concentrations of the dye, using UV–Visible spectroscopy, thus allowing evaluations of the amounts adsorbed as a function of time.

This study shows that rates of sorption of EB and TCP on M100 were about two orders of magnitude faster than those observed on AC.

Sorption kinetics is considered a limiting factor in water purification devices because polluted water needs to reach equilibrium with the sorbent to optimize the processes. Thus, the results presented in this study might be developed for broad environmental applications.

Materials and methods

Wyoming montmorillonite (SWy-2) was purchased from the Source Clays Repository of The Clay Minerals Society (Columbia, MO, USA). The CEC of the clay was reported to be 0.8 mol kg^{-1}, with Ca^{2+} and Na^{+} as main exchangeable cations [14]. CV was obtained from Fluka Chemica (Fluka Chemie AG, Buchs, Switzerland). EB was purchased from Spectrum (Gardena, CA, USA). TCP was obtained from Aldrich (Germany). High-quality C4386 activated carbon was obtained from Sigma (Germany). All materials were used without further treatment or purification.

An organoclay with CV up to 100% of the CEC (denoted as M100) was prepared by adding 1 g dry clay to 200 ml of distilled water, and stirring it for several minutes, until homogenous suspension was observed. CV powder was added slowly, and stirring continued for 2 h. The amount of CV adsorbed was calculated by sampling and filtering the suspension and measuring the remaining dye in the supernatant by UV–Visible spectroscopy using an HP 8452A diode array spectrophotometer, at 588 nm. Almost no dye remained in solution, indicating complete adsorption (0.8 mol CV per kilogram crude clay).

Adsorption experiments of EB on M100 or AC suspensions were performed by preparing a 1-mM EB stock solution and adding the desired volume of EB solution to the sorbent suspension, bringing the final volume to 100 ml. Measurements of the dye concentration as a function of time were performed by two different and independent methods:

(a) Filtering: The experiment was prepared in 100 ml batch vessels at constant stirring. At each time step, 5 ml was sampled and filtered using a 0.45 μm syringe filter (Minisart, Sartorius AG. Göttingen, Germany). Previous experiments showed that the filters do not adsorb EB or TCP. EB concentration was calculated by measuring optical density of the remaining dye in the filtrated solution at 526 nm, using a UV–Visible HP 8452A spectrophotometer.
(b) In situ measurement: The experiment was performed in situ using a 5-cm length cuvette placed directly on the HP 8452A spectrophotometer stand. This allows very fast measurements, but can be performed only at low sorbent concentrations. The whole spectrum was measured (190–820 nm) and was mathematically deconvoluted to the spectra of the dye, the adsorbed dye, and the sorbent, using a spectra-subtraction computer program prepared using MATLAB (Gonen, unpublished results). As seen in Fig. 1, both techniques yielded similar results.

Adsorption experiments of TCP were performed using the filtering method, and the pollutant concentration was measured at 244 nm using a HP 8452A spectrophotometer.

Results

Figure 1 shows changes of the ratio between measured EB concentration as a function of time (C_{EB}) and its initial concentration ($C_{EB,0}$). At sorbent amounts of 0.02 g l^{-1}, and $C_{EB,0}$=1 μM (0.880 mg EB per liter), equilibrium is reached in less than 10 min for M100, while for AC equilibrium, time was at least 80 min. In both cases, the

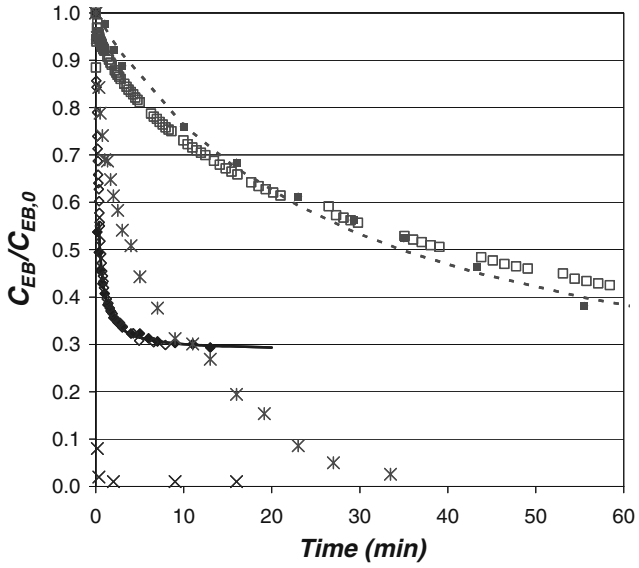

Fig. 1 Ratio of concentration of EB (C_{EB}) to its initial concentration ($C_{EB,0}$) as a function of time. For all the following, initial sorbent concentration is 0.02 g l^{-1} and $C_{EB,0}$=1 μM: ■ —AC filtered; □ — AC in situ; *dashed line*—AC calculated; ◆ —M100 filtered; ◇ — M100 in situ; *full line*—M100 calculated. The following indicate initial sorbent concentration of 1 g l^{-1}, and $C_{EB,0}$=100 μM: ✻ —AC filtered, ×—M100 filtered

equilibrium concentration is similar (about 30% $C_{EB,0}$), indicating similar capacities of sorption for both sorbents at those conditions. To quantitatively compare the results with previously published studies, the adsorbed amounts as evaluated from the remaining dye in solution using method (a) were adapted to a pseudo second-order model, using the equation [15, 16]:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t$$

where t is the time (in minutes), q_e is the equilibrium amount sorbed (gram per kilogram), and k is the rate of sorption (kilogram per gram per minute). The calculated values for q_e for both sorbents were relatively similar: 62.8 and 78.7 g kg^{-1} for M100 and AC, respectively. However, the rates of sorption (k) differed by more than two orders of magnitude, yielding 7.76×10^{-2} kg g^{-1} min^{-1} for M100 and 4.45×10^{-4} kg g^{-1} min^{-1} for AC. As seen in Fig. 1, method (b) (in situ direct measurement) yielded similar results.

To compare with previously reported values, we performed also experiments at sorbent amounts of 1 g l^{-1} and $C_{EB,0}$=100 μM (88 mg l^{-1}). When compared with the 0.02 g l^{-1} experiments, sorption kinetics was considerably faster for both M100 and AC (see Fig. 1), reaching complete removal of the dye from the solution, for both sorbents. In the case of AC, equilibrium is reached in about 30 min, and k_{AC} increases to 3.17×10^{-3} kg g^{-1} min^{-1}. Similar values for pseudo second-order kinetic coefficients were reported for adsorption of dyes ($0.18–0.38\times10^{-3}$ kg g^{-1} min^{-1}) and phenol ($2.22–3.46\times10^{-3}$ kg g^{-1} min^{-1}) to activated carbon prepared from bagasses [17], and dyes ($0.12–0.88\times10^{-3}$ kg g^{-1} min^{-1}) to chitosan [18]. However, for M100, equilibrium and complete removal of the dye are observed after less than 0.5 min. An accurate evaluation of k_{M100} at such fast process is impossible. The complete removal at such short period of time implies that $k_{M100}\geq1.0$ kg g^{-1} min^{-1}, thus at least three orders of magnitude larger than the sorption rate to AC at the same conditions. Such fast sorption was measured in all experiments performed with M100 concentration larger than 0.25 g l^{-1}.

Figure 2 shows a similar trend for the adsorption of TCP on M100 and AC, with sorbent amounts of 0.25 g l^{-1} and $C_{EB,0}$=20 μM (16.72 mg l^{-1}), performed using the filtering method. As in the EB case, the calculated values for q_e for both sorbents were relatively similar: 15.6 and 17.2 g kg^{-1} for M100 and AC, respectively. The rates of sorption (k) were calculated as from Fig. 2, where 2.45×10^{-2} kg g^{-1} min^{-1} is for AC, with complete adsorption achieved only after more than 20 min; whereas for M100, equilibrium and almost complete removal are observed in less than 0.5 min. To obtain such fast sorption process, $k_{M100}\geq8.2$ kg g^{-1} min^{-1}, thus at least two orders of magnitude larger than the sorption rate to AC at the same conditions.

The results shown indicate that organoclay particles based on montmorillonite saturated with CV presented sorption rates of EB and a phenolic pollutant at least two orders of magnitude faster than AC. Considering that sorption kinetics is one of the limiting factors in the removal of organic pollutants from water, a fast sorbent

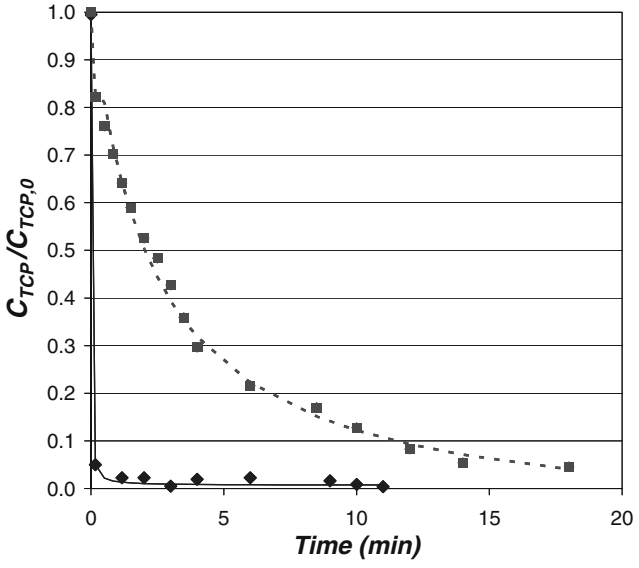

Fig. 2 Ratio of concentration of TCP (C_{TCP}) to the initial concentration ($C_{TCP,0}$) as a function of time. Initial sorbent concentration is 0.25 g l^{-1} and $C_{TCP,0}$=20 μM: ■ —AC filtered; ◆ —M100 filtered; *dashed line*—AC calculated; *full line*—M100 calculated

such as the organoclay compound presented in this study might have wide environmental uses. For example, Mogyorosi et al. [19] presented photocatalysis of 2-chlorophenol on an organoclay based on montmorillonite treated with hexadecylpyridinium. Combination of the fast sorbent presented in this study and such photocatalysis processes might lead to an effective adsorbent that can be used without the need of regeneration.

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