

Removal of tributyltin from shipyard process wastewater by fly ash, activated carbon and fly ash/activated carbon composite: adsorption models and kinetics

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Abstract

BACKGROUND: The removal of tributyltin (TBT) from shipyard process wastewater using fly ash, activated carbon and fly ash/activated carbon composite was investigated.

RESULTS: Adsorption experiments performed on TBT-contaminated artificial process wastewater revealed that the adsorption capacity of TBT increases with increase in the adsorbent amount, contact time, pH, stirring speed and initial TBT concentration. The adsorption isotherms and the kinetic data were well described by the Freundlich and pseudo-second-order kinetic model, respectively. The negative values of the Gibbs energy change (ΔG°) indicated the spontaneous nature of the adsorption and the positive values of the enthalpy change (ΔH°) showed that the adsorption process is endothermic. Optimal conditions for the adsorption of TBT from contaminated artificial process wastewater were applied to TBT removal from natural shipyard process wastewater and the results showed that 94.2%, 99.2% and 99.8% TBT were removed by the fly ash, activated carbon and fly ash/activated carbon composite, respectively.

CONCLUSION: This study showed that the precursors as well as the composite could be employed as efficient adsorbents for the removal of TBT from contaminated shipyard process wastewater with the composite material exhibiting the highest adsorption efficiency.

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Keywords: organotin; tributyltin; shipyard process wastewater; adsorption; activated carbon and fly ash composite; GC-FPD

NOTATION

q_e	amount of TBT adsorbed at equilibrium per unit weight of the adsorbent (mg g^{-1})
q_t	amount of TBT adsorbed at any time (mg g^{-1})
k_1	pseudo-first-order rate constant (min^{-1})
k_2	rate constant of pseudo-second-order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$)
h_o	initial adsorption rate ($\text{mg g}^{-1} \text{min}^{-1}$)
C_a	amount of adsorbed TBT on the adsorbent (mg g^{-1})
C_e	equilibrium concentration of TBT in the bulk solution (mg L^{-1})
C_o	initial concentration of the TBT aqueous solution
R	gas constant ($\text{J mole}^{-1} \text{K}^{-1}$)
k_L	Langmuir isotherm constant
A_{max}	maximum monolayer TBT adsorption capacity (mg g^{-1})
k_F	Freundlich isotherm constant
n_F	exponent in Freundlich isotherm
ΔG°	standard Gibbs free energy (kJ mol^{-1})
ΔH°	standard enthalpy change (kJ mol^{-1})
ΔS°	standard entropy change ($\text{J K}^{-1} \text{mol}^{-1}$)

T	absolute temperature
K_c	thermodynamic equilibrium constant

INTRODUCTION

Tributyltin (TBT) is an organic tin compound that is widely used in biocides, wood preservatives and antifouling paints. The use of TBT has led to serious contamination of the environment and causes harmful effects on aquatic organisms such as imposex in gastropods and abnormal embryonic development in sea urchins and marine invertebrates.¹ Although the use of TBT-containing paints has been banned, developing countries are still using TBT in

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antifouling paints because of its effectiveness, hence, high concentrations of TBT can still be found in the marine environment. Efforts are therefore being made to reduce the concentration of TBT in shipyard process wastewater to >99% reduction before discharge into the aquatic environment. The suitability of anode materials to remove TBT from shipyard process waters has been reported by Calmano and Arevalo.² Tam *et al.*³ also investigated the biosorption and biodegradation of TBT by free cells of a resistant microalgal species. Hoch *et al.*⁴ studied the adsorption and desorption behavior of TBT from aqueous solution to clay-rich sediments. Song *et al.*⁵ reported the removal of TBT from wastewater by extraction with diesel oil. Prasad and Schafran⁶ reported the use of a full-scale process train consisting of coagulation–flocculation, dissolved air flotation, sand filtration and a series of two granular activated carbon (GAC) filters for removal of TBT, and Vreysen *et al.*⁷ investigated the removal of TBT from shipyard wastewaters by a one-step adsorption–flocculation method.

Activated carbon is a very efficient adsorbent for removing varieties of environmental pollutants including TBT⁶ from wastewater due to its high surface area, porosity, and physicochemical characteristics; however, its use is limited due to its high cost and low selectivity.⁸ Fly ash, a by-product of coal combustion process, is a low cost adsorbent, and is effective for the removal of contaminants in water and wastewater.^{9,10} Fly ash/activated carbon composite preparations results in improved physicochemical properties and reduces the cost of using activated carbon alone for the remediation of environmental pollutants. The kinetics and equilibrium data on the sorption of TBT from wastewaters to carbon are limited and no work has been reported on the use of fly ash and/or fly ash/activated carbon composite for the removal of TBT.

In the present work, adsorption characteristics of fly ash, activated carbon and fly ash/activated carbon composite have been studied with a view to demonstrating the role of these materials in controlling TBT pollution. Adsorption data have been analyzed with adsorption models to determine the mechanistic parameters associated with the adsorption process, the kinetics of adsorption were also investigated and the results obtained on the effect of temperature at optimum conditions have been used to determine the thermodynamic parameters.

METHODS AND MATERIALS

Adsorbents

Fly ash from Matla power station, Mpumalanga, South Africa was used in this study. Activated carbon (100–400 mesh) was purchased from Sigma Aldrich, USA. Composite material involving fly ash and activated carbon in the ratio 1:1 was prepared by the method reported by Fatoki *et al.*⁸ The physicochemical properties of the precursors and the composite are listed in Table 1.

Chemical reagents

Tributyltin chloride (purity 98%), methanol, hexane, acetic acid, sodium hydroxide and sodium tetraethylborate (NaBEt₄) were purchased from Sigma Aldrich, USA while carbonate, sulphate and chlorides salts for the preparation of artificial seawater were supplied by Merck. Stock solution containing 1000 mg L⁻¹ TBT was prepared by dissolving the organotin compound in methanol, and was stored in the dark at 4 °C. Working solutions were prepared daily. Working solutions of the derivatization agent were made up daily by dissolving 1.0 g NaBEt₄ in 100 mL of methanol (1% NaBEt₄) while acetate buffer (3 mL acetic acid, 4.0 g sodium acetate, in 1 L of Milli-Q water resulting in pH 4.5) was also prepared.

Table 1. Physicochemical properties of fly ash, activated carbon and fly ash/activated carbon composite

Characteristics	Activated carbon	Fly ash	Fly ash/activated carbon
pH	3.30	10.70	3.52
PZC	2.06	12.17	3.19
Surface area (m ² g ⁻¹)	1156.60	1.06	5.30
Micropore area (m ² g ⁻¹)	442.7	0.38	0.19
Ash content (%)	0.45 ± 0.07	97.40 ± 0.14	46.30 ± 0.14
Carbon content (%)	71.40	1.54	36.83
Nitrogen content (%)	0.35	BD	BD
Hydrogen content (%)	2.82	BD	2.72

BD- below detection limit.

TBT-contaminated shipyard process wastewater was simulated in the laboratory, prepared by spiking artificial seawater with TBT stock solution. The artificial seawater was prepared by the addition of 86.6 mL of 5 mol L⁻¹ NaCl, 9.0 mL of 1.0 mol L⁻¹ KCl, 9.27 mL of 1.0 mol L⁻¹ CaCl₂·2H₂O, 4.68 mL of 4.9 mol L⁻¹ MgCl₂·2H₂O, 12.75 mL of 2.0 mol L⁻¹ MgSO₄·7H₂O and 2.15 mL of 1.0 mol L⁻¹ NaHCO₃ all diluted to 1 L with Milli-Q water, which resulted in pH 8 (marine condition). TrisHCl-buffer was not used in the preparation of artificial seawater because it resulted in a lower pH.¹² TrisHCl-buffer and NaOH solution were used to adjust the pH during study of the effect of pH. The physicochemical properties of the shipyard process wastewater obtained from Cape Town harbor were: turbidity (3.26 NTU), pH (7.5), conductivity (37.56 mS cm⁻¹), TDS (18.78 ppt), salinity (22.65 psu), resistivity (26.60 ohms) and 4.615 mg L⁻¹ TBT concentration.

Analysis of tributyltin

The concentration of TBT in artificial or natural shipyard process wastewater before and after the adsorption studies was determined after derivatization by the addition of 1 mL of acetate buffer (pH = 4.5) and 1.0 mL of 1% NaBEt₄ and extraction into hexane by horizontal shaking in a separation funnel. The extracts were reduced to 1 mL and analysed by gas chromatography–flame photometric detector (GC-FPD) (Shimadzu GC-2010 Plus) with a capillary column HP 5 (5% phenyl methyl siloxane, 30 m × 0.25 mm i.d., film thickness 0.25 μm). The temperature was programmed as follows: initially at 60 °C hold for 1 min, then heated to 280 °C at 10 °C min⁻¹, hold for 4 min. The injection and detector temperatures were 270 °C and 300 °C, respectively, and the carrier gas was high purity helium.

The limit of detection and quantification of the analytical method were determined according to EURACHEM guidelines.¹³ Blank matrices without sample were injected, and the blank signal measured. The limit of detection (LOD = 0.0001 mg L⁻¹) and limit of quantification (LOQ = 0.0010 mg L⁻¹) were calculated from the mean and standard deviation of 10 blank measurements with 95% confidence level.

The regression analysis carried out on signal intensities obtained for 6.25, 12.5, 25, 50 and 100 mg L⁻¹ working standards of TBT, showed a correlation coefficient of 0.9985. The linearity of the standards calibration concentration of TBT analyzed under the same conditions was 38.75 ± 0.05 mg L⁻¹ and the precision of measurement was represented by the relative standard deviation (RSD) which ranged from 8.83–10.5% for the between-sample reproducibility aliquots of TBT.

Adsorption experiments

The adsorption experiments of TBT onto fly ash, activated carbon and fly ash/activated carbon composite were conducted in batch mode, which permits complete evaluation of parameters that influence the adsorption process. Adsorption experiments were conducted in which TBT-contaminated artificial process wastewater was introduced into 250 mL Erlenmeyer flasks containing accurately weighed amounts of the adsorbent. The flasks were shaken by orbital shaker at room temperature (20 °C) for a prescribed length of time to obtain equilibrium. The adsorbents were then 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 initial and final TBT concentrations. The adsorption capacities were obtained by mass balance equation:

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

where q is the equilibrium adsorption capacity per gram dry weight of the adsorbent, mg g^{-1} ; c_o is the initial concentration of TBT in the solution, mg L^{-1} ; c_e is the final or equilibrium concentration of TBT in the solution, mg L^{-1} ; V is the volume of the solution, L; and W is the dry weight of the adsorbent, g.

The adsorption kinetics experiments were conducted at room temperature using 100 mg L^{-1} of TBT solutions with 0.5 g of adsorbents per 25 mL keeping pH at 8, a stirring speed of 200 rpm and a contact time of 10–70 min. The data obtained were analyzed with pseudo-first-order and pseudo-second-order kinetic models.

The adsorption isotherms were investigated by varying the initial TBT concentration from 12.5 to 200 mg L^{-1} at optimized adsorbent dose, contact time, pH and stirring speed established after optimization of working parameters. The equilibrium data were fitted by Langmuir and Freundlich isotherm models.

The effect of pH on TBT adsorption was studied by varying the pH in the range 3 to 9. The effect of stirring speed on TBT adsorption was studied by varying the mixing speeds from 160 to 200 rpm. The effect of temperature on the adsorption of TBT was evaluated after optimization of all the working parameters for TBT adsorption at an initial TBT concentration of 100 mg L^{-1} solution with 0.5 g of adsorbents per 25 mL, pH 8, contact time 60 min and stirring speed 200 rpm from where the thermodynamic parameters of TBT adsorption in artificial process wastewater were obtained.

RESULTS AND DISCUSSION

Optimization of the adsorbent dose and contact time

The effect of adsorbent dose on the adsorption of TBT by the fly ash, activated carbon and fly ash/activated carbon composite is shown in Fig. 1. It was observed that the percentage adsorption increased with increasing adsorbent dose, reaching an optimum at 0.5 g for the fly ash, activated carbon and fly ash/activated carbon composite, corresponding to 89.1%, 99.7% and 99.6% removal, respectively.

The increase in the adsorption yields with increasing amounts of adsorbent can be explained by more adsorptive binding sites due to more adsorbent in the medium at higher dosages. The later constant trend in adsorption yields may be due to saturation of these sites on the adsorbent surface by the TBT molecules.¹⁴ Determination of an optimum amount of adsorbent is important for TBT removal in order to provide a cost-effective adsorption system.¹⁵ 0.5 g was therefore selected as the optimum adsorbent amount utilized for further studies.

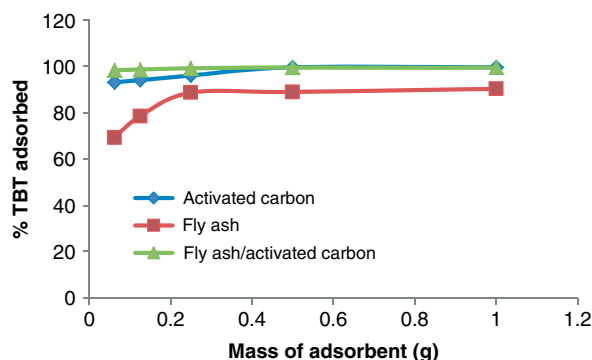


Figure 1. Adsorption efficiencies of TBT onto fly ash, activated carbon and fly ash/activated carbon composite. Experimental conditions: concentration of TBT = 100 mg L^{-1} ; volume of TBT solution = 25 mL, contact time = 60 min; stirring speed = 160 rpm, temperature = 20 °C.

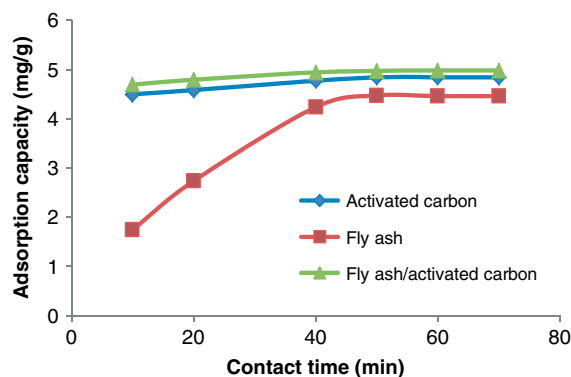


Figure 2. Effect of contact time on TBT adsorption onto fly ash, activated carbon and fly ash/activated carbon composite. Experimental conditions: concentration of TBT = 100 mg L^{-1} ; volume of TBT solution = 25 mL, mass of adsorbent = 0.5 g; stirring speed = 160 rpm, temperature = 20 °C.

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

The figure indicates that the adsorption rate was fast in the beginning of the process for all the adsorbents. It was also observed that equilibrium was achieved within approximately 60 min and the corresponding TBT removal for fly ash, activated carbon and fly ash/activated carbon composite of an initial concentration of 5.0 mg g^{-1} TBT reached 4.458 mg g^{-1} , 4.841 mg g^{-1} and 4.979 mg g^{-1} , respectively. A contact time of 60 min was therefore selected as the optimum contact time used in further studies.

Kinetic modeling

In order to investigate the mechanism and to determine the rate controlling step of the adsorption of TBT on fly ash, activated carbon and fly ash/activated carbon composite, kinetic models were used. The rate constants were calculated by pseudo-first-order and pseudo-second-order kinetic models.¹⁶

Pseudo-first-order model

The pseudo-first-order model is generally expressed as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} (t) \quad (2)$$

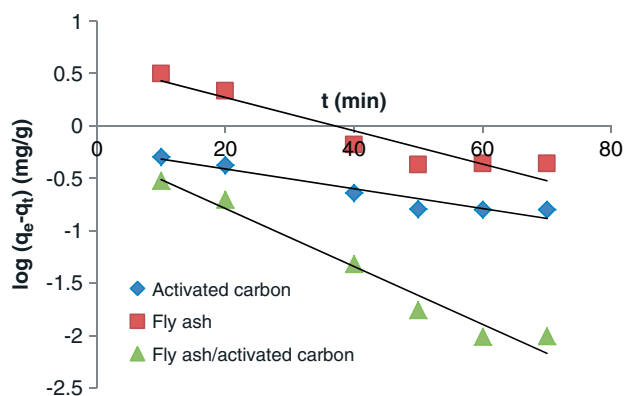


Figure 3. Pseudo-first-order rate equation plot for TBT adsorption onto fly ash, activated carbon and fly ash/activated carbon composite.

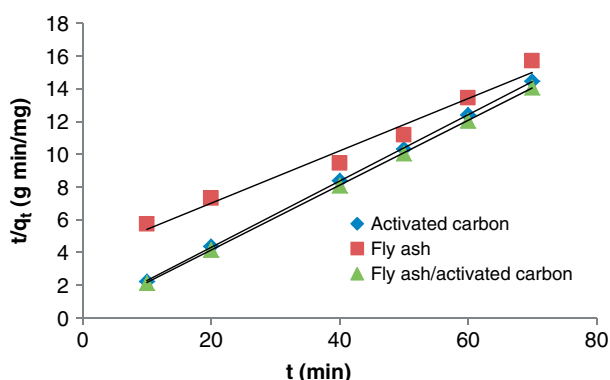


Figure 4. Pseudo-second-order rate equation plot for TBT adsorption onto fly ash, activated carbon fly ash/activated carbon composite.

where q_e is the amount of TBT adsorbed per unit weight of adsorbent at equilibrium, i.e. adsorption capacity (mg g^{-1}), q_t is the amount of adsorbent adsorbed (mg g^{-1}) at any time t and k_1 is the rate constant. The value of k_1 was calculated from the slope of the linear plot of $\log(q_e - q_t)$ versus t .

The pseudo-second-order rate model

The pseudo-second-order rate model is given as follows:

$$\frac{t}{q_t} = \frac{1}{h_o} + \frac{1}{q_e} (t) \tag{3}$$

where k_2 is the rate constant. The values of k_2 can be determined from the plot of $\frac{t}{q_t}$ versus t , furthermore, the initial rate of adsorption (h) ($\text{mg g}^{-1} \text{min}^{-1}$), when $t \rightarrow 0$, can also be calculated using following formula:

$$h = k_2 q_e^2 \tag{4}$$

Figure 3 and 4 show the pseudo-first-order and pseudo-second-order kinetic plots, respectively, and Table 2 provides the evaluated parameters of the kinetic models.

The value of the correlation coefficient (R^2) of the pseudo-second-order kinetic model (>0.97) is higher than the correlation coefficient of the pseudo-first-order model, indicating that the best kinetic model for the adsorption of TBT onto the precursors and composites is pseudo-second-order. The value of the initial

Table 2. Kinetic model parameters for TBT adsorption onto activated carbon, fly ash and fly ash/activated carbon composite			
Models	Activated carbon	Fly ash	Fly ash/activated carbon
Pseudo-first-order			
k_1 (min^{-1})	0.0216	0.0366	0.0638
q_e (mg g^{-1})	0.5944	3.8824	0.5812
R^2	0.9200	0.8925	0.9680
Pseudo-second-order			
q_e (mg g^{-1})	4.9309	6.2617	5.0480
h_o ($\text{mg g}^{-1} \text{min}^{-1}$)	4.0650	0.2617	5.8038
k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	0.1672	0.0067	0.2278
R^2	0.9999	0.9762	0.9999

adsorption rate, h_o , obtained for the pseudo-second-order kinetics decreased as follows: $5.8038 \text{ mg g}^{-1} \text{min}^{-1}$ (fly ash/activated carbon composite) $> 4.0650 \text{ mg g}^{-1} \text{min}^{-1}$ (activated carbon) $> 0.2617 \text{ mg g}^{-1} \text{min}^{-1}$ (fly ash) indicating that fly ash/activated carbon composite and activated carbon can sorb TBT more rapidly than fly ash.

The pseudo-second-order kinetic model depends on the assumption that chemisorption is the rate-limiting step for the adsorption of TBT on the adsorbents. In chemisorption, the TBT ions stick to the adsorbent surface by forming a chemical (usually covalent) bond and tend to find sites that maximize their coordination number with the surface.¹⁷

Optimization of pH and stirring speed

The effect of pH on the adsorption of TBT onto the adsorbents was studied at pH 3–9. It was observed (Fig. 5) that the percentage of TBT adsorbed by the adsorbents steadily increased as the pH of the solution was increased from pH 3 to pH 8, and reached equilibration at $\text{pH} \geq 8$. This is in support of the results obtained by Fang et al.¹⁸ and Weidenhaupt et al.¹⁹

Maximum adsorption capacity was therefore recorded within the pH range of normal saline water (pH 8). About 89.5%, 96.9%, and 99.6% of TBT were removed from the initial concentration of 5 mg g^{-1} TBT by the fly ash, activated carbon and fly ash/activated

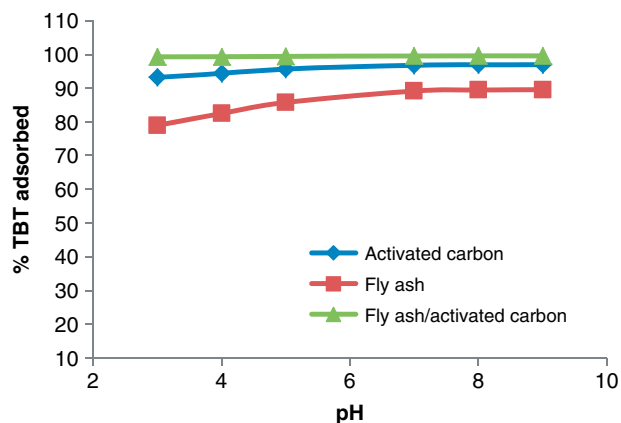


Figure 5. Effect of pH on TBT adsorption onto fly ash, activated carbon and fly ash/activated carbon composite. Experimental conditions: concentration of TBT = 100 mg L^{-1} ; volume of TBT solution = 25 mL, mass of adsorbent = 0.5 g; contact time = 60 min; stirring speed = 160 rpm, temperature = 20°C .

carbon composite, respectively, at a contact time of 60 min, stirring speed 160 rpm, temperature 20 °C and pH 8. The order of decreasing adsorption capacity was thus fly ash/activated carbon composite > activated carbon > fly ash. pH 8 was chosen as the optimum pH and was used for further studies.

The effect of stirring speed on the adsorption of TBT onto the adsorbents was studied at stirring speeds 160–200 rpm. The adsorption capacity of the adsorbents increased as the stirring speed of the mixture was increased, reaching equilibration at 200 rpm. Maximum amount of 4.726 mg g⁻¹, 4.963 mg g⁻¹ and 4.988 mg g⁻¹ of TBT were removed from the initial concentration of 5 mg g⁻¹ TBT by the fly ash, activated carbon and fly ash/activated carbon composite, respectively, at a contact time of 60 min, pH 8, temperature 20 °C and a stirring speed 200 rpm (Fig. 6). A stirring speed of 200 rpm was therefore used for further studies.

Effect of initial TBT concentration

Figure 7 shows that the adsorption of TBT on the adsorbents increased as the initial TBT concentration was increased from 12.5 to 100 mg L⁻¹, indicating that adsorption is also favorable for the higher TBT concentrations investigated. The increase in adsorption capacity with increase in initial TBT concentration is as a result of the increase in driving force due to the concentration gradient developed between the bulk solution and surface of the adsorbents. At higher TBT concentrations, the active sites of the adsorbents were surrounded by more TBT and the process of adsorption continues, leading to an increased uptake of TBT from the solution.

Adsorption isotherm parameters

Adsorption isotherms were determined to quantify the interaction between solute and the adsorbents, critical in optimizing the purification process. Two isotherm models (Langmuir and Freundlich) were employed to understand the equilibrium data and deduce an adsorption mechanism. The linear form of the Langmuir model²⁰ is:

$$\frac{c_e}{c_a} = \frac{1}{A_{\max}k_L} + \frac{1}{A_{\max}}c_e \quad (5)$$

where c_e (mg L⁻¹) is the equilibrium concentration of TBT in the solution, c_a (mg g⁻¹) is the TBT adsorption capacity for the adsorbents at equilibrium, A_{\max} (mg g⁻¹) is the maximum monolayer TBT adsorption capacity, and k_L (L mg⁻¹) is the Langmuir

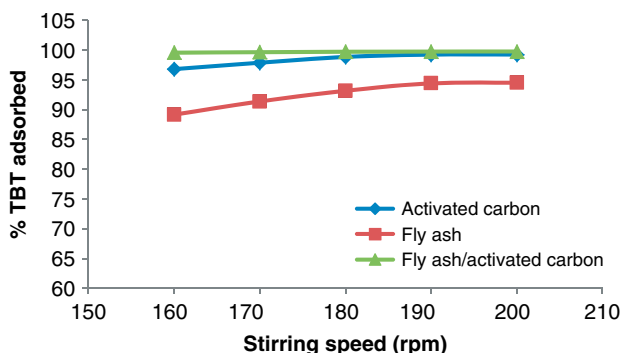


Figure 6. Effect of stirring speed on TBT adsorption onto fly ash, activated carbon and fly ash/activated carbon composite. Experimental conditions: concentration of TBT = 100 mg L⁻¹; volume of TBT solution = 25 mL, mass of adsorbent = 0.5 g; contact time = 60 min; pH 8; temperature = 20 °C.

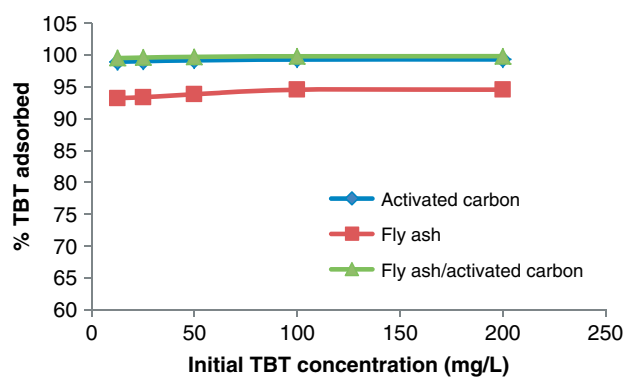


Figure 7. Percentage TBT adsorbed by the fly ash, activated carbon and fly ash/activated carbon composite at various initial TBT concentrations. Experimental conditions: volume of TBT solution = 25 mL, mass of adsorbent = 0.5 g; pH = 8; stirring speed = 200 rpm; contact time = 60 min; temperature = 20 °C.

isotherm constant related to the free energy of adsorption. When $\frac{c_e}{c_a}$ is plotted against c_e and the data are regressed linearly, A_{\max} and k_L constants are calculated from the slope and the intercept.

The linear form of the Freundlich model²⁰ is:

$$\log c_a = \log k_F + \frac{1}{n_F} \log c_e \quad (6)$$

The constant k_F [mg g⁻¹ (L mg⁻¹)^{1/n}] is related to the adsorption capacity of the adsorbents, and $\frac{1}{n_F}$ is related to the surface heterogeneity. When $\log c_a$ is plotted against $\log c_e$ and the data are analyzed by linear regression, $\frac{1}{n_F}$ and k_F constants can be determined from the slope and intercept.

The adsorption isotherm parameters²¹ obtained from the two models are given in Table 3. The experimental data fitted the Freundlich model well for all the adsorbents.¹² It is thus a more suitable model for describing the adsorption process because the regression coefficient (R^2) values (>0.98) are higher than for the Langmuir model (Table 3). The result therefore suggests the formation of multilayer coverage of TBT molecules at the outer surface of the adsorbents.²² The value of k_F determines the adsorption capacity of adsorbent at equilibrium concentration in a solution.²³ A higher k_F value corresponds to a higher adsorption capacity. According to the k_F values listed in Table 3, the adsorption capacity of TBT is higher for fly ash/activated carbon composite than for activated carbon, and that for activated carbon is in turn higher than for fly ash. The value of n_F , for all the adsorbents, falling in the range 1–10 also indicates favourable adsorption.

The negative value of the Langmuir constants, A_{\max} (mg g⁻¹) and k_L (L mg⁻¹) for TBT adsorption indicates the inadequacy of fitting of experimental data to the Langmuir model.²⁴ Thus, the Freundlich model was the best model to explain the adsorption behavior of TBT onto the adsorbents.

The solid residues before and after the adsorption processes were subjected to scanning electron microscopy (SEM) analysis and results are presented in Fig. 8. Micrographs of the adsorbents before and after adsorption showed that the spherical particles of fly ash²⁵ and the aggregated surfaces of activated carbon and fly ash/activated carbon composite were clearly seen before adsorption whereas TBT was deposited on the surfaces of these adsorbents after the adsorption process.

Table 3. Isotherms constants for the adsorption of TBT onto fly ash, activated carbon and fly ash/activated carbon composite

Equilibrium models	Activated carbon	Fly ash	Fly ash/activated carbon
Freundlich			
k_F (mg/g (L/mg) ^{1/n})	6.6589	0.6856	36.610
n_F	0.8375	0.9048	0.6799
R^2	0.9977	0.9990	0.9873
Langmuir			
k_L (L mg ⁻¹)	-0.2494	-0.0213	-1.4239
A_{max} (mg g ⁻¹)	-19.0476	-32.573	-7.3692
R^2	0.6952	0.7577	0.6622

Effect of temperature and thermodynamics

To investigate the effect of temperature on the adsorption process, K_c was calculated using Equation (7). The standard Gibbs free

energy ΔG° (kJ mol⁻¹) was obtained from Equation (8), while the values of the standard enthalpy change ΔH° (kJ mol⁻¹) and standard entropy change ΔS° (J K⁻¹ mol⁻¹) were calculated from the intercept and the slope of the linear plot of log K_c versus 1/T (Equation (9)).

$$K_c = \frac{c_a}{c_e} \tag{7}$$

$$\Delta G^\circ = -RT \ln K_c \tag{8}$$

$$\log K_c = \frac{\Delta S^\circ}{2.303R} - \frac{\Delta H^\circ}{2.303R} \cdot \frac{1}{T} \tag{9}$$

where c_a (mg L⁻¹) is the amount of TBT (mg) adsorbed on the adsorbent per liter of the solution at equilibrium, c_e (mg L⁻¹) is the equilibrium concentration of TBT in the solution, R is the universal gas constant, 8.314 J mol⁻¹ K⁻¹; T is absolute temperature and K_c is the thermodynamic equilibrium constant.

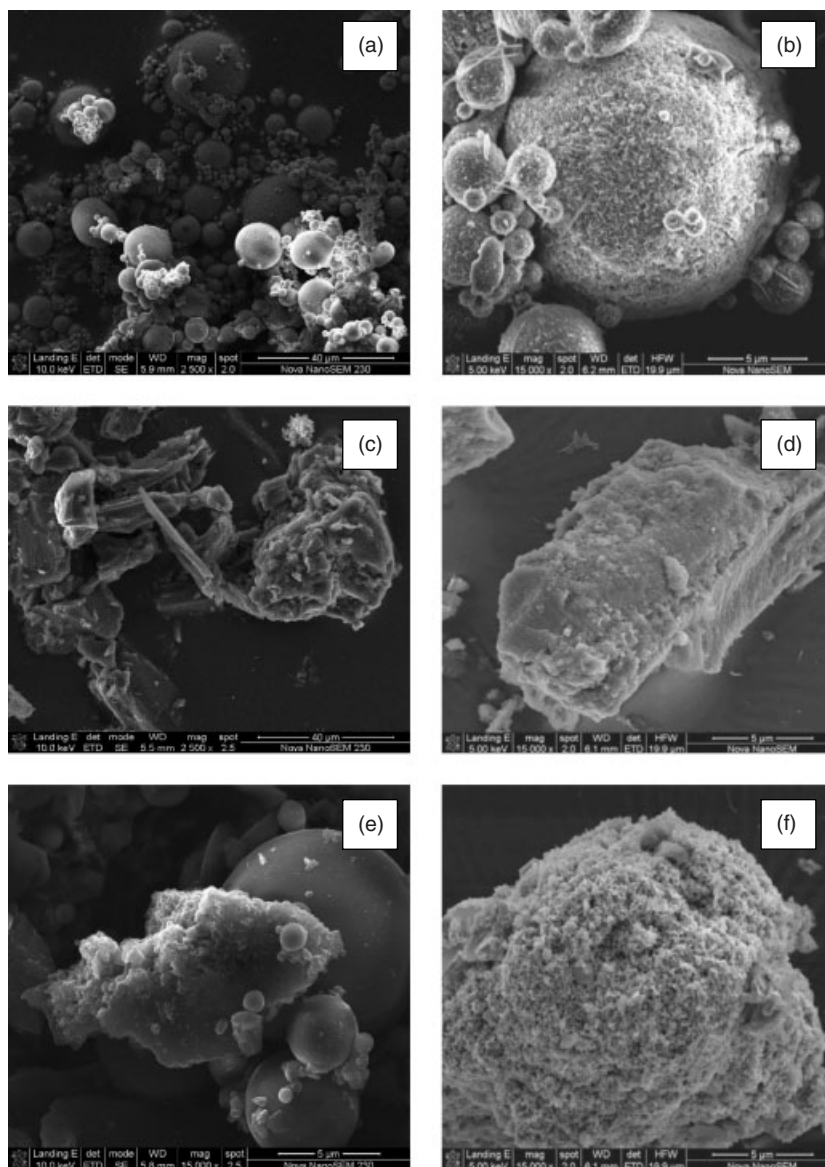


Figure 8. SEM of fly ash before (a) and after (b) TBT adsorption, activated carbon before (c) and after (d) TBT adsorption, and fly ash/activated carbon composite before (e) and after (f) TBT adsorption.

The adsorption data obtained in the temperature range 40–80 °C shows that the adsorption capacity of TBT onto all the adsorbents increases with increase in the solution temperature. This indicates that the adsorption of TBT onto the precursors and the composite is endothermic. 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 adsorbate species and also between the adjacent molecules of the adsorbed phases.²⁶

Approximately 95.7%, 99.9%, and 99.9% of TBT were removed from the initial concentration of 5 mg g⁻¹ TBT by the fly ash, activated carbon and fly ash/activated carbon composite, respectively, after a contact time of 60 min, at pH 8 and a stirring speed 200 rpm.

Figure 9 shows the Van't Hoff plot²⁷ for the adsorption of TBT and the thermodynamic parameters (ΔH° , ΔS° , ΔG° and K_c) are presented in Table 4.

The positive values of ΔH° for the intervals of temperatures also showed the endothermic nature of the adsorption process. The positive values of ΔS° correspond to an increase in degree of freedom of the adsorbed TBT and suggest an increase in

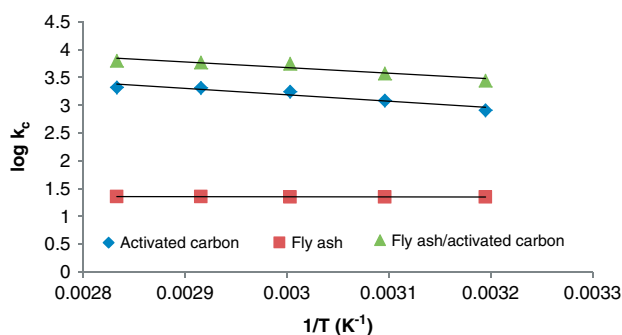


Figure 9. Van't Hoff plot for the adsorption of TBT onto fly ash, activated carbon and fly ash/activated carbon composite.

Table 4. Thermodynamic parameters for adsorption of TBT onto fly ash, activated carbon and fly ash/activated carbon composite

Temperature (°C)	ΔG° (kJ mol ⁻¹)	ΔS° (J K ⁻¹ mol ⁻¹)	ΔH° (kJ mol ⁻¹)	K_c
Fly ash				
40	-8.036	27.5853	0.5970	21.941
50	-8.312			22.100
60	-8.580			22.180
70	-8.867			22.414
80	-9.138			22.507
Activated carbon				
40	-17.434	127.830	22.293	812.00
50	-19.080			1218.5
60	-20.679			1753.4
70	-21.731			2039.8
80	-22.425			2082.3
Fly ash/activated carbon				
40	-20.634	128.414	19.363	2776.8
50	-22.066			3702.7
60	-23.872			5554.6
70	-24.751			5881.4
80	-25.651			6249.0

the concentration of adsorbate at the solid–solution interface, indicating an increase in adsorbate concentration onto the solid phase.²⁸

It is evident from Table 4 that ΔG° values were more negative as the temperature increased, indicating that the adsorption efficiency of TBT onto precursors and composite increased with increase in temperature and the adsorption of TBT onto all the adsorbents is a thermodynamically feasible process.²⁶

Application of optimized operating factors to the sorption of TBT in shipyard process wastewater

Optimal conditions for the adsorption of TBT from artificial process wastewater were applied to TBT removal from contaminated natural shipyard process wastewater. The result showed that approx. 94.2%, 99.2% and 99.8% TBT were removed by 0.5 g of fly ash, activated carbon and fly ash/activated carbon composite, respectively after a contact time of 60 min, at a temperature of 20 °C and stirring speed of 200 rpm under normal atmospheric condition.

CONCLUSION

The study has shown the potential of fly ash, activated carbon and fly ash/activated carbon composite to remove tributyltin from shipyard process wastewater. The TBT removal efficiency was in the order: fly ash/activated carbon composite > activated carbon > fly ash. The adsorption data suggest that all the operating factors considered in this study are important for the control of TBT adsorption. The percentage adsorption increases with increasing adsorbent dose, contact time, pH, stirring speed, initial TBT concentration and temperature. It is therefore evident that maximum adsorption can be achieved at normal saline water conditions (pH 8). The equilibrium data fit Freundlich isotherm model satisfactorily and the kinetic data were well described by the pseudo-second-order model. Thermodynamic analysis also showed that the adsorption process was endothermic and spontaneous in nature. The results of this experimental study are highly useful and the adsorbents may be extended to other organic pollutants in wastewater.

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