REMOVAL OF ENDOCRINE DISRUPTORS FROM WASTEWATER WITH ADSORPTION ONTO TIN PILLARED MONTMORILLONITE

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ABSTRACT –SnO_2 pillared montmorillonite clay was prepared and examined as adsorbent in the adsorption of endocrine disruptors compounds (EDCs) and compared with its starting material. The pillared samples showed a considerable increase in EDCs adsorption capacity in comparison to the natural clay mineral. This effect can be related to the textural and structural changes produced during the pillaring process. Consequently, Tin pillared clays could be the new material to be used in studied environmental process. Kinetics studies indicated that the multicomponent adsorption equilibrium was reached within 1 h and followed pseudo-second-order kinetics. The Langmuir, Freundlich, Redlich-Peterson and Temkin models were used to evaluate the EDCs adsorption capacity by pillared clay. The Freundlich model was found to be suitable for all compounds in a multicomponent system.

1. INTRODUCTION

The escalating problem in pollution has recently caught global attention due to its environmental and health hazards. Among the various types of pollutants, endocrine disrupting compounds (EDCs) are of particular concern because of their potential to interfere with the function of the endocrine system in wildlife and humans (Vidal et al. 2014). Currently, the majority of the EDCs that have been reported are found in municipal wastewater, once some of these compounds are not completely removed by conventional wastewater treatment systems, due to their high resistance to biodegradation (DeRudder et al. 2004; Fukahori et al. 2011). Moreover, researchers have also detected various EDCs in seawater sources; their presence could possibly be attributed to the transport of contaminated wastewater effluent by rivers into larger water bodies such as oceans and seas (Pessoa et al. 2012). To reduce the potential risk caused by EDCs in treated wastewater discharged to aquatic environments, their removal is considered as significantly important.

The use of adsorption to remove EDCs is one of the most promising techniques (Fukahori et al. 2011). Among the adsorbents for the decontamination of water, the clay minerals are usually selected by their low cost, wide distribution and its preference to adsorb specific contaminants. The clay

minerals have proved to be promising materials for the removal of several contaminants from wastewater (Jalil et al. 2013).

Montmorillonite (Mt), is a typical inorganic material and very rich clay mineral, consists of layers of two tetrahedral silica sheets sandwiching one octahedral alumina sheet. The cationic layered clays can be transformed into the highly porous structures by following three-step synthesis procedure: polymerization of a multivalent cation (such as Al^{3+}, Ga^{3+}, Ti^{4+}, Zr^{4+}, Sn^{+4}, Fe^{3+}, and Cr^{3+}, among others), leading to polycations; intercalation of these polycations into the interlayer space of clays, involving the substitution of natural exchangeable charge-compensating cations; and calcination at moderate temperatures. The latter step is necessary because the solids obtained after the second one, usually called intercalated clays, are metastable, like the polycations themselves. Calcination transforms the polycations into stable oxi-hydroxide phases named pillars, the solids obtained thus being called pillared clays (Gil et al. 2011).

Over the past few years nanostructures of tin oxide like; nano-wire, nano-tubes, nano-rods, nano-sheets, nano-particles and nano-pillars have been reported with their diversifying properties and, hence, functionalities (Sharma et al. 2013). Our choice of tin oxide pillared Mt is also motivated by their technological importance. Tin oxide has been studied by different research groups due to its capacity to adsorb molecules in the gas phase (Mendoza et al. 2014). There are few studies in the literature using tin oxide in the clays pillaring process (Gyftopoulou et al. 2005), thus requiring more studies to prove the efficiency of tin oxide in clays pillaring process.

Tin oxide exists in two different form namely; stannous oxide/tin monoxide (SnO) and stannic oxide/tin dioxide (SnO_2). The existence of these two oxides reflects the dual valency of tin with valence states of 2+ and 4+, respectively. During the pillaring processes SnO is easily oxidized to SnO2. Moreover, the large surface area of the clays and their enhanced acidity could very well promote the reactions of hydrated Sn(II) ions, leading to polyoxo/hydroxo species that are likely to precipitate onto the clay surfaces.

In this work, a Montmorillonite from Brazil and one SnO_2-pillared clay synthesized from this natural clay mineral were used to removal EDCs from real wastewater in order to evaluate if the pillaring of the Raw Mt improves the adsorption process.

2. MATERIALS AND METHODS

Montmorillonite was supplied from Bentonisa of Brazil Campina Grande (PB). The cation exchange capacity (CEC) of Mt was 718 mmol/100 g which was estimated using the ammonium acetate method (Vidal et al. 2012).

A stock solution of 1000 mg/L of compounds was prepared in methanol (HPLC grade, VETEC-Brazil), and the standards for EDCs (trimethoprim (TMP), estrone (E1), 17β-estradiol (E2) and 17α ethynilestradiol (EE2)) were purchased from Sigma- Aldrich-USA. Then working solutions were prepared doping the real wastewater samples to a concentration of 10 mg/L.

Wastewater samples for this study were collected from one full-scale wastewater treatment plant (WWTP) , located in the State of Ceará, a semi-arid zone locate in Brazil, which consists of one Upflow anaerobic sludge blanket (UASB) with post-chlorination disinfection.

The samples were collected in glass flasks, transferred to 1 L amber glass bottles and preserved by addition of 10 mL.L-1 formaldehyde. The samples were transported to the laboratory in cooling boxes and immediately (no longer than 48 h) used for adsorption tests. The pillaring agent was prepared by allowing a solution of 50 mL KOH 0.4 mol.L^{-1} under stirring until the temperature reached 60°C. Afterwards, 50 mL of tin chloride (II) 0.4 mol.L-1 was added dropwise to the initial solution of KOH.

Mt (5.0 g) was dispersed into 400 mL of deionized water and left briefly stirred, and a gieven amout (100 mL) of pillaring agent was added into the clay suspension. The mixture reaction was stirred at 60 °C for 24 h. The resulting suspension was centrifuged and washed several times with deionized water, thereafter dried at 80°C and calcined at 500 °C for 3 h.

X-Ray powder diffraction (XRD) patterns were recorded at XRD diffractometer (Philips X'Pert X-ray diffractometer) with a CuKα radiation for crystalline phase with a routine power of 1600 W (40 kV, 40 mA). Nitrogen isotherms were measured at -196 °C using an ASAP2020 instrument (Micromeritics). Prior to each measurement, the samples were outgassed at 120 °C to vacuum 4 mm Hg. The surface area, S_{BET}, was calculated from the isotherms. The pore size distribution (PSD) was determined using the BJH method.

In order to compare the efficiency of adsorption on clays (Raw Mt and pillared Mt), the adsorptions of EDCs was studied using a batch procedure and results were indicated in the form of adsorption capacity (Q), as shown in Equation 1. For each run, 150 mg of adsorbent were added to glass flasks containing 40 mL of EDCs in doped real wastewater and pH was adjusted to 3 using 0.1 M HCl solution. The flasks were agitated in an incubated rotatory shake for 24 h at 300 rpm. The suspension were then filtered and analyzed in HPLC.

$$Q = \frac{V*(C_i - C_f)}{w} \qquad (1)$$

where Q is the amount of EDCs adsorbed (mg) per g of pillared Mt, V is the volume of solution (L), Ci is the initial EDCs concentration (mg/L), Cf is the final EDCs concentration (mg/L) and w is the weight of adsorbent (g). Isotherms were taken running the adsorption experiments with various initial EDCs concentrations (Co = 0.5-60 mg/L) for 5 hours as contact time. Kinetic tests were performed using 10 mg/L as initial concentration at 25 °C (the pH of solution was adjusted at 3) for fixed time-intervals during adsorption (tads = 0-8 h).

Qualitative and quantitative analyses of effluent samples were carried out with the use of a liquid chromatograph HPLC Shimadzu (20A prominence) with UV-DAD detector (SPD-M20A) (230 nm), C18, 5-μm column, 250 × 4.6mm i.d (Hichrom5), acetonitrile/ HCl 0.1% as mobile phase.

Analyses were carried out in a programmed gradient: increase of 10–100% acetonitrile in 10 min, returning to 10% in four minutes. The initial flow was 1.4 mL/ min; and after five minutes, the flow was increased to 2.0 mL/ min. The column was thermostated during analysis at 35°C.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD of the Raw Montmorillonite (Mt) and SnO2-Mt samples. A typical diffraction peak (101) for montmorillonite clays at $2\theta = 6.6°$ corresponds to a basal spacing of 1.33 nm. After modification with tin this peak moves to a low angle at 4.1°, which correspond to a basal spacing of 2.16 nm. Similar result were found by Jalil et al. 2013. This result indicate that SnO2 exists within the interlayer space of the modify clay and these species were introduced via ion exchange process. Moreover, the XRD patterns of SnO_2-Mt show a characteristic diffraction peak for tin oxide at $2\theta = 33.8$, indicating the presence of SnO_2 crystalline particles in the modified Mt (Klementová et al. 2000).
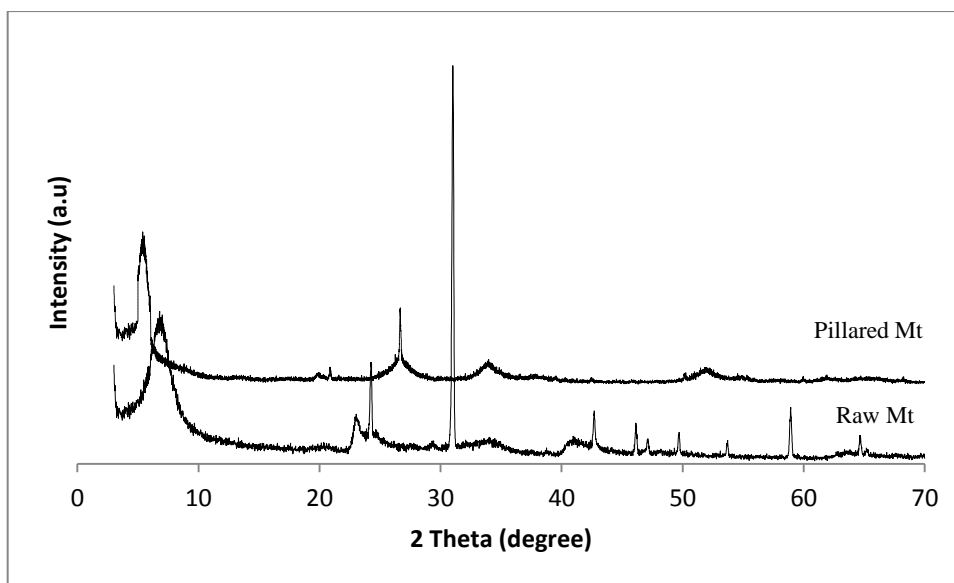

Figure 1 –XRD patterns of samples before and after modification.

Previous adsorption studies were performed in order to confirm the better efficiency of adsorption Pillared Mt with respect to Raw Mt and the results are presented in Fig. 2. The results reveal that the adsorption capacities of the pillared Mt are much higher than those of the Raw Mt. According to Jalil et al. (2013), the highest hydrophobicity of the pillared clays could be contributing to a better selectivity for the organic molecules compared to the natural clay mineral.
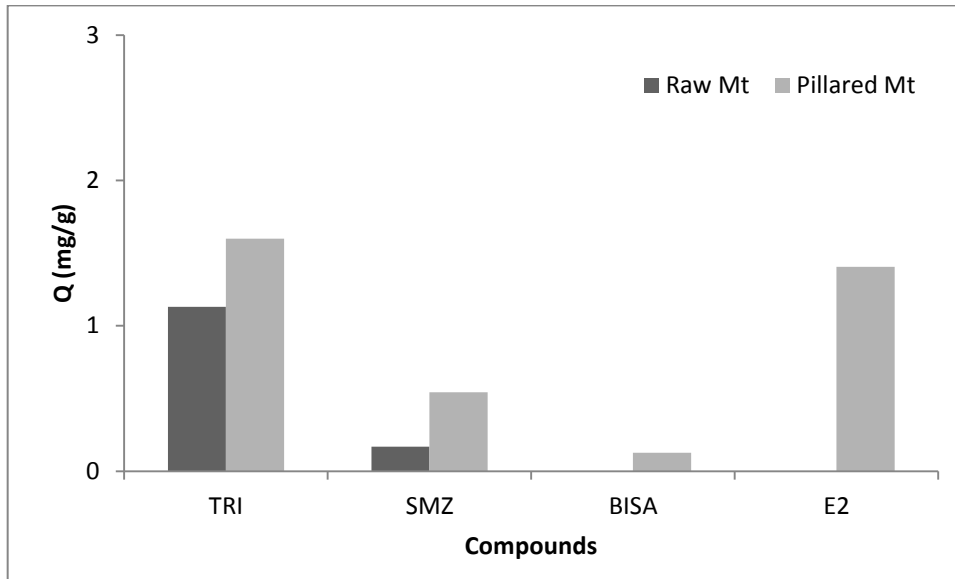
Figure 2 – Adsorption capacity of EDCs on Raw Mt and Pillared Mt. Conditions: C_0: 10 mg/L; mass of adsorbent: 150 mg, volume: 40 mL, temperature: 28 ± 2 °C.

Adsorption isotherms of the EDCs studied onto pillared Mt were obtained by plotting the concentration of each compound adsorbed on the solid phase (Q) versus its concentration in the liquid phase (Ce). The Langmuir, Freundlich, Redlich-Peterson and Temkin models were applied to the experimental data in isotherms and the parameters determined for each model are given in Table 1

Table 1 - Parameters of multicomponent adsorption isotherm models.

		TMP	E1	E2	EE2
Langmuir	$q_{máx}$	18.37	25.38	45.88	53.59
	K_L	0.08	0.003	0.001	0.001
	R^2	0.9679	0.9500	0.8846	0.8851
	E	1.99	0.19	0.89	4.64
Freundlich	K_F	1.52	0.45	0.12	0.3
	$1/n$	1	1.5	2	1.5
	R^2	0.9735	0.9857	0.9886	0.9674
	E	1.6480	0.05	0.0881	1.3182
Temkin	B	1.60	0.68	0.59	1.63
	K_t	4.77	2.89	3.26	0.79
	R^2	0.8804	0.89	0.5384	0.6344
	E	7.44	0.37	3.58	14.77
Redlich-Peterson	K_{RP}	26.69	0.64	0.5202	0.5786
	A	16.49	0.02	0.2559	0.4804
	B	0.2509	0	0	0
	R^2	0.9734	0.9430	0.8858	0.8871

	E	1.6528	0.1840	0.88	4.56

The parameters calculated from the models revealed that the Freundlich model adequately described the adsorption mechanism in this system for all EDCs studied, as shown by the values of the coefficients of determination R^2 and the error functions. The adsorption capacities (Q_{max}) followed the order: EE2 > E2 > E1 > TMP.

Fig. 3 shows the kinetics process of EDCs on pillared Mt. Equilibrium concentrations of EDCs appear to be achieved after 1 h of adsorption, which is consistent with the rapid equilibrium times observed in other studies (Joseph et al., 2011).
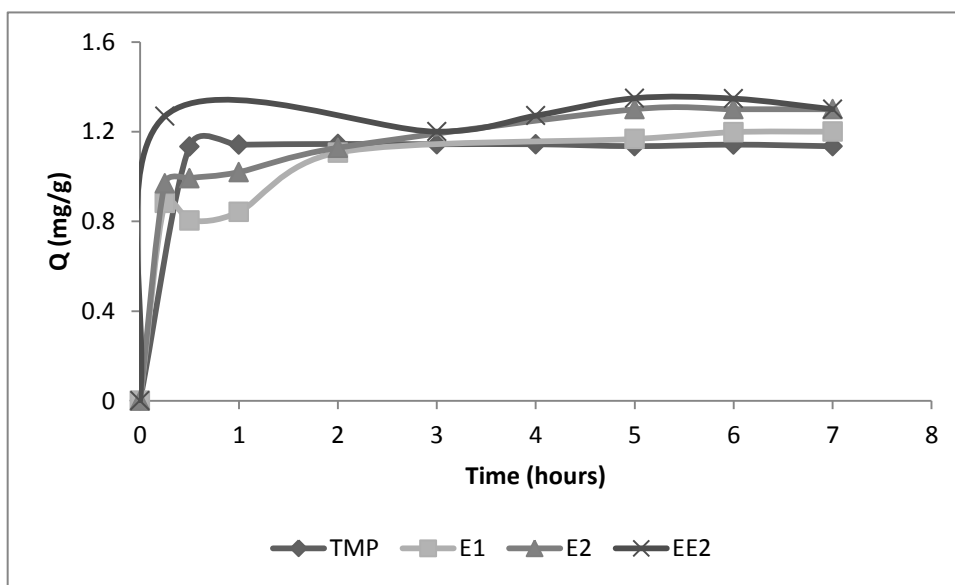

Figure 3 - Multicomponent adsorption kinetics of EDCs on pillared Mt.

According to Cooney (1999), the adsorption kinetics is initially fast because adsorption takes place predominantly onto the outer surface, followed by a slow adsorption step onto the inner surface of the adsorbent. A short time required to reach equilibrium, besides being beneficial to the process, is regarded as an indicator that the adsorption is controlled by chemical interactions rather than by diffusion.

The adsorption rate is also important because the prediction of the rate at which the target compound is removed from aqueous solutions allows for the design of appropriate adsorption systems (Fukahori et al. 2011). In order to analyze in depth the adsorption process, the kinetic data here reported have been fitted to three commonly accepted kinetic models namely the pseudo-first order (Ho and McKay, 1998) and pseudo-second order (Ho and McKay, 1998).

Both angular and linear coefficients of the equations were used in the calculations of constants K_1 and K_2 (not shown). The experimental adsorption capacity values (qe) were found to be in agreement with those of the theoretical adsorption capacity (qc) that were calculated with the pseudo-

second order model. The use of the pseudo-second-order model to describe the adsorption mechanism and the obtained results were supported by the R^2 values and error functions. It may be observed that this model provides an excellent fitting of the experimental data (Figure 4), all values of $R^2 > 0.99$. Therefore, it can be assumed that the pseudo-second order model describes the adsorption of the EDCs studied in a more accurate manner.
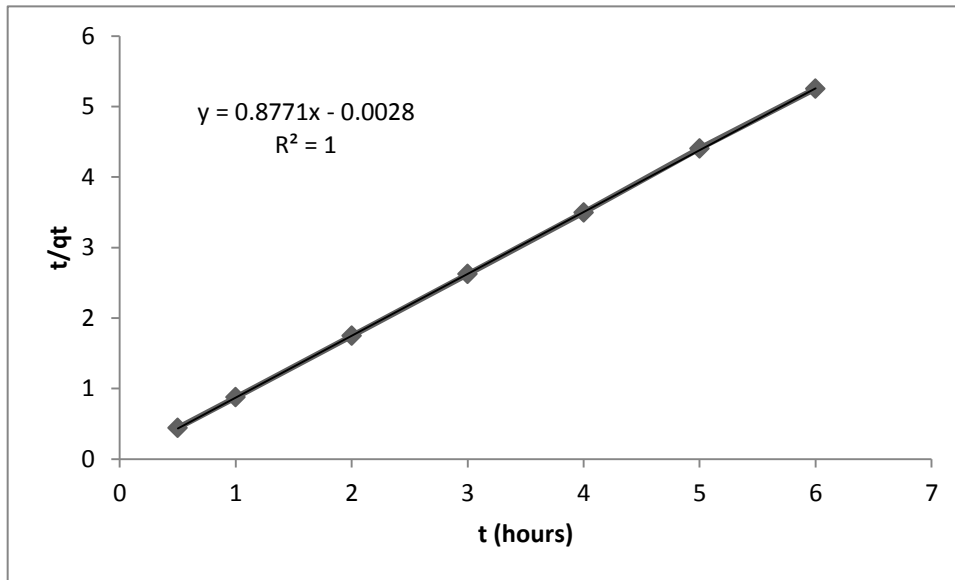

Figure 4 – Pseudo-second order model for TMP compound.

Azizian et al. 2004 reported on a theoretical approach to adsorption rate kinetics and concluded that adsorption kinetics fit better to a pseudo-second-order model when the initial concentration of the solute is not high. In this study, the initial concentration of EDCs was low (10 mg/L).

4. CONCLUSIONS

SnO_2 pillared montmorillonite clay was prepared and examined as adsorbent in the adsorption of endocrine disruptors compounds (EDCs) and compared with its starting material. The pillared sample showed a considerable increase in EDCs adsorption capacity in comparison to the natural clay mineral. This effect can be related to the textural and structural changes produced during the pillaring process. Consequently, Tin pillared clays could be the new material to be used in studied environmental process. Kinetics studies indicated that the multicomponent adsorption equilibrium was reached within 1 h and followed pseudo-second-order kinetics. The Langmuir, Freundlich, Redlich-Peterson and Temkin models were used to evaluate the EDCs adsorption capacity by pillared clay. The Freundlich model was found to be suitable for all EDCs compounds in a multicomponent system.

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