

KINETICS OF REMOVAL OF PETROLEUM HYDROCARBONS FROM AQUEOUS SOLUTION USING BENTONITE ORGANOCCLAY AS ADSORBENT

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ABSTRACT: This work evaluated the potential of Spectrogel C organoclay to remove petroleum hydrocarbons from aqueous solution. The adsorption tests were carried out with gasoline, diesel, kerosene, iso-octane and n-hexadecane. The kinetics curves were obtained through agitated batch systems at 250 rpm and 25°C and the removal was evaluated on graduated cylinders. The results showed that this organoclay has greater affinity and faster adsorption for hydrocarbons mixtures rather than the pure ones. Pseudo first order, pseudo second order and Mass Transfer on External Layer models were adjusted to all experimental data through non-linear fit. All kinetic curves were well fit by pseudo second order model. The removal of contaminant at equilibrium were over 96%, 97% and 99% for gasoline, kerosene and diesel respectively, while it ranged from 25% to 38% for n-hexadecane and from 46% to 100% for iso-octane. These results support the potential uses of Spectrogel C on water treatment.

KEYWORDS: kinetics, hydrocarbons, gasoline, kerosene, diesel, adsorption, organoclay, montmorillonite.

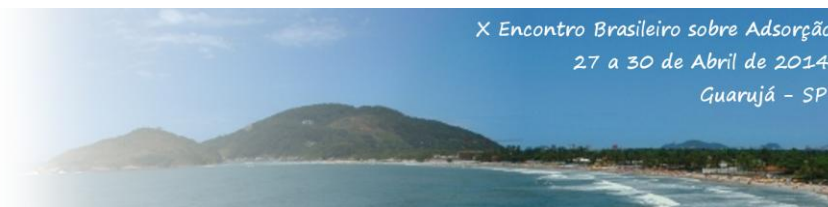
1. INTRODUCTION

The main threat to groundwater are petroleum hydrocarbons from gas stations activity (Tiburtius *et al*, 2005; Smith *et al*, 2003; Corseuil *et al*, 1998) mainly due the lack of maintenance, their old fuel storages are likely to leak as surveyed by Environmental Protection Agency (USEPA, 2013) on late 80's in USA and by Environmental Company of São Paulo State (CETESB, 2012) nowadays in Brazil.

These hydrocarbons, like BTEX used as fuel additives, are troublesome for the environment due their know toxicity, carcinogenic and mutagenic properties (Wang, 2013), but the fuels themselves also affects the environment reducing soil permeability to water and damaging the flora (Zhang, 2006).

The treatment of contaminated groundwater can be done by process like oxidation (Tiburtius *et al*, 2005), biodegradation (Corseuil *et al*, 1998) and adsorption (Smith *et al*, 2003), reduction, air stripping, among others. The advantages of adsorption over other process are the easy handling and its ability to work well on very low concentrations of pollutants, effectively reducing the contamination acceptable legal levels (Sutherland *et al*, 2004).

The drawback of adsorption lies on adsorbent costs as activated carbon and other materials, like resins and foams, used with great results are still costly. In this sense, there is a quest for alternative adsorbents that can be either raw or requires less process steps to produce. Therefore studies evaluating the removal of petroleum hydrocarbons using organoclays (Bertagnolli and Silva, 2012; Souza *et al.*, 2011.), sugarcane



bagasse (Brandão *et al.*, 2010, Said *et al.*, 2009), walnut shell (Srinivasan and Viraraghavan, 2008), kapok fiber, cattail fiber, wood chip, rice husk, coconut husk, polyester fiber (Khan *et al.*, 2004) and recycled wool (Radetic *et al.*, 2003) have been widely carried out.

Organoclays are chemically modified clays capable of adsorbing organic fluids instead of water. What makes them competitive as adsorbent is that their base material is clay in general, which is abundant, therefore, cheap and its great variety allows the application on many adsorption systems depending on the organic salt used in the organophilization process.

Aivalioti *et al.* (2012) studied adsorption of BTEX, MTBE and TAME on raw, chemically, thermally and both chemically and thermally treated diatomite. The kinetics curves were best fit by pseudo second order model. The equilibrium was reached after 20 hours or more, explained by the unfavorable isotherms.

Souza *et al.* (2011) successfully used raw red mud for the treatment of benzene, observing fast adsorption and removal of 98%.

Bertagnolli and Silva (2010) compared two bentonite organoclays in the removal of BTX from aqueous solution and sorption tests with diesel and gasoline.

Whereas there are many adsorptions studies for BTEX and other hydrocarbons, tests using fuels are missing in the literature. Thus, this study aimed for the removal of petroleum hydrocarbons, specifically gasoline, diesel, kerosene, iso-octane and n-hexadecane, from aqueous systems using a commercial organoclay, named Spectrogel C.

2. MATERIALS AND METHODS

2.1. Materials

The organophilic bentonite clay was kindly provided by Spectrochem® Company - Londrina-PR/Brazil. Its origin and organophilization method was not informed.

The diameter of 0.655 mm used in the experiments was obtained by milling the raw organoclay and sieving it with Tyler sieves.

The sorbates tested were commercial gasoline, diesel oil and kerosene, sigma-aldrich n-hexadecane 99% and iso-octane P.A. cetec.

2.2. Kinetic curves models

Adsorption kinetics was evaluated on two different concentrations of hydrocarbon and two masses of organoclay as described in the Table 1.

Table 1: Mass of organoclay used (g) and volume of hydrocarbon added (mL) and their ratio.

Organoclay mass (g)	Hydrocarbon Volume (mL)	Hydrocarbon/Organoclay Ratio
1.5	15	10
1.5	9	6
3	15	5
3	9	3

Firstly, using graduated cylinders, 75 mL of water and the respective volume of hydrocarbon were measured. Then, they were mixed on a third graduated cylinder in case of some hydrocarbon be dissolved in water. The new organic phase volume was then measured. These mixtures were transferred to erlenmeyer flasks. The organoclay was added, the flask sealed and then subjected to agitation at 250 rpm and 25 °C for pre-set contact times, i.e., (5, 15, 30, 45, 60, 90, 150 and 300 minutes). At the end of each experiment, the system was filtered and the remaining organic phase was measured in graduated cylinders after proper decantation.

The adsorption capacities were determined according to Equation 1:

$$q = \frac{(V_i - V_f)}{m} \quad (1)$$

where V_i (mL) and V_f (mL) are, respectively, the initial and final volume of the organic phase, m (g) is the organoclay mass utilized and q_{eq} (mL.g⁻¹) is the adsorbed volume per gram of organoclay.

The kinetic curves were adjusted by pseudo first order (Equation 2), pseudo second order (Equation 3) models (HO, 1998):

$$\frac{\partial q}{\partial t} = k_1(q_{eq} - q) \quad (2)$$

$$\frac{\partial q}{\partial t} = k_2 (q_{eq} - q)^2 \quad (3)$$

where q (mL.g^{-1}) is the volume (mL) of hydrocarbon adsorbed per unit mass of adsorbent at t (min), q_e (mL.g^{-1}) is the volume (mL) of hydrocarbon adsorbed per unit mass of adsorbent at equilibrium, and k_1 (min^{-1}) and k_2 ($\text{g.mL}^{-1} \cdot \text{min}^{-1}$) are the kinetic model constants.

The model of Mass Transfer on External Layer (MTEL) (Equation 4) (Puranik, *et al*, 1998) was also adjusted to the data.

$$\frac{\partial C_l}{\partial t} = \frac{vk_{tm}}{mq_{\max}k_l} (1 + k_l C_l)^2 (C - C_l) \quad (4)$$

Where C_l is the concentration in the external layer of the adsorbent (mL mL^{-1}), C is the concentration at the solution (mL mL^{-1}), k_l is the Langmuir isotherm adsorption constant (g^{-1}), q_{\max} is the maximum adsorption capacity (ml g^{-1}), m is the adsorbent mass used (g), v is the total volume of solution (mL), and k_{tm} is the constant of mass transfer (s^{-1}).

3. RESULTS AND DISCUSSION

The gasoline kinetic curves showed an almost instant adsorption for all conditions tested, with equilibrium time equal or under 5 minutes, as can be seen on Figure 1.

Table 2. Pseudo First Order (PFO), Pseudo Second Order (PSO) and MTEL parameters adjusted for gasoline adsorption

Condition (mL g^{-1})	Model	q_e (mL g^{-1})	K_1 (min^{-1})	K_2 ($\text{g mL}^{-1} \text{min}^{-1}$)	K_{tma}	R^2
10	PFO	7.834	12.507			0.995
	PSO	7.834		2.42×10^{14}		0.995
	MTEL	7,834			29,757	0,993
6	PFO	4.572	0.418			0.977
	PSO	4.623		0.34		0.972
	MTEL	4,500			26,651	0,982
5	PFO	3.661	2.55×10^8			0.989
	PSO	3.672		4.618		0.989

Using sugarcane bagasse and gasoline at similar conditions Brandão *et al.* (2010) observed fast adsorption kinetics as well.

The sugarcane achieved 83% to 85% of removal at equilibrium, while the organoclay achieve 100% on all experimental conditions tested.

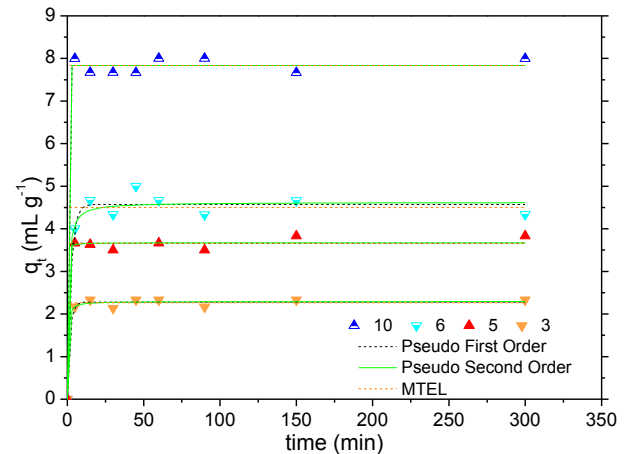


Figure 1: Kinetic curves for gasoline and their adjustments to pseudo first, pseudo second order and MTEL models. Legend: Hydrocarbon / Organoclay ratio (mL.g^{-1}).

The adjusted parameters from pseudo first order, pseudo second order MTEL models for gasoline are displayed on Table 2. No meaningful difference can be seen between the models.

	MTEL	3,661		32,658	0,995
	PFO	2.281	0.599		0.988
3	PSO	2.293		1.612	0.988
	MTEL	2,266		29,757	0,993

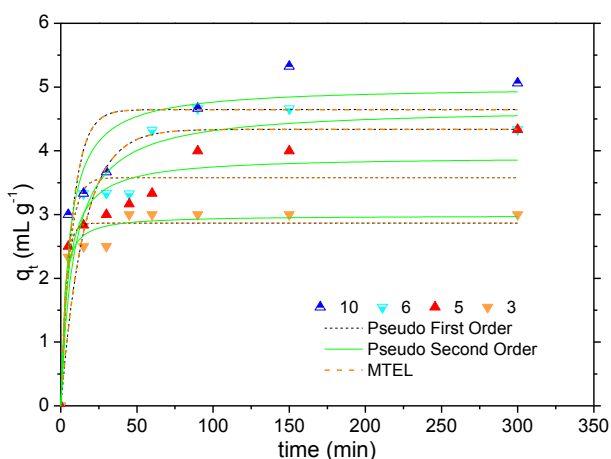


Figure 2: Kinetic curves for iso-octane and their adjustments to pseudo first, pseudo second order and MTEL models. Legend: Hydrocarbon / Organoclay ratio ($\text{mL}\cdot\text{g}^{-1}$).

Hua (2011) studied diesel adsorption on salty sand and observed a fast adsorption in the first 10 min and much slower rate until reach equilibrium at 1080 min. His data were best fitted by the pseudo second order model.

The kinetics curves for diesel (Figure 3) showed fast adsorption for ratios of 3 and 5 but the ratio of 6 and 10 needed 50 min and 90 min, respectively, to reach equilibrium.

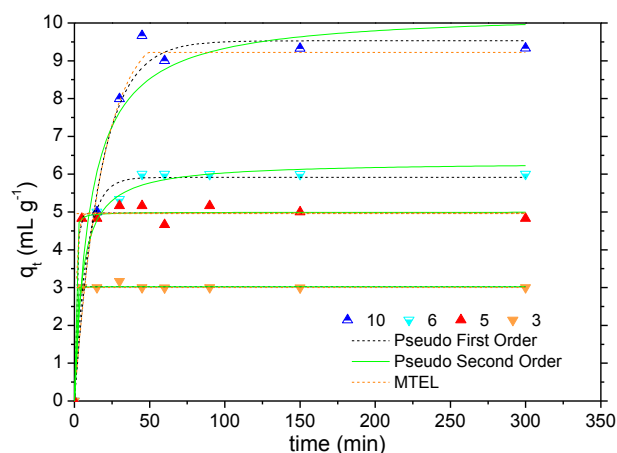


Figure 3: Kinetic curves for diesel and their adjustments to pseudo first, pseudo second and MTEL models. Legend: Hydrocarbon / Organoclay ratio ($\text{mL}\cdot\text{g}^{-1}$).

Table 4 shows the parameters of diesel adsorption for pseudo first order, pseudo second order and MTEL models. The pseudo second order models showed a slightly higher q_e with the same correlation coefficients.

Table 3. Pseudo First Order (PFO), Pseudo Second Order (PSO) and MTEL parameters adjusted for iso-octane adsorption.

Condition ($\text{mL}\cdot\text{g}^{-1}$)	Model	q_e ($\text{mL}\cdot\text{g}^{-1}$)	K_1 (min^{-1})	K_2 ($\text{g}\cdot\text{mL}^{-1}\cdot\text{min}^{-1}$)	K_{ma}	R^2
10	PFO	4.646	0.134			0.851
	PSO	5.012		0.038		0.935
	MTEL	4.645			0.062	0.937
6	PFO	4.337	0.066			0.902
	PSO	4.678		0.025		0.937

	MTEL	4.336		0.048	0.958
	PFO	3.580	0.196		0.839
5	PSO	3.912		0.058	0.915
	MTEL	3.579		0.121	0.927
	PFO	2.865	0.322		0.948
3	PSO	2.985		0.191	0.972
	MTEL	2.865		0.307	0.9769

Table 4. Pseudo First Order (PFO), Pseudo Second Order (PSO) and MTEL parameters adjusted for diesel adsorption.

Condition (mL g ⁻¹)	Model	q _e (mL g ⁻¹)	K ₁ (min ⁻¹)	K ₂ (g mL ⁻¹ min ⁻¹)	K _{ma}	R ²
	PFO	9.53	0.058			0.982
10	PSO	10.307		0.009		0.944
	MTEL	9.220			0.052	0.872
	PFO	5.915	0.13			0.99
6	PSO	6.325		0.033		0.991
	MTEL	5.915			0.129	0.960
	PFO	4.976	0.702			0.987
5	PSO	4.995		1.157		0.987
	MTEL	4.976			0.698	0.994
	PFO	3.023	0.974			0.997
3	PSO	3.023		16.454		0.997
	MTEL	3.000			5.380×10 ⁷	0.999

The adsorption equilibrium reached by N-hexadecane was significantly lower compared to diesel's as shown on Figure 4. Again, the equilibrium time increased as the hydrocarbon/organoclay ratio increased.

For n-hexadecane the MTEL model fitted better the experimental data than PSO and PFO

models for all conditions except the ratio of 10 (mL g⁻¹) (Table 5).

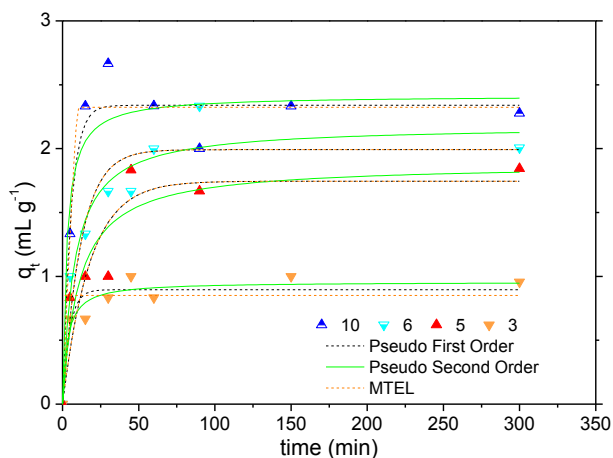


Figure 4: Kinetic curves for n-hexadecane and their adjustments to pseudo first, pseudo second order and MTEL models. Legend: Hydrocarbon / Organoclay ratio (mL.g^{-1}).

The adsorption process seems to be fast for kerosene either, as shown in Figure 5, being the ratio of 10 (mL.g^{-1}) the only condition that not reached equilibrium under 5 minutes.

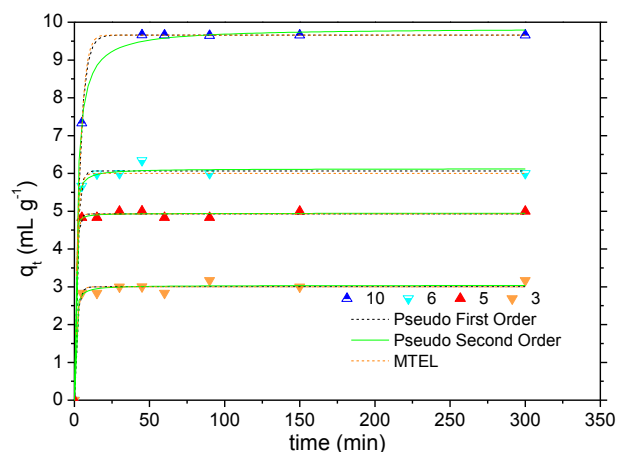


Figure 5: Kinetic curves for kerosene and their adjustments to pseudo first, pseudo second order and MTEL models. Legend: Hydrocarbon / Organoclay ratio (mL.g^{-1}).

Table 5. Pseudo First Order (PFO), Pseudo Second Order (PSO) and MTEL parameters adjusted for n-hexadecane adsorption.

Condition (mL.g^{-1})	Model	q_e (mL.g^{-1})	K_1 (min^{-1})	K_2 ($\text{g mL}^{-1} \text{min}^{-1}$)	K_{tma}	R^2
10	PFO	2.339	0.186			0.943
	PSO	2.416		0.1580		0.894
	MTEL	9.220			0.029	0.996
6	PFO	1.992	0.084			0.898
	PSO	2.180		0.060		0.939
	MTEL	5.915			0.027	0.996
5	PFO	1.745	0.0560			0.817
	PSO	1.880		0.050		0.860
	MTEL	4.976			0.02	0.928
3	PFO	0.895	0.223			0.883
	PSO	0.957		0.343		0.933
	MTEL	0.850			15.638	0.914

The adjusted parameters for kerosene kinetics are shown on Table 4. As can be seen, both models fitted quite well, with correlation coefficient over 0.98 on all cases and similar values for q_e .

The adsorption capacity order observed, from the greatest to smallest among the pollutants tested, was:

diesel > kerosene > gasoline > iso-octane >> n-hexadecane

This difference may be due because, as a mixture of hydrocarbons, gasoline, diesel and kerosene, may have smaller hydrocarbons which would have higher mobility and be adsorbed faster. Also, these fuels have many additives that can play a role in the process (ADAM et. al., 2002).

Table 6. Pseudo First Order (PFO), Pseudo Second Order (PSO) and MTEL parameters adjusted for kerosene adsorption.

Condition (mL g ⁻¹)	Model	q _e (mL g ⁻¹)	K ₁ (min ⁻¹)	K ₂ (g mL ⁻¹ min ⁻¹)	K _{ma}	R ²
10	PFO	9.659	0.285			1.000
	PSO	9.846		0.0600		0.999
	MTEL	9.659			0.266	0.999
6	PFO	6.066	0.543			0.996
	PSO	6.124		0.427		0.996
	MTEL	6.000			0.578	0.998
5	PFO	4.928	0.7860			0.997
	PSO	4.945		1.522		0.998
	MTEL	4.928			0.774	0.999
3	PFO	3.000	0.576			0.984
	PSO	3.038		0.722		0.987
	MTEL	3.000			0.576	0.993

4. CONCLUSIONS

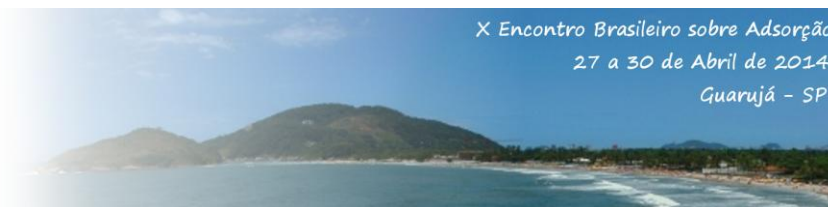
The organoclay presented higher adsorption for all three fuels tested (gasoline, diesel and kerosene), compared to the pure components (iso-octane and hexadecane).

The highest adsorption capacities observed for each hydrocarbon studied were 10.307 mL g⁻¹ for diesel, 9.659 mL g⁻¹ for kerosene, 7.834 mL g⁻¹ for gasoline, 5.012 mL g⁻¹ for iso-octane and 2.416 mL g⁻¹ for n-hexadecane.

Tests with other hydrocarbons of different sizes and polarities may give a hint on this adsorption process.

In this process, n-hexadecane and iso-octane cannot be considered pure components representatives for diesel and gasoline, respectively.

The MTEL model adjusted well for the data suggesting low intraparticle diffusion and rapid equilibrium between the layer and the adsorbent. Also it showed higher mass transfer rates for lower contaminant/organoclay ratios.



This clay may not be suitable for batch adsorption as the sticky consistency acquired with gasoline, diesel and kerosene, adhering to the recipient walls of the vessel. However, its use on continuous process cannot be disposed yet. A better use of it might be as reactive/contention barrier, acting on preventing the contamination. Since the contaminated organoclay floats on water it could also be powdered for oil spill contention.

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6. ACKNOWLEDGEMENTS

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