ARTICLE IN PRESS

Colloids and Surfaces A xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Colloids and Surfaces A

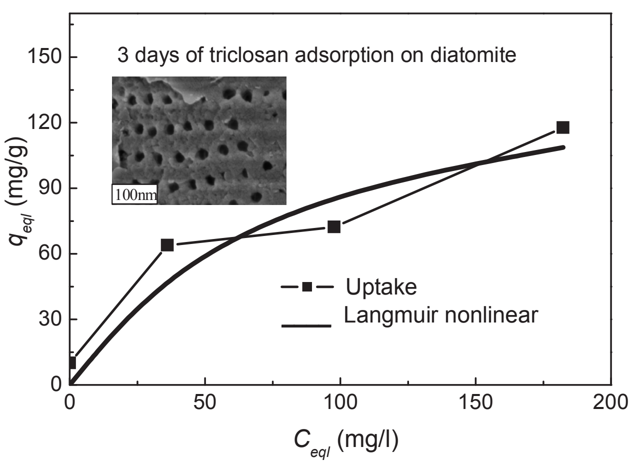
journal homepage: www.elsevier.com/locate/colsurfa

# Triclosan adsorption from model system by mineral sorbent diatomite

Altynay A. Sharipova[a,b,*], Saule B. Aidarova[a], Neila Ye. Bekturganova[a], Aiym Tleuova[a,b], Moldir Kerimkulova[c], Orynkul Yessimova[c], Talmira Kairaliyeva[b], Olena Lygina[d], Svitlana Lyubchik[d], Reinhard Miller[b]

[a] Kazakh National Research Technical University named after K.I. Satpayev, Almaty, Kazakhstan
[b] Max-Planck Institute of Colloids and Interfaces, Potsdam, Golm, Germany
[c] Kazakh national university named after al-Farabi, Kazakhstan
[d] Universidade Nova de Lisboa, Lisboa, Portugal

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Keywords:*
Triclosan
Adsorption
Diatomite
Sorbents
Adsorption isotherms

## ABSTRACT

Adsorption of model systems of triclosan by mineral sorbent diatomite is studied. The triclosan equilibrium concentration was measured spectrophotometrically, the morphology of the diatomite characterized using scanning electron microscopy and the amount of the adsorbed triclosan on the diatomite quantified by a mass balance. Adsorption isotherms were analyzed according to the linear/nonlinear form of Langmuir, Freundlich, Sips and Toth isotherm models isotherms, using AMPL software. It is shown that nonlinear Langmuir and Sips isotherm model provided suitable fitting results and no pronounced difference in adsorption efficiency between isotherms measured after 1, 2 and 3 days adsorption was observed. Determined maximum adsorption capacity of diatomite towards triclosan $q_s$ is 140 mg/g. Averaged calculated values of $\Delta G$ are −9.9 and −9.6 kJ/mol for Langmuir and Sips models respectively. The negative sign of such values indicates spontaneous, physical in nature adsorption.

* Corresponding author at: Kazakh National Research Technical University named after K.I. Satpayev, Almaty, Kazakhstan.
*E-mail addresses:* altynay.sharipova@mpikg.mpg.de, a_sharipova85@mail.ru (A.A. Sharipova).

http://dx.doi.org/10.1016/j.colsurfa.2017.06.012
Received 25 October 2016; Received in revised form 4 April 2017; Accepted 7 June 2017
0927-7757/ 

Please cite this article as: Sharipova, A.A., Colloids and Surfaces A (2017), http://dx.doi.org/10.1016/j.colsurfa.2017.06.012

**Table 1**
Chemical structure of diatomite sorbent.

| Sorbent | $SiO_2$ % | $Al_2O_3$ | $Fe_2O_3$ % | CaO % | $TiO_2$ % | MgO % | $Na_2O$ % | $K_2O$ % |
|---|---|---|---|---|---|---|---|---|
| Diatomite | 64–83 | 0.08–16.3 | 2–8 | 0.2–3.5 | 0.72 | 0.7–1.8 | 0.3–0.8 | 0.7–1.0 |

## 1. Introduction

Triclosan is a common synthetic antimicrobial agent widely used in domestic and consumer care products such as toothpaste, mouthwash, and soaps [1–22]. Triclosan is additionally used as a stabilizing agent in many cosmetics and detergents [1]. It inhibits bacterial growth by blocking the biosynthesis of lipids [2–4]. Triclosan has also been linked to a number of health and environmental effects, such as irritation of skin, susceptibility to allergies, as well as other environmental toxicities of the aquatic and terrestrial environment [5,6]. For example, triclosan has an impact on earthworms (Eisenia fetida) [7] and the Japanese medaka fish [8].

Its widespread use resulted in increased concentrations of triclosan in wastewater treatment plants and sewage water intakes. That is why triclosan biodegradation in the environment and wastewater has recently become an important research topic [1–23]. It was shown that 79% of triclosan was removed from biological wastewater treatment processes due to the presence of triclosan-degrading bacteria in the activated sludge [9]. A removal of about 90% was measured in wastewater treatment plants (WWTP) employing a conventional activated sludge process of which 40–60% was due to biodegradation while the remainder was due to sorption to the sludge [3,9,10].

Nowadays, one of the most promising challenges is the processing of natural raw materials, the utilization of wastes and attraction of ecologically friendly secondary products in economic recycling. At present, different sorbents are used for the treatment of industrial waste water [11–25], including special artificial adsorbents with hierarchical nanostructures [23–25]. Aluminosilicates like diatomite, kaolinite, bentonite and etc. [13,14,22] can be interesting to study as sorbents for waste water treatment due to their folded structure which is reflected in high dispersity, hydrophilicity and good ion exchange properties. Moreover, they are low cost sorbents with excellent sources of raw materials.

Diatomite (SiO2·nH2O), or diatomaceous earth, is a soft lightweight rock available in large deposits around the world [22]. This pale colored sedimentary rock consists principally of silica microfossils of aquatic, unicellular alga varying in shape and size of diatom [26]. Diatomite is highly porous, with its structure containing up to 80–90% voids. It is used in a number of industrial applications, e.g. as filtration medium for various beverages, and inorganic and organic chemicals, and as adsorbent for pet litter and oil spills [27]. Although diatomite has a unique combination of physical and chemical properties its use as an adsorbent in waste water treatment has not been extensively investigated yet [28,29].

In this paper we present results of triclosan adsorption from model systems by the mineral sorbent diatomite. The triclosan equilibrium concentration was measured spectrophotometrically, the morphology of the diatomite was characterized by scanning electron microscopy, and the amount of the triclosan adsorbed on the diatomite was quantified by a mass balance method.

## 2. Experiment

Triclosan (97%) was purchased from Aldrich. The adsorption process of triclosan was studied in a static mode at the adsorption equilibrium in "triclosan-sorbent" systems. Each adsorption run was performed for a model solution of triclosan at a given pH in two different batch modes: at varied triclosan concentrations (from 10 to 400 ppm) and at fixed sorbent loading (at 1 g/l), respectively, aiming at studies of the equilibrium conditions. This process was carried out at constant temperature (24 ± 1 °C). At the end of the experiments, the adsorbent was removed by filtration through membrane filters with a pore size of 0.45 μm. The triclosan equilibrium concentration was measured spectrophotometrically with a Cary 50 Cons at a fixed wavelength of 280 nm [30,31].

The experiments on triclosan adsorption were performed from ethanol solutions instead of standard aqueous solutions [32,33]. Such step allows a large increase in the concentration of the adsorbate in solution due to its 100% solubility in ethanol, and hence it was possible to fully explore the adsorption capacity of diatomite towards triclosan.

As a sorbent, we used the mineral diatomite produced in the Aktobe deposit of West Kazakhstan. Low temperature Nitrogen adsorption analyzed by the BET method was used to characterize diatomite.

The chemical structure and characteristics of the diatomite is given in Tables 1 and 2. As it is shown the basic components of diatomite are silicium dioxide $SiO_2$ (60–70%) and aluminium oxide (9%) with specific surface area equaled to 32 $m^2/g$.

The structure of the sorbent was studied using cryo-scanning electron microscopy, SEM (Zeiss Gemini LEO 1550). For the characterization, a droplet of the aqueous particle suspension was placed on a sample holder and left to dry at atmospheric pressure and room temperature and followed by sputtering with a gold/palladium mixture to avoid electron charging of the samples during SEM analysis. The samples were studied using an operating voltage of 3 kV and different magnification.

The amount of the adsorbed triclosan on the diatomite was quantified by a mass balance method. The adsorption capacity of the sorbent ($q_{eql}$) can be expressed in terms of the triclosan amount adsorbed per unit of sorbent mass, i.e. the uptake (mg/g) is given by:

$$q_{eql} = \frac{(C_{init} - C_{eql})}{m} \tag{1}$$

The sorption efficiency of the system (*Rem%*) indicated by the percentage of removed triclosan relative to the initial amount, i.e. Rem in% is given by

$$Rem\ \% = \frac{(C_{init} - C_{eql})}{C_{init}} \times 100 \tag{2}$$

where $C_{init}$ and $C_{eql}$ are, respectively, the initial and equilibrium concentrations of triclosan in solution (mg/l) and m is the sorbent dosage (g/l).

Fitting the experimental adsorption data was performed by several well-known isotherm models.

### 2.1. Langmuir isotherm

This model assumes monolayer coverage and constant binding energy between surface and adsorbate [34]:

**Table 2**
Characteristics of diatomite.

| Sorbent | Density, ρ, $cm^3/g$ | Specific surface area, $m^2/g$ | Sizes of pores, nm |
|---|---|---|---|
| Diatomite | 2.17–2.26 | 32 | 3.8 |