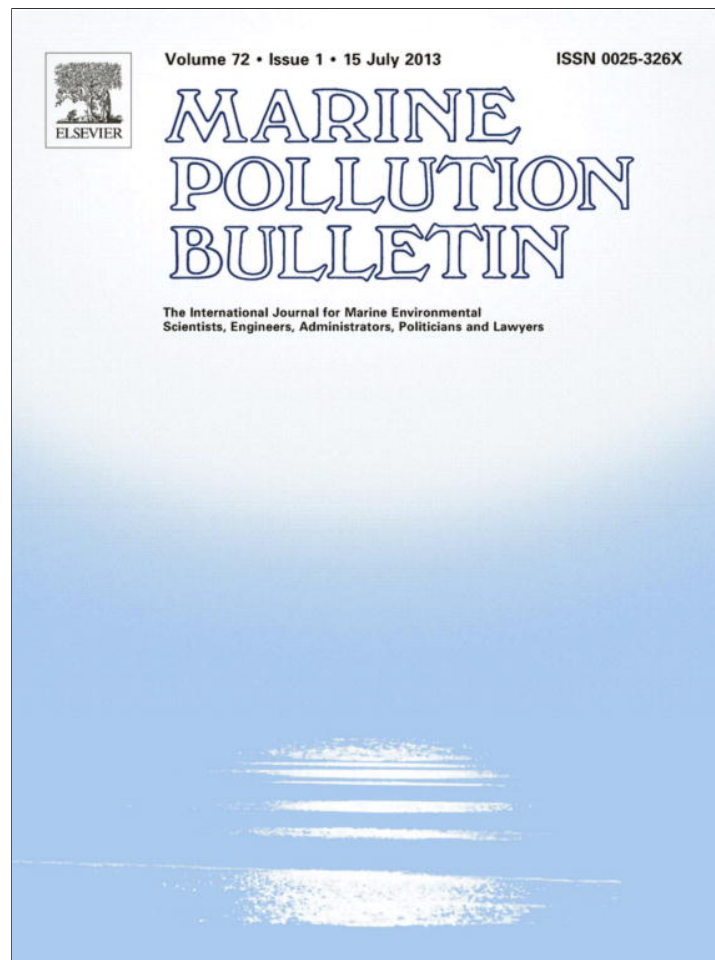


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Kinetics and equilibrium models for the sorption of tributyltin to *n*ZnO, activated carbon and *n*ZnO/activated carbon composite in artificial seawater

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ABSTRACT

The removal of tributyltin (TBT) from artificial seawater using *n*ZnO, activated carbon and *n*ZnO/activated carbon composite was systematically studied. The equilibrium and kinetics of adsorption were investigated in a batch adsorption system. Equilibrium adsorption data were analyzed using Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) isotherm models. Pseudo first- and second-order, Elovich, fractional power and intraparticle diffusion models were applied to test the kinetic data. Thermodynamic parameters such as ΔG° , ΔS° and ΔH° were also calculated to understand the mechanisms of adsorption. Optimal conditions for the adsorption of TBT from artificial seawater were then applied to TBT removal from natural seawater. A higher removal efficiency of TBT (>99%) was obtained for the *n*ZnO/activated carbon composite material and for activated carbon but not for *n*ZnO.

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1. Introduction

Tributyltin (TBT) is an organotin compound (OTC) that is used in the manufacturing of antifouling paints and is highly effective against fouling organisms. TBT is used to prevent the growth of fouling organisms on marine structures and vessels. TBT toxicity has been a large problem in aquatic environments. High concentrations of TBT have been found in the tissues of marine mammals and its presence has been linked to marine mammal mass mortalities. TBT causes imposex and calcification abnormalities in mollusks. TBT exposure in humans is thought to come from the consumption of seafood, which is believed to be the most probable source of TBT. Although the use of paints that contain TBT has been banned (Brandli et al., 2009), these paints are still applied to large shipping vessels, and some third world countries still apply them to smaller vessels. Therefore, high concentrations of TBT are still found in the marine environment.

Song et al. (2005) reported that TBT could be removed from wastewater by extraction with diesel oil. Arevalo and Calmano (2007) evaluated the suitability of anode materials to eliminate TBT electrochemically from shipyard process water, and Kotrikla (2009) reported the use of hydrogen peroxide as a photocatalyst to enhance the rate of photodegradation of TBT. However, adsorption has proven to be a reliable treatment method because it has a low capital investment cost, it is simple to design, it is easy to operate and it is insensitive to toxic substances (Bazrafshan

et al., 2012). Adsorption is therefore an important process that can be used to reduce the concentration of TBT in harbors and/or in wastewaters before they are discharged into the marine environment. The adsorption of TBT onto sediments, clay (Hoch et al., 2002), mineral surfaces (Weidenhaupt et al., 1997), dead and live cells of microalgal species (Tam et al., 2002), municipal solid waste compost (Said-Pullicino and Vella, 2005) and iron oxides (Ottosen et al., 2005) has been reported; however, the use of oxides for the remediation of OTC usually resulted in between 56% and 76% OTC removal (Honda and Takahashi, 2006). Microbial remediation (Tam et al., 2002) also appears to be a possible removal method but only if the concentration of OTC is not too high. Some of the available organotin remediation techniques take 1–2 weeks of adsorption processes before notable percentages of OTC can be removed. Data on the sorption of TBT from seawater to oxides and to carbon are limited, and work describing the use of composite materials for the adsorption of TBT has not been conducted.

In this work, the adsorption potential of *n*ZnO, of activated carbon and of a composite prepared from these precursors (*n*ZnO/activated carbon composite) in removing TBT from artificial seawater was examined. The effects of the adsorbent amount, the contact time, the pH, the stirring speed, the initial concentration and the temperature on the adsorption capacity of the precursors and of the composite were investigated. The experimental results were analyzed using kinetic and isotherm models. Thermodynamic parameters, such as the Gibbs free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°), were also calculated. The adsorbents before and after adsorption were characterized using a scanning electron microscope (SEM). Finally, optimal

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Nomenclature

q_e	amount of TBT adsorbed at equilibrium per unit weight of the adsorbent (mg/g)	A_{\max}	maximum monolayer TBT adsorption capacity (mg/g)
q_t	amount of TBT adsorbed at any time (mg/g)	k_F	Freundlich isotherm constant
k_1	pseudo first-order rate constant (min)	n_F	exponent in Freundlich isotherm
k_2	rate constant of pseudo second-order adsorption (g/mg min)	k_T	Temkin isotherm constant
h_o	initial adsorption rate (mg/g/min)	b_T	constant in Temkin isotherm (J/mol)
α	constant in the Elovich rate equation (g min ² /mg)	n_T	constant in Temkin isotherm
β	constant in the Elovich rate equation (g min/mg)	k_{D-R}	Dubinin–Radushkevich (D–R) isotherm constant
k_p	rate coefficient for particle-diffusion controlled process	ε	Polanyi potential = $RT \ln(1 + 1/c_e)$
k	fractional power rate constant	E	mean free energy (J/mol)
c_a	amount of adsorbed TBT on the adsorbent (mg/g)	q_m	maximal substance amount of adsorbate per gram of the adsorbent
c_e	equilibrium concentration of TBT in the bulk solution (mg/L)	ΔG°	standard Gibbs free energy (kJ/mol)
c_o	initial concentration of the TBT aqueous solution	ΔH°	standard enthalpy change (kJ/mol)
R	gas constant (J/mole K)	ΔS°	standard entropy change (J/K/mol)
k_L	Langmuir isotherm constant	T	absolute temperature
		K_c	thermodynamic equilibrium constant

conditions for the adsorption of TBT from artificial seawater were applied to remove TBT from natural seawater.

2. Methods and materials

2.1. Adsorbents

Activated carbon (100–400 mesh) and Zinc oxide NanoGard® (particle size 40–100 nm APS powder) were purchased from Sigma–Aldrich, USA. A composite material made from these adsorbents (activated carbon and nZnO, ratio 1:1) was prepared following methods reported by Ayanda et al. (2013). The physicochemical properties of the precursors and of the composite are listed in Table 1.

2.2. Chemical reagents

Tributyltin chloride (purity 98%), methanol, hexane, acetic acid, sodium hydroxide and sodium tetraethylborate (NaBEt₄) were purchased from Sigma–Aldrich, USA, while carbonate, sulfate and chloride salts, which were used to prepare the artificial seawater, were supplied by Merck. The stock solution containing 1000 mg/L TBT was prepared daily by dissolving TBT in methanol. This solution was stored in the dark at 4 °C. Working solutions of the derivatizing agent were made daily by dissolving 1.0 g NaBEt₄ in 100 mL of methanol. An acetate buffer (3 mL acetic acid plus 4.0 g sodium acetate filled to 1 L with deionized water) with a pH of 4.5 was also prepared.

Artificial seawater was prepared by adding 86.6 mL of 5 M NaCl, 9.0 mL of 1.0 M KCl, 9.27 mL of 1.0 M CaCl₂·2H₂O, 4.68 mL of 4.9 M MgCl₂·2H₂O, 12.75 mL of 2.0 M MgSO₄·7H₂O and 2.15 mL of 1.0 M NaHCO₃ and diluting the seawater with 1 l of Milli-Q water. This artificial seawater solution had a pH of 8 (marine condition). A tris-HCl-buffer was not used in the solution because it resulted in a lower pH (Brandli et al., 2009). A trisHCl-buffer and NaOH solution was used, however, to adjust the pH during the study when the effect of pH was examined.

2.3. Analysis of tributyltin

The concentration of TBT in artificial and natural seawater before and after the adsorption studies was determined after derivatization by adding 2 mL of acetate buffer (pH = 4.5) and 1.0 mL of 1% NaBEt₄ and extracting the solution into hexane by horizontally

Table 1

Physicochemical properties of activated carbon, nZnO and nZnO/activated carbon composite.

Characteristics	Activated carbon	nZnO	nZnO/activated carbon
pH	3.30	6.71	6.47
PZC	2.06	6.80	6.24
Surface area (m ² /g)	1156.6	14.41	275.49
Micropore area (m ² /g)	442.7	3.18	82.62
Ash content (%)	0.45 ± 0.07	99.2 ± 0.14	44.25 ± 0.07
Carbon content (%)	71.4	0.42	34.72
Nitrogen content (%)	0.35	BD	0.23
Hydrogen content (%)	2.82	BD	2.08

BD-below detection limit.

shaking it in a separation funnel. The extracts were reduced to 1 mL and were analyzed using a GC-FPD (Shimadzu GC-2010 Plus) with a capillary column HP 5 (5% phenyl methyl siloxane, 30 m × 0.25 mm, i.d. and film thickness 0.25 μm). The temperature was initially set to 60 °C, and the extract remained this temperature for 1 min. Then, the temperature rose to 280 °C at a rate of 10 °C/min, and the extract remained this temperature for 4 min. The injection and detector temperatures were 270 °C and 300 °C, respectively, and the carrier gas was high purity helium.

2.4. Adsorption experiments

TBT in artificial seawater was poured into 250 mL Erlenmeyer flasks containing accurately weighed amounts of the adsorbent to conduct the adsorption experiments. The flasks were shaken at room temperature (20 °C) for a prescribed length of time to obtain equilibrium. The adsorbents were removed by filtration, and the equilibrium concentrations of TBT were determined. The concentration of TBT remaining in the solution was calculated by taking the difference of the initial and the final TBT concentrations. Adsorption capacities were obtained using a mass balance equation (Ayanda et al., 2012):

$$q = \frac{(c_o - c_e)V}{W} \quad (1)$$

where q is the equilibrium adsorption capacity per gram dry weight of the adsorbent (mg/g), c_o is the initial concentration of TBT in the

solution (mg/L), c_e is the final or equilibrium concentration of TBT in the solution (mg/L), V is the volume of the solution (L), and W is the dry weight of the adsorbent (g).

The adsorption kinetic experiments were conducted at room temperature using 100 mg/L of the TBT solution with 0.5 g of adsorbents per 25 mL; pH remained at 8, the stirring speed was 160 rpm and the contact time was 10–70 min. The adsorption isotherms were investigated by varying the initial TBT concentrations from 12.5 to 200 mg/L at an optimized adsorbent dose, contact time, pH and stirring speed, which were established after optimizing the working parameters. The equilibrium data were fitted using Langmuir, Freundlich, Temkin and Dubinin–Radushkevich (D–R) isotherm models.

The effect of pH on TBT adsorption was studied by varying the pH from 4 to 9. The effect of stirring speed on TBT adsorption was studied by varying the mixing speeds from 160 to 200 rpm. Finally, the effect of temperature on the adsorption of TBT was evaluated after optimizing all of the working parameters for TBT adsorption at initial TBT concentrations of 100 mg/L solution with 0.5 g of adsorbents per 25 mL, pH 8, contact time of 60 min and a stirring speed of 200 rpm. Here, the thermodynamic parameters of TBT adsorption in artificial seawater were obtained.

3. Theory

3.1. Adsorption kinetics

Pseudo first-order, pseudo second-order, Elovich, fractional power and intraparticle diffusion rate equations have been used to model the kinetics of TBT adsorption. The pseudo first-order equation is generally expressed as:

$$d_q/d_t = k_1(q_e - q_t) \quad (2)$$

where q_e is the amount of TBT adsorbed at equilibrium per unit weight of the adsorbent (mg/g), q_t is the amount of TBT adsorbed at any time (mg/g) and k_1 is the pseudo first-order rate (constant/min).

After the equation is integrated and boundary conditions ($t = 0-t$ and $q_t = 0-q_t$) are applied the equation becomes:

$$\log(q_e - q_t) = \log q_e - k_1 t / 2.303 \quad (3)$$

The values of $\log(q_e - q_t)$ were linearly correlated with t . The plot of $\log(q_e - q_t)$ versus t should give a linear relationship from which k_1 and q_e can be determined from the slope and intercept of the relationship, respectively.

The pseudo second-order adsorption kinetic rate equation is expressed as:

$$d_q/d_t = k_2(q_e - q_t)^2 \quad (4)$$

where k_2 is the rate constant of the pseudo second-order adsorption equation (g/mg min). For the boundary conditions ($t = 0-t$ and $q_t = 0-q_t$), the integrated form of Eq. (4) becomes:

$$t/q = 1/h_0 + 1/q_e(t) \quad (5)$$

where h_0 is the initial adsorption rate. If the second-order kinetic equation is applicable, the plot t/q against t in Eq. (5) should give a linear relationship from which the constants q_e and h_0 can be determined.

When t tends to 0, h_0 is defined as:

$$h = k_2 q_e^2 \quad (6)$$

where k_2 is the pseudo second-order rate constant (g/mg/min), and k_2 is calculated for the adsorption of TBT in artificial seawater (Basha and Murthy, 2007).

The Elovich model is generally described as:

$$(dq_t/dt) = \alpha \exp(-\beta q_t) \quad (7)$$

Ho and McKay (2002). After applying the boundary conditions ($q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$), the simplified form of the Elovich equation is expressed as:

$$q_t = (1/\beta) \cdot \ln(\alpha/\beta) + (1/\beta) \cdot \ln(t) \quad (8)$$

where q_t is the amount of adsorbate per unit mass of sorbent at time (t), and α and β are the constants during any one experiment (α is the initial adsorbate sorption rate and β is the desorption constant). A plot of q_t versus $\ln(t)$ should be linearly related with a slope of $(1/\beta)$ and an intercept of $[(1/\beta) \cdot \ln(\alpha/\beta)]$.

The Fractional Power or Power Function model can be expressed as:

$$q_t = kt^v \quad (9)$$

The linearized form of Eq. (9) is given as:

$$\log q_t = \log k + v \log t \quad (10)$$

where q_t is the amount of sorbate per unit mass of sorbent, k is a constant, t is time, and v is a positive constant (<1). A plot of $\log q_t$ versus $\log(t)$ should be linearly related with a slope of v and an intercept of $\log k$.

The intra-particle diffusivity is expressed as:

$$\ln(1 - \alpha) = -k_p t \quad (11)$$

where α is fractional attainment to equilibrium, k_p is the rate coefficient for particle-diffusion controlled process corresponding to the particle size of the adsorbent, t is time and $\ln(1 - \alpha)$ is a measure of the intra-particle diffusivity (Igwe et al., 2008). $\ln(1 - \alpha)$ was plotted against time t and the rate coefficient (k_p) was calculated from the slope of the line.

3.2. Adsorption isotherm modeling

Isotherms are the equilibrium relationships between the concentration of adsorbate in the solid phase and in the liquid phase. The maximum adsorption capacity can be obtained from the isotherms. Data from isotherms provide information on the capacity of the sorbent or on the amount required to remove a unit mass of pollutant under the system conditions. These data were subjected to four different adsorption isotherms.

Langmuir isotherm models are usually used to describe the adsorption of solute from liquid solutions. This model assumes monolayer adsorption onto a homogeneous surface with a finite number of identical sites. The linearized form of the Langmuir isotherm model can be written as:

$$\frac{c_e}{c_a} = \frac{1}{A_{\max} k_L} + \frac{1}{A_{\max}} \cdot c_e \quad (12)$$

where c_e is the equilibrium concentration of TBT in the solution (mg/L), c_a is the TBT adsorption capacity for the adsorbents at equilibrium (mg/g), A_{\max} is the maximum monolayer TBT adsorption capacity (mg/g), and k_L is the Langmuir isotherm constant related to the free energy of adsorption (L/mg) (Lin et al., 2011). The values of A_{\max} and k_L can be calculated from the intercept and the slope of the linearized form of the Langmuir isotherm.

The Freundlich isotherm model is applicable to both monolayer (chemisorption) and multilayer adsorption (physisorption) and is based on the assumption that the adsorbate adsorbs onto the heterogeneous surface of an adsorbent. The linearized form of the Freundlich isotherm model can be written as:

$$\log c_a = \log k_F + \frac{1}{n_F} \log c_e \quad (13)$$

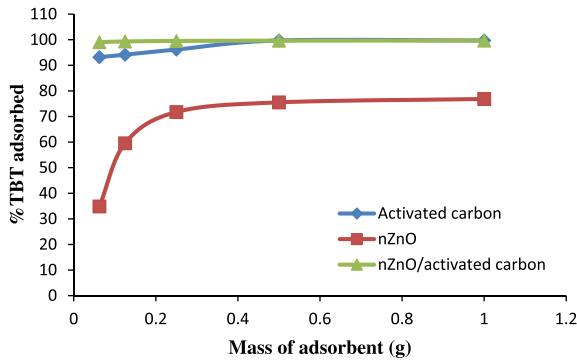


Fig. 1. Adsorption efficiencies of TBT onto activated carbon, nZnO and nZnO/activated carbon composite. *Experimental conditions:* TBT concentration = 100 mg/L, TBT solution volume = 25 mL, contact time = 60 min, stirring speed = 160 rpm, and temperature = 20 °C.

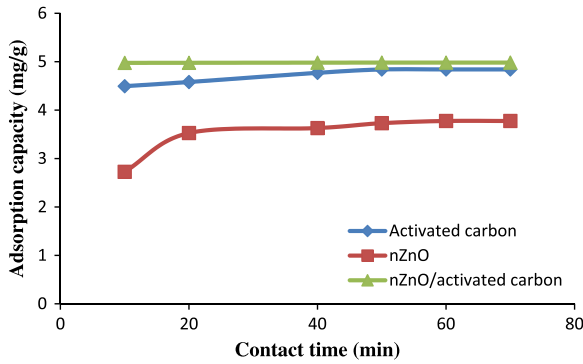


Fig. 2. The effect of contact time on TBT adsorption onto activated carbon, nZnO and nZnO/activated carbon composite. *Experimental conditions:* TBT concentration = 100 mg/L, TBT solution volume = 25 mL, mass of adsorbent = 0.5 g, stirring speed = 160 rpm, and temperature = 20 °C.

where k_F and n_F are the Freundlich constants [$\text{mg/g} (\text{L}/\text{mg})^{1/n}$], which are related to the adsorption capacity and adsorption intensity, respectively (Sheela et al., 2012). The values of k_F and n_F can be calculated from the intercept and the slope of the linearized form of the Freundlich isotherm, respectively.

The Temkin isotherm model assumes that the adsorption energy decreases linearly with the surface coverage due to adsorbent–adsorbate interactions. The linearized form of the Temkin isotherm model can be written as:

$$c_a = n_T \ln k_T + n_T \ln c_e \quad (14)$$

where $n_T = RT/b_T$, b_T is the Temkin constant related to the heat of sorption (J/mol), and k_T is the Temkin isotherm constant (L/g) (Boparai et al., 2010). The values of n_T , b_T and k_T can be calculated from the intercept and the slope of the linearized form of the Temkin isotherm.

The D–R isotherm model is a semi-empirical equation where adsorption follows a pore filling mechanism. It assumes that the adsorption has a multilayer character involving van der Waals forces and it is applicable for physical adsorption processes (Hudson and Yang, 1997). The linear form of the D–R isotherm model is expressed as:

$$\ln c_a = \ln q_m - k_{D-R} \varepsilon^2 \quad (15)$$

where q_m is the maximum TBT adsorption capacity (mg/g), k_{D-R} is the D–R constant related to free energy, R is the gas constant (8.314 J/mol K), T is the absolute temperature (K) and ε is the Polanyi potential which is defined as:

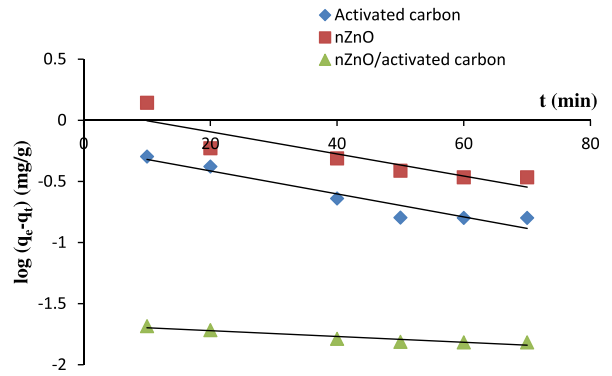


Fig. 3. Pseudo first-order rate equation plot for TBT adsorption onto activated carbon, nZnO and nZnO/activated carbon composite.

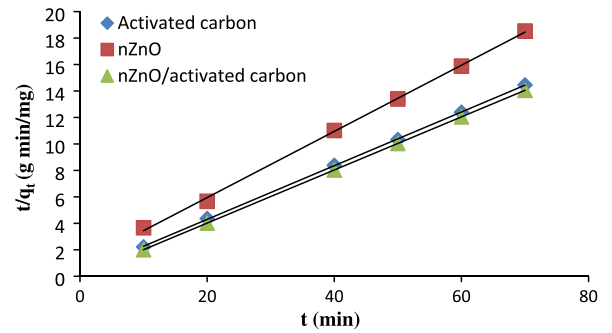


Fig. 4. Pseudo second-order rate equation plot for TBT adsorption onto activated carbon, nZnO and nZnO/activated carbon composite.

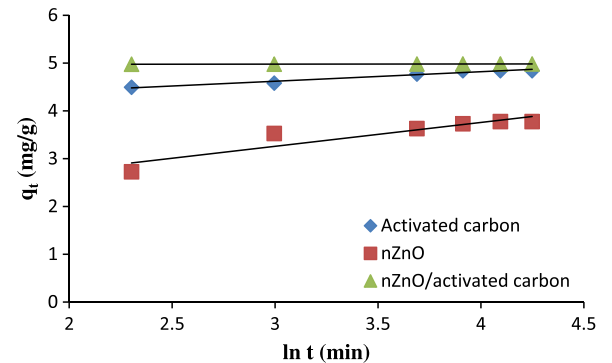


Fig. 5. Elovich rate equation plot for TBT adsorption onto activated carbon, nZnO and nZnO/activated carbon composite.

$$\varepsilon = RT \ln(1 + 1/c_e) \quad (16)$$

The values of q_m and k_{D-R} can be calculated from the intercept and the slope of the linearized form of the D–R isotherm, while the mean free energy (E) can be calculated using:

$$E = 1/\sqrt{2}k_{D-R} \quad (17)$$

3.3. Thermodynamic parameters

Thermodynamic parameters can be determined from the thermodynamic equilibrium constant, K_c : (Eq. (18)). The standard Gibbs free energy ΔG° (kJ/mol) was calculated using Eq. (19), while the values of the standard enthalpy change ΔH° (kJ/mol) and the

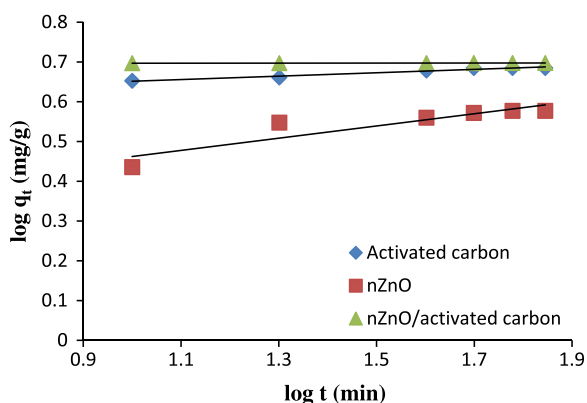


Fig. 6. Fractional power rate equation plot for TBT adsorption onto activated carbon, nZnO and nZnO/activated carbon composite.

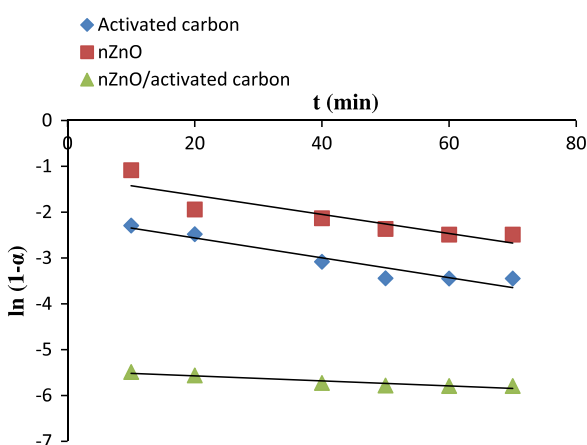


Fig. 7. Intraparticle diffusivity plot for TBT adsorption onto activated carbon, nZnO and nZnO/activated carbon composite.

Table 2

Kinetic model parameters for TBT adsorption onto activated carbon, nZnO and nZnO/activated carbon composite.

Models	Activated carbon	nZnO	nZnO/activated carbon
<i>Pseudo first-order</i>			
k_1 (min^{-1})	0.0216	0.0207	0.0055
q_e (mg/g)	0.5944	1.2209	0.0212
R^2	0.9200	0.8152	0.9098
<i>Pseudo second-order</i>			
q_e (mg/g)	4.9309	4.00	4.9826
h_0 (mg/g/min)	4.0650	1.0549	294.1176
k_2 (g/mg/min)	0.1672	0.0659	11.8470
R^2	0.9999	0.9991	1.000
<i>Elovich</i>			
β (g min/mg)	5.0025	2.002	322.58
α (g min^2 /mg)	2.712×10^9	67.9095	3.9431×10^{698}
R^2	0.9651	0.8530	0.9734
<i>Fractional power</i>			
v (min^{-1})	0.0428	0.1538	0.0006
k_3 (mg/g)	4.0616	2.0342	4.9682
k_3v (mg/g/min)	0.1738	0.3129	0.0029
R^2	0.9660	0.8327	0.9734
<i>Intraparticle diffusivity</i>			
k_p (min^{-1})	0.0217	0.0208	0.0055
R^2	0.9200	0.8152	0.9098

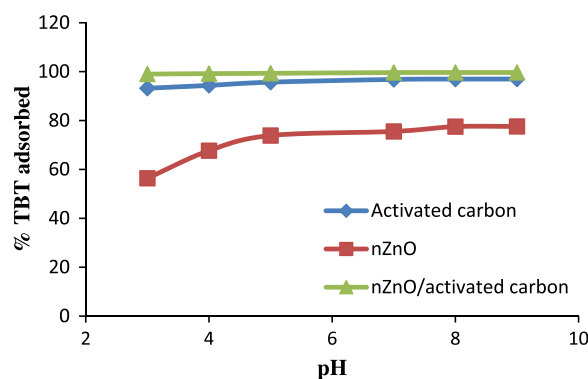


Fig. 8. The effect of pH on TBT adsorption onto activated carbon, nZnO and nZnO/activated carbon composite. Experimental conditions: TBT concentration = 100 mg/L, TBT solution volume = 25 mL, mass of adsorbent = 0.5 g, contact time = 60 min, stirring speed = 160 rpm, and temperature = 20 °C.

standard entropy change ΔS° (J/K/mol) were calculated from the intercept and the slope of the linear plot of $\log K_c$ versus $1/T$.

$$K_c = c_a/c_e \quad (18)$$

$$\Delta G^\circ = -RT \ln k_c \quad (19)$$

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303RT} \quad (20)$$

where c_a is the amount of TBT (mg) adsorbed on the adsorbent per liter of the solution at equilibrium (mg/L), c_e is the equilibrium concentration of TBT in the solution (mg/L), R is the universal gas constant, 8.314 J/mol K, T is absolute temperature, and K_c is the thermodynamic equilibrium constant.

4. Results and discussion

4.1. Effect of adsorption dose

The effect of adsorbent dose on the adsorption of TBT by the activated carbon, the nZnO and the nZnO/activated carbon composite is shown in Fig. 1. The percentage of adsorption increased with increasing adsorbent dose, reaching an optimum at 0.5 g for activated carbon, nZnO and nZnO/activated carbon composite. This corresponded to a 99.71%, 75.53% and 99.63% removal of TBT, respectively. Therefore, 0.5 g was selected to be the optimum adsorbent dose that was utilized for further studies.

4.2. Effect of contact time

Fig. 2 shows the effect of contact time on adsorption of TBT by the precursors and by the composite material. The TBT removal efficiencies at different time intervals ranging from 10 to 70 min were obtained.

The adsorption of TBT increased with time and gradually attained equilibrium after 60 min. The corresponding TBT removal efficiency for activated carbon, nZnO and nZnO/activated carbon composite reached 4.84 mg/g, 3.78 mg/g and 4.98 mg/g, respectively.

4.3. Adsorption kinetics

Figs. 3–7 show the pseudo first-order, pseudo second-order, Elovich, fractional power and intraparticle diffusivity kinetic plots, respectively, and Table 2 provides the evaluated parameters of all the kinetic models. The R^2 value of the pseudo second-order kinetic model was very high ($R^2 > 0.999$) when compared to the other models and the calculated q_e value was in good agreement with the experimental value. This suggests that the pseudo second-order kinetic model is useful for describing the adsorption kinetic

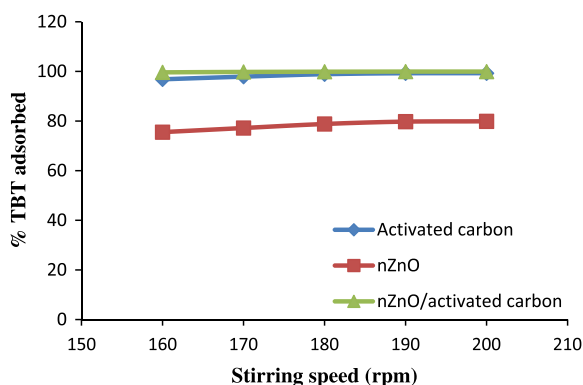


Fig. 9. The effect of stirring speed on TBT adsorption onto activated carbon, nZnO and nZnO/activated carbon composite. *Experimental conditions:* TBT concentration = 100 mg/L, TBT solution volume = 25 mL, mass of adsorbent = 0.5 g, contact time = 60 min, and temperature = 20 °C.

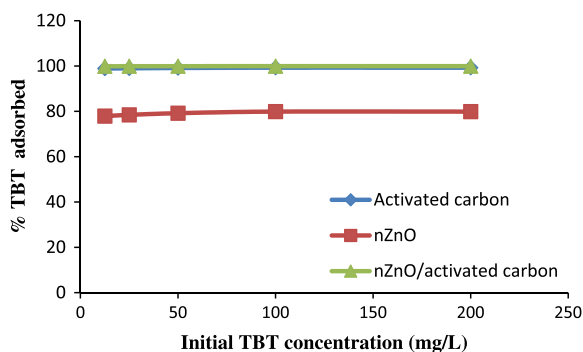


Fig. 10. Percentage of TBT adsorbed by activated carbon, nZnO and nZnO/activated carbon composite at various initial TBT concentrations. *Experimental conditions:* TBT solution volume = 25 mL, mass of adsorbent = 0.5 g, pH = 8, stirring speed = 200 rpm, contact time = 60 min, and temperature = 20 °C.

Table 3

Isotherm constants for the adsorption of TBT onto activated carbon, nZnO and nZnO/activated carbon composite.

Equilibrium models	Activated carbon	nZnO	nZnO/activated carbon
<i>Freundlich</i>			
k_F (mg/g (L/mg) ^{1/n})	6.6589	0.1686	120.14
n_F	0.8375	0.9536	0.8403
R^2	0.9977	0.9999	0.9980
<i>Langmuir</i>			
k_L (L/mg)	-0.2494	-0.0028	-2.7377
A_{max} (mg/g)	-19.0476	-64.52	-19.960
R^2	0.6952	0.6934	0.6683
<i>Temkin</i>			
n_T (L/g)	3.8895	2.7075	3.9179
k_T (mg/L)	6.1492	0.2989	69.6048
b_T (J/mol)	626.30	899.72	621.76
R^2	0.8899	0.8759	0.8953
<i>Dubinin–Redushkevich</i>			
k_{D-R} (J ² /mol ²)	8×10^{-8}	3×10^{-6}	2×10^{-8}
q_m (mg/g)	8.1858	3.7833	21.91
E (J/mol)	2500	408.25	5000
R^2	0.9279	0.7392	0.9922

data of TBT onto the precursors and onto the composite. The intraparticle coefficients for the adsorption of TBT by the precursors and by the composite were also calculated. The experimental data gave linear plots for the fractional attainment of the equilibrium concept. Hence, the adsorption process followed the particle diffusion process.

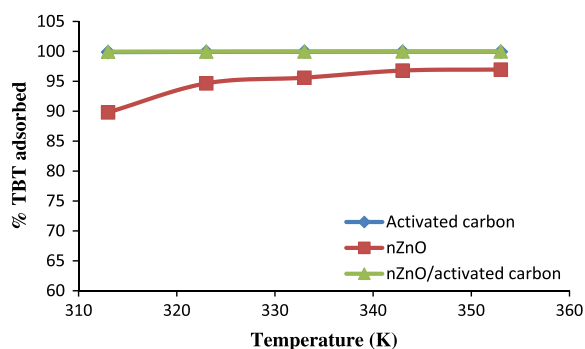


Fig. 11. The effect of temperature on TBT adsorption onto activated carbon, nZnO and nZnO/activated carbon composite. *Experimental conditions:* TBT concentration = 100 mg/L, TBT solution volume = 25 mL, mass of adsorbents = 0.5 g, contact time = 60 min, pH = 8, and stirring speed = 200 rpm.

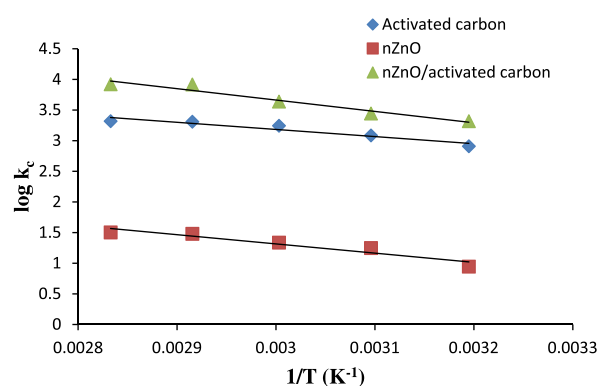


Fig. 12. van't Hoff plot for the adsorption of TBT onto activated carbon, nZnO and nZnO/activated carbon composite.

Table 4

Thermodynamic parameters for the adsorption of TBT onto activated carbon, nZnO and nZnO/activated carbon composite.

Temperature (°C)	ΔG° (kJ/mol)	ΔS° (J/K/mol)	ΔH° (kJ/mol)	K_c
<i>Activated carbon</i>				
40	-17.434	127.830	22.293	812.0
50	-19.080			1218.5
60	-20.679			1753.4
70	-21.731			2039.8
80	-22.425			2082.3
<i>nZnO</i>				
40	-5.663	111.639	28.816	8.81
50	-7.719			17.71
60	-8.523			21.73
70	-9.719			30.21
80	-10.158			31.85
<i>nZnO/activated carbon</i>				
40	-19.88	176.843	35.568	2082.3
50	-21.29			2776.8
60	-23.19			4346.8
70	-25.72			8263.5
80	-26.50			8332.3

The solid residues before and after adsorption (the optimal condition) were subjected to SEM analysis (Fig. 13). The micrographs show that the surface morphology of all the adsorbents changed after adsorption.

The initial adsorption rates (h) calculated from the pseudo second-order rate equation for TBT by activated carbon, nZnO and nZnO/activated carbon composite were 4.0650, 1.0549, and 294.1176 mg/g min, respectively. This indicates that the nZnO/acti-

Table 5
Physicochemical properties of natural seawater.

Parameters	
Turbidity (NTU)	3.26
pH	7.5
Conductivity (mS/cm)	37.56
TDS (ppt)	18.78
Salinity (psu)	22.65
Resistivity (ohms)	26.6
TBT conc. (mg/L)	4.615

ivated carbon composite had a higher adsorption rate than the precursors.

In addition, the power function model satisfactorily described the time-dependence of TBT on various adsorbents because the value of the constant ν was less than 1 and because the regression

coefficients for activated carbon and for the $n\text{ZnO}$ /activated carbon composite were greater than 0.96.

4.4. Effect of pH

The pH of an aqueous solution is an important variable that governs the adsorption of TBT onto adsorbents. The pH affects both the adsorbent and adsorbate chemistry in a solution. The effect of pH on the adsorption of TBT onto the adsorbents was examined for pH values ranging from 3 to 9. Fig. 8 demonstrates that the percentage of TBT adsorbed by the adsorbents steadily increased as the pH of the solution increased from 3 to 8, where equilibrium was attained. This finding supports the results obtained by Weidenhaupt et al. (1997) and Fang et al. (2010). It is therefore evident that the maximum adsorption rate was recorded within the pH range of normal saline water (pH = 8). Activated carbon, $n\text{ZnO}$

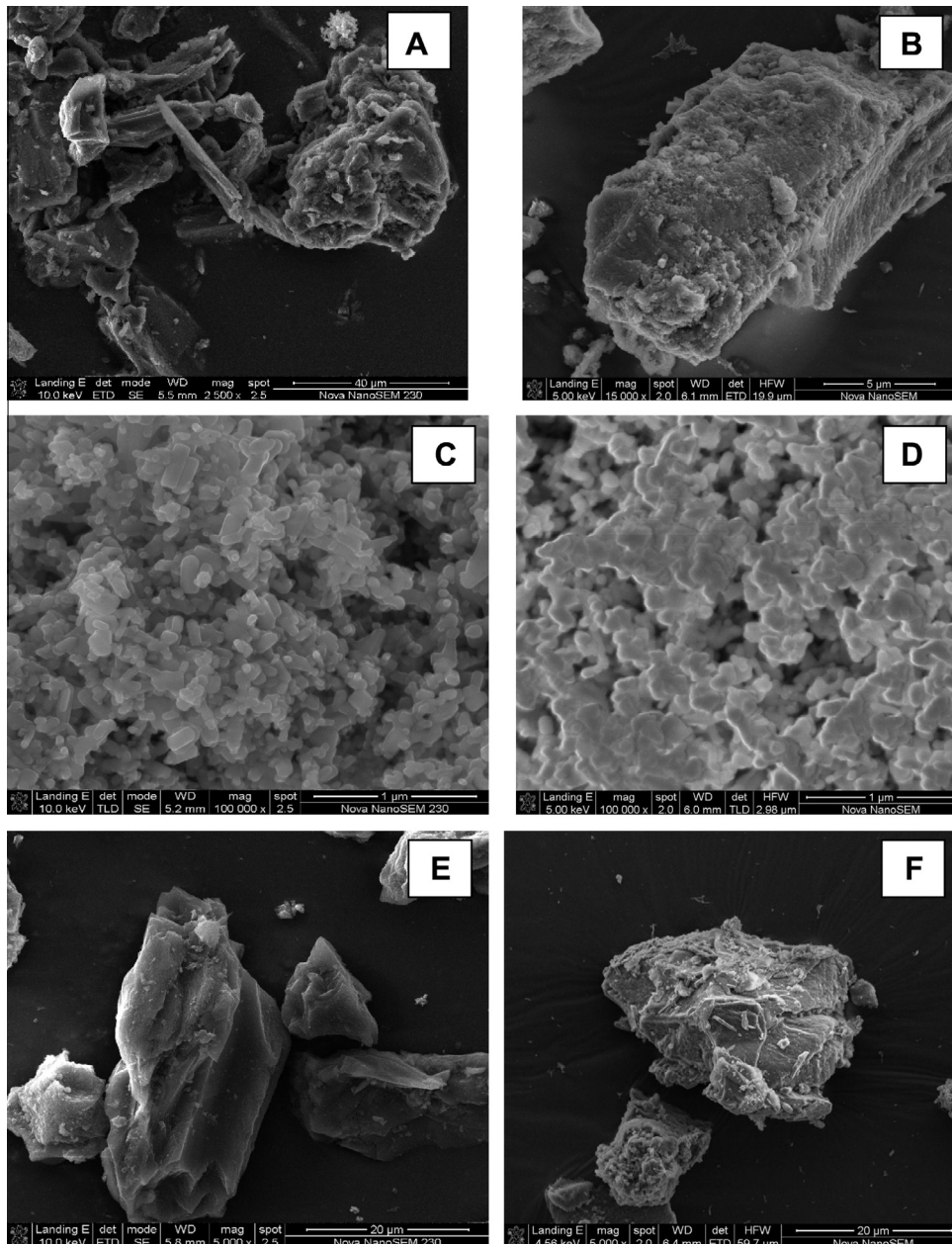


Fig. 13. SEM of activated carbon before (A) and after (B) TBT adsorption, $n\text{ZnO}$ before (C) and after (D) TBT adsorption and $n\text{ZnO}$ /activated carbon composite before (E) and after (F) TBT adsorption.

and an *n*ZnO/activated carbon composite removed 96.94%, 77.50%, and 99.66% of TBT, respectively, from the initial concentration of 5 mg/g TBT using a contact time of 60 min, stirring speed of 160 rpm, pH 8 and temperature of 20 °C. The order of decreasing adsorption capacity was: *n*ZnO/activated carbon composite > activated carbon > *n*ZnO.

4.5. Effect of stirring speed

The effect of stirring speed on the adsorption of TBT onto the adsorbents was examined for stirring speeds ranging between 160 and 200 rpm. The adsorption capacity of the adsorbents also increased with increasing stirring speed. The maximum amounts of 99.27%, 79.90% and 99.94% TBT were removed from the initial concentration of 5 mg/g TBT by the activated carbon, *n*ZnO and *n*ZnO/activated carbon composite, respectively, using a contact time of 60 min, pH 8, temperature of 20 °C and a stirring speed of 200 rpm (Fig. 9). The order of decreasing adsorption capacity was: *n*ZnO/activated carbon composite > activated carbon < *n*ZnO.

4.6. Adsorption isotherm

Fig. 10 shows that the adsorption of TBT onto activated carbon increased as the initial TBT concentration increased from 12.5 to 100 mg/L, indicating that adsorption was favorable for the higher TBT concentrations that were investigated. The increase in adsorption capacity with increasing initial TBT concentrations is a result of the increase in the driving force due to the concentration gradient that developed between the bulk solution and the surface of the adsorbents (Kumar et al., 2010). At higher TBT concentrations, the active sites of the adsorbents were surrounded by much more TBT, and the process of adsorption continued, leading to an increased uptake of TBT from the solution. Therefore, the values of c_a increased with increasing initial TBT concentrations.

Based on the values of the correlation coefficient, R^2 , summarized in Table 3, the adsorption of TBT onto all of the adsorbents can be described by the Freundlich adsorption isotherm. This is most likely due to the real heterogeneous nature of the surface sites involved in the process of adsorption. In addition to the Freundlich model, the adsorption of TBT by *n*ZnO/activated carbon composite also fit well with the D–R isotherm model (>0.99). Moreover, the negative value of the Langmuir constant, A_{\max} (mg/g) for TBT adsorption, indicated that the Langmuir model could not adequately explain the process (Maarof and Hameed, 2004). Thus, the Freundlich model explained the adsorption behavior of TBT onto the adsorbents better than all of the other models examined in this study.

4.7. Effect of temperature

The adsorption capacity increased with increasing solution temperatures (Fig. 11). This indicates that the adsorption of TBT on the precursors and on the composite is endothermic in nature. The increase in the rate of adsorption with the increase in temperature may be attributed to the strong adsorptive forces between the active sites of the adsorbents and the adsorbate species and also between the adjacent molecules of the adsorbed phases.

Approximately 99.95%, 96.96%, and 99.99% of TBT were removed from the initial concentration of 5 mg/g TBT by the activated carbon, the *n*ZnO and the *n*ZnO/activated carbon composite, respectively, using a contact time of 60 min, pH 8 and a stirring speed of 200 rpm. The order of decreasing adsorption capacity was: *n*ZnO/activated carbon composite < activated carbon < *n*ZnO.

Fig. 12 shows the van't Hoff plot for the adsorption of TBT. In this plot, the variation in the extent of adsorption with respect to

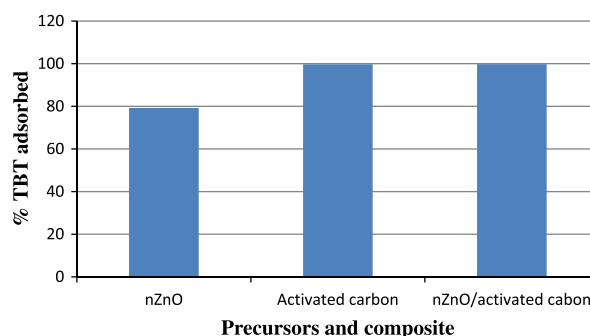


Fig. 14. Percentage of TBT removed from natural seawater.

temperature is explained by the change in enthalpy (ΔH°), change in entropy (ΔS°) and change in free energy (ΔG°) (Table 4).

The positive values of ΔH° for the intervals of temperatures also shows the endothermic nature of the adsorption process. The positive values of ΔS° correspond to an increase in degrees of freedom of the adsorbed TBT and suggests that the increase in adsorbate concentration in the solid–solution interface indicates an increase in adsorbate concentration onto the solid phase. ΔG° values were more negative as the temperatures increased (Table 4), which indicates spontaneous adsorption and that the degree of spontaneity of the reaction increases with temperature increases.

4.8. Practical application of TBT adsorption to natural seawater

Optimal conditions for the adsorption of TBT from artificial seawater were applied to TBT removal from natural seawater obtained from Cape Town harbor. The physicochemical properties of the seawater and the percentage of TBT removed after the adsorption of TBT contained in 25 mL of natural seawater by 0.5 g of adsorbent, using a contact time of 60 min and a stirring speed of 200 rpm under natural conditions, are shown in Table 5 and Fig. 14, respectively.

5. Conclusion

The precursors and the composite used in this study can be used as effective adsorbents to remove TBT from seawater. The composite had a higher removal efficiency (>99.8%) of TBT than the precursors. Increasing the contact time, the pH, the stirring speed and the temperature increased the TBT adsorption rate. The pseudo second-order kinetic model accurately described the adsorption kinetics. The *n*ZnO/activated carbon composite showed a better fit to Freundlich and D–R adsorption isotherm models, whereas the Freundlich isotherm model could be used to describe the adsorption of TBT onto activated carbon and *n*ZnO. A thermodynamic analysis showed that the adsorption process was endothermic and spontaneous in nature. A SEM analysis before and after the adsorption studies (Fig. 13) confirmed that TBT was adsorbed onto the precursors and onto the composite particles. The results from this study suggest that the materials are effective adsorbents for TBT from natural seawater. A total of 99.88%, 99.71%, and 80.42% of TBT was adsorbed from natural seawater by *n*ZnO/activated carbon composite, activated carbon and *n*ZnO, respectively.

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