Application of nano zinc oxide (nZnO) for the removal of triphenyltin chloride (TPT) from dockyard wastewater

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ABSTRACT

The use of triphenyltin chloride (TPT), a persistent organic pollutant, as a biocide has led to serious contamination of the marine environment. The potential of nano zinc oxide (nZnO) for the removal of TPT from contaminated dockyard wastewater was investigated. The adsorption of TPT onto nZnO has been found to depend on the adsorbent dose, contact time, pH, stirring speed, and temperature. Equilibrium data fitted well with the Freundlich model and the experiments showed that 97.0% TPT removal was achieved by treating 0.643 mg·ℓ^{-1} TPT contaminated dockyard wastewater with 0.5 g nZnO at optimal conditions. The kinetic data for the adsorption process obeyed a pseudo second-order kinetic model, suggesting that the adsorption process is chemisorption. The nZnO investigated in this study showed good potential for the removal of TPT from contaminated dockyard wastewater systems.

Keywords: persistent organic pollutants, triphenyltin chloride, nano zinc oxide, adsorption, dockyard wastewater

INTRODUCTION

Persistent organic pollutants (POPs) are organic compounds that are resistant to environmental degradation through chemical, biological, and photolytic processes (Ritter et al., 2005; Reindl et al., 2013). POPs are pollutants of global concern due to their widespread occurrence, strong resistance, long-range transportation and high level of bioaccumulation (Xu et al., 2013). They include organohalogens (i.e halogenated dioxins and furans, polychlorinated biphenyl (PCBs), hexachlorobenzene, mirex, toxaphene, heptachlor, chlordane and DDT), polycyclic aromatic hydrocarbons (PAHs), organotin compounds (tributyltin chloride (TBT) and triphenyltin chloride (TPT)), and certain brominated flame-retardants. POPs are toxic and highly hazardous and can therefore have severe negative effects on the health of ecosystems, wildlife, and humans (Vested et al., 2014). Many of these compounds act as endocrine disruptors, which disrupt reproductive cycles of humans and wildlife (Colborn and Smolen, 1996; Gregoraszczuk and Ptak, 2013). The usage of POPs has been banned in many countries. Some developing countries, however, are still using these compounds because of their low cost and versatility in industry, agriculture and public health (Tanabe et al., 1994; El-Naggar et al., 2013). TPT is a biocide that has been used to prevent fouling of boats and ships, to preserve wood, kill molluscs and pests, and for many other purposes (Kimbrough, 1976; Evans, 1981). The chemical structure of TPT is shown in Fig. 1. The relative persistence of this compound, its tendency to bioaccumulate, and its toxicity have been of great concern. Hence, there is a need to remove this pollutant from dockyard and/or industrial wastewater before discharge into the environment.
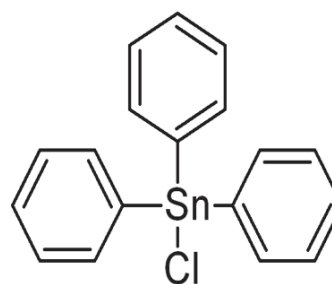
Figure 1
Triphenyltin chloride (TPT)

Activated carbon has been widely investigated for the adsorption of organic pollutants (Najm et al., 1991; Nigam et al., 2000; Daneshvar et al., 2007; Fang et al., 2010). There has been growing interest in the use of other effective alternatives to activated carbon, such as fly ash (Ayanda et al., 2013a; Ayanda et al., 2013b), clay minerals (Alverez-Ayuzo and Garcia-Sanchez, 2003), sawdust (Hamdaoui, 2006), peat (Ho and McKay, 1998), wood powder (Ferrero, 2007), and oxides (Yamashita et al., 2010; Liang et al., 2011; Ghasemi et al., 2012). However, reports on the adsorption of organic pollutants from aqueous solution onto nano metal oxides, viz., kinetic, isotherm and thermodynamic studies are limited. The application of nanoscale materials and structures, usually ranging from 1 to 100 nm, is an emerging field of research.

Nano zinc oxide (nZnO) is low cost and can be readily produced on a large-scale. It has been studied as a potential nontoxic semiconductor photocatalyst and adsorbent for organic pollutants (Khani and Sohrabi, 2012; Zhang et al., 2013). In this study the evaluation of TPT adsorption onto nZnO and its degradation are reported. The objectives investigation were to understand the way in which TPT interacts with nZnO and to study the adsorption mechanism of TPT onto nZnO. To

achieve this aim, the adsorption studies were carried out in the laboratory on simulated contaminated dockyard wastewater and the optimal conditions obtained were applied to real polluted dockyard wastewater.

METHODS AND MATERIALS

Chemical reagents and adsorbents

Nano zinc oxide (nZnO), TPT, methanol, n-hexane, acetic acid, sodium hydroxide and sodium tetraethylborate (NaBEt$_4$) were purchased from Sigma Aldrich, USA. A stock solution of 1 000 mg·ℓ^{-1} TPT was prepared by dissolving the TPT in methanol. This was then stored in the dark at 4°C. Simulated dockyard wastewater was prepared daily by spiking the artificially prepared seawater (Keller et al., 1987) with the TPT stock solution. A working solution of the derivatization agent was made up daily by dissolving 1.0 g NaBEt$_4$ in 100 mℓ of methanol while acetate buffer (3 mℓ acetic acid, 4.0 g sodium acetate, filled up to 1 ℓ with deionised water resulting in a pH of 4.5) was also prepared.

Experimental set-up

To study the effect of important parameters, such as adsorbent dose, contact time, pH, stirring speed, and temperature, on the adsorptive removal of TPT adsorption experiments were carried out by adding varying quantities of nZnO to 100 mℓ of TPT-contaminated simulated seawater in 250 mℓ conical glass flasks and shaking these in a shaking thermostat at a constant speed of 160 r·min^{-1}. Samples were withdrawn at appropriate time intervals, derivatized, and determined by a gas chromatography–flame photometric detector (GC-FPD) (Shimadzu GC-2010 Plus) (Ayanda et al., 2013a). The pH (4.0–9.0) of TPT-contaminated simulated dockyard wastewater solution was adjusted with TrisHCl-buffer and NaOH solutions using a Mettler-Toledo pH meter. Inductively coupled plasma-atomic emission spectroscopic (ICP-AES; Thermo Icap 6300) analysis of the filtrates was conducted in order to confirm that the nZnO was not dissolving at these pH values. To verify the effect of stirring speed on adsorption, 100 mℓ of 100 mg·ℓ^{-1} TPT-contaminated simulated dockyard wastewater solution was contacted with 0.5 g nZnO at a stirring speed of 160 to 200 r·min^{-1}. The experiments were conducted at 40, 50, 60, 70, and 80°C to study the effect of temperature on adsorption time and to evaluate sorption thermodynamic parameters. The kinetics of adsorption were determined by analysing adsorptive uptake of the TPT from contaminated simulated dockyard wastewater at different time intervals. For adsorption isotherm determination, TPT-contaminated simulated dockyard wastewater solutions of different concentrations were agitated with known amounts of adsorbent until equilibrium was achieved at 20°C. All of the experiments were performed in triplicate and a GC–MS instrument (Agilent 6890N GC with CTC CombiPAL autosampler and Agilent 5975B MS) was used for the confirmation of TPT concentrations after all adsorption experiments. Table 1 shows the GC–MS instrument operating parameters.

The amount of TPT adsorbed (mg·g^{-1}) by nZnO was calculated using Eq. (1):

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

where:
q is the equilibrium adsorption capacity per gram dry weight of the adsorbent, mg·g^{-1}

TABLE 1 GC-MS operating parameters for the confirmation of TPT	
GC injection parameters	
Mode	Splitless
Temperature	270°C
Pressure	98.6 kPa
Purge flow	50.0 mℓ·min^{-1}
Purge time	10.00 min
Total flow	54.3 mℓ·min^{-1}
Gas saver	On
Saver flow	50.0 mℓ·min^{-1}
Saver time	2.00 min
Gas type	Helium
Column parameters	
Column information	Rtx®-5MS, Restek 12723-127
Max. temperature	330°C
Normal Length	30 m, 0.25 mm ID, 0.25 µm film thickness
Oven programme	Initially at 60°C hold for 1 min, then heated to 280°C at 10°C·min^{-1}, hold for 7 min
Mode	Constant flow
Initial flow	1.6 mℓ·min^{-1}
Normal initial pressure	98.6 kPa
Average velocity	46 cm·s^{-1}
Inlet	Front inlet
Outlet	MSD
Outlet pressure	Vacuum

C_0 is the initial concentration of TPT in the solution, mg·ℓ^{-1}
C_e is the final or equilibrium concentration of TPT in the solution, mg·ℓ^{-1}
V is the volume of the solution, ℓ
W is the dry weight of the adsorbent, g

RESULTS AND DISCUSSION

CHARACTERISATION OF NZNO

The Brunauer, Emmett and Teller (BET) surface area and porosity determination for the nZnO used showed that the nano oxide has a surface area of 14.4 ± 0.04 m²·g^{-1}, a micropore area of 3.2 m²·g^{-1}, and an average pore diameter of 98.5 Å. X-ray diffraction (XRD) analysis showed the presence of ZnO characterised by sharp peaks. Scanning electron micrographs (SEM) showed that the nZnO particles consisted of uniform granules with regular surfaces (Fig. 2).

Effect of adsorbent amount

To study the effect of nZnO amount on adsorption of TPT from contaminated simulated dockyard wastewater, adsorbent amount was varied from 0.0625–1.0 g, concentration of TPT was 100 mg·ℓ^{-1} and other parameters were also kept constant. Figure 3 shows that the percentage of TPT adsorbed by nZnO increases as the amount of nZnO increases from 0.0625–0.50 g, after which equilibration was attained. Thus 0.50 g of nZnO was able to remove 95.4% of the TPT from the contaminated simulated dockyard wastewater solution.
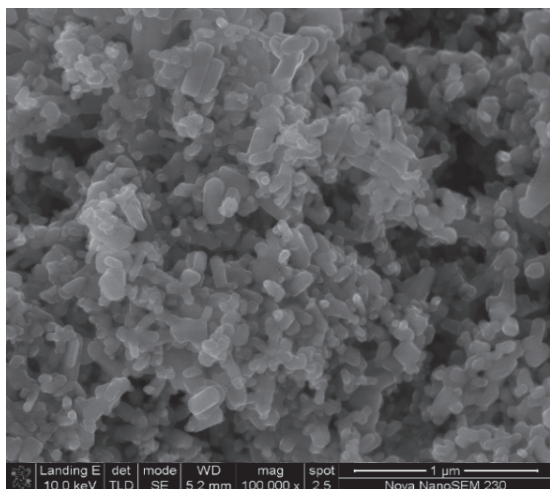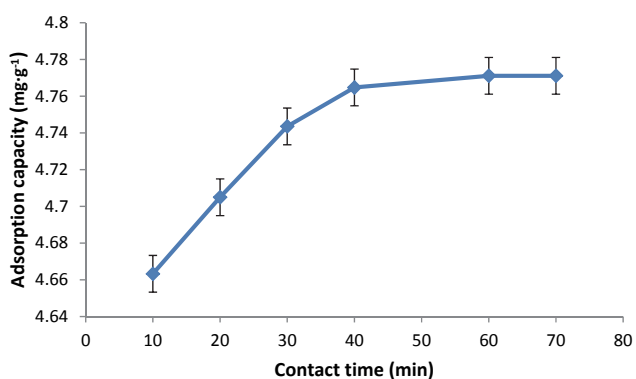
Figure 2
SEM of nZnO
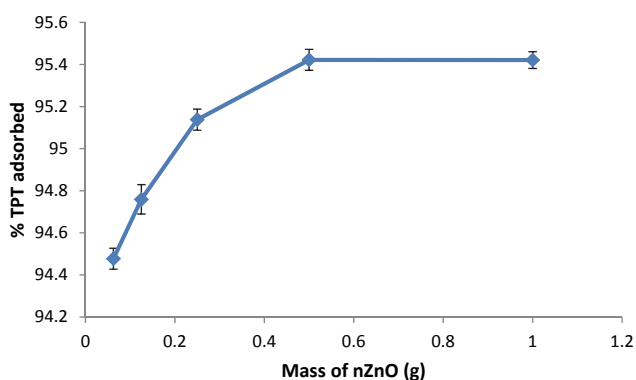
Figure 3
Adsorption efficiencies for TPT onto nZnO. Experimental conditions: concentration of TPT = 100 mg·ℓ⁻¹; volume of TPT solution = 25 mℓ, contact time = 60 min; stirring speed = 160 r·min⁻¹, temperature = 20 °C.
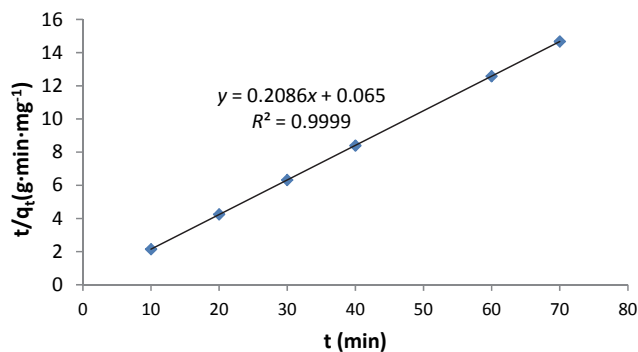

Figure 4
Effect of contact time on TPT adsorption onto nZnO. Experimental conditions: concentration of TPT = 100 mg·ℓ⁻¹; volume of TPT solution = 25 mℓ, mass of nZnO = 0.5 g; stirring speed = 160 r·min⁻¹, temperature = 20°C.

Effect of contact time and kinetics

The effect of contact time on percentage TPT removal was examined at 100 mg·ℓ⁻¹ TPT concentration, for various time intervals from 10 to 70 min. As can be seen from Fig. 4, the

Figure 5
Pseudo second-order rate equation plot for TPT adsorption onto nZnO

removal efficiency for TPT onto nZnO by adsorption is initially rapid from a contact time of 10 to 40 min and then slows down gradually until it attains equilibrium. The graph also shows that an increase in the amount of TPT adsorbed by nZnO from 4.66 mg·g⁻¹ (93.3%) to 4.77 mg·g⁻¹ (95.4%) (Fig. 4) was observed from 10 to 60 min. After that, there is no significant change observed. The pseudo first-order (Batzias and Sidiras, 2004), and pseudo second-order (Waranusantigul et al., 2003) have been used for modelling the kinetics of TPT adsorption onto the nZnO (Eqs (2) and (3)).

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

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}(t) \tag{3}$$

where:

k_1 and k_2 are the pseudo first-order, and pseudo second-order constants, respectively

Figure 5 thus shows the pseudo second-order kinetic plot and Table 2 provides the evaluated parameters of the kinetic model. The value of the regression coefficient (R^2) of pseudo second-order kinetic model (> 0.99) is higher than the R^2 value of the pseudo first-order models indicating that the kinetic model for the adsorption of TPT onto the nZnO is pseudo second-order. This shows that the rate-limiting step is chemisorption (Ungarish and Aharoni, 1981).

| TABLE 2 Pseudo second-order kinetic parameters for TPT adsorption onto 0.5g of nZnO	
Pseudo second-order	
q_e (mg·g⁻¹)	4.79
h_o (mg·g⁻¹·min⁻¹)	15.3
k_2 (g·mg⁻¹·min⁻¹)	0.669
R^2	0.9999

Effect of pH and stirring speed

Figure 6 illustrates the effect of pH on the adsorption of TPT for initial TPT concentration of 100 mg·ℓ⁻¹ at 20°C. It was observed in Fig. 6 that the percentage of TPT adsorbed by the nZnO steadily increases as the pH of the solution increases
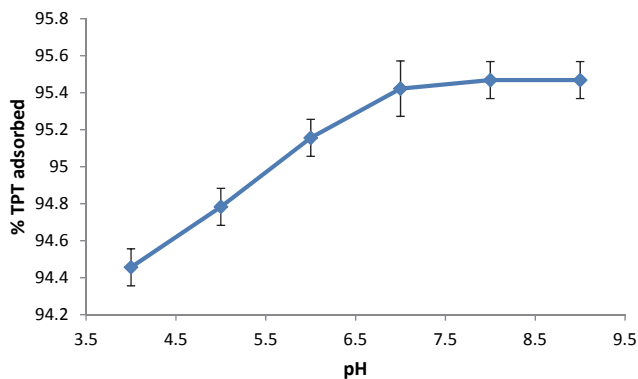
Figure 6
Effect of pH on TPT adsorption onto nZnO. Experimental conditions: concentration of TPT = 100 mg·ℓ⁻¹; volume of TPT solution = 25 mℓ, mass of nZnO = 0.5 g; contact time = 60 min; stirring speed = 160 r·min⁻¹, temperature = 20°C.
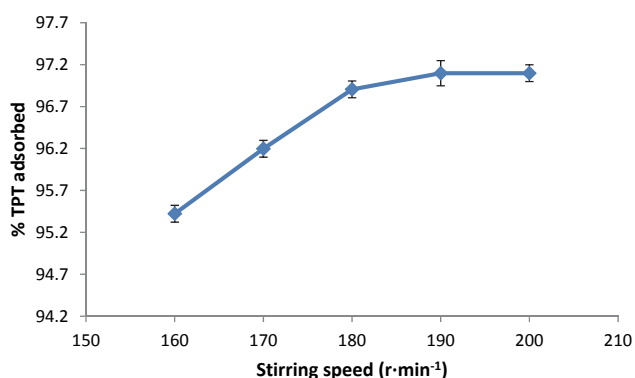
Figure 7
Effect of stirring speed on TPT adsorption onto nZnO. Experimental conditions: concentration of TPT = 100 mg·ℓ⁻¹; volume of TPT solution = 25 mℓ, mass of nZnO = 0.5 g; contact time = 60 min; temperature = 20°C.

from pH 4 to pH 8, and reaches equilibration at pH ≥ 8. About 95.5% of 100 mg·ℓ⁻¹ TPT was removed by nZnO at a contact time of 60 min, stirring speed of 160 r·min⁻¹, temperature of 20°C and pH 8.

The effect of stirring speed on the percentage of TPT removal was examined at 100 mg·ℓ⁻¹ TPT concentration, contact time of 60 min, pH of 8 and a temperature of 20 °C. The adsorption capacity for adsorption of TPT onto nZnO increases as the stirring speed of the mixture increases from 160 to 200 r·min⁻¹ (Fig. 7). Equilibration was attained afterwards. Figure 7 shows that 97.1% of TPT was removed by nZnO for an initial TPTconcentration of 100 mg·ℓ⁻¹, a contact time of 60 min, pH 8.0, temperature 20°C and stirring speed of 200 r·min⁻¹.

Adsorption isotherms

The adsorption isotherms for the adsorption of TPT onto nZnO were investigated by varying the initial TPT concentration from 12.5 to 200.0 mg·ℓ⁻¹ at optimised adsorbent dose, contact time, pH and stirring speed (established after optimisation of working parameters). The equilibrium data were fitted using Langmuir (Langmuir, 1918), and Freundlich (Freundlich, 1906) (Eqs (4) and (5)) isotherms:

$$\frac{c_e}{c_a} = \frac{1}{A_{max} k_L} + \frac{1}{A_{max}} c_e \qquad (4)$$
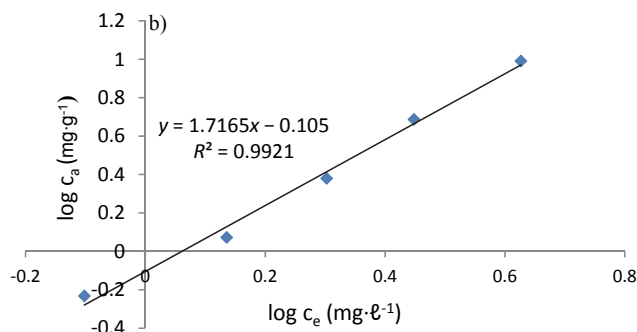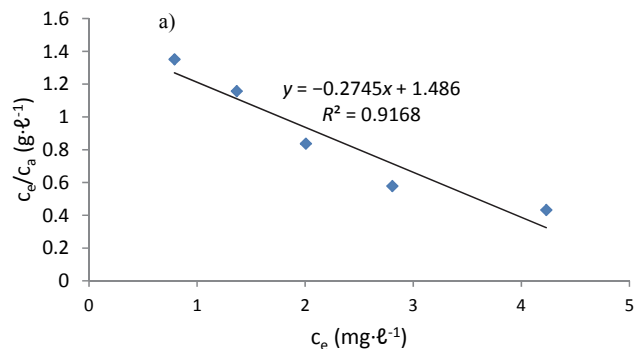
Figure 8
Langmuir isotherm (a) and Freundlich isotherm (b) for adsorption of TPT onto nZnO

$$\log C_a = \log k_F + \frac{1}{n_F} \log C_e \qquad (5)$$

where:

C_e (mg·ℓ⁻¹) is the equilibrium concentration of TPT in the solution
C_a (mg·g⁻¹) is the TPT adsorption capacity for the adsorbents at equilibrium
A_{max} (mg·g⁻¹) is the maximum monolayer TPT adsorption capacity
k_L (ℓ·mg⁻¹) is the Langmuir isotherm constant related to the free energy of adsorption
k_F [mg·g⁻¹ (ℓ·mg⁻¹)¹/ⁿ] and n_F are the Freundlich constants related to the adsorption capacity and adsorption intensity, respectively (Freundlich, 1906)

The constants k_L, A_{max}, k_F, and n_F were calculated from the intercept and the slope of the plots.

TABLE 3 Isotherms constants for the adsorption of TPT onto nZnO	
Equilibrium models	
Freundlich	
k_F [mg·g⁻¹ (ℓ·mg⁻¹)¹/ⁿ]	0.785
n_F	0.583
R^2	0.9921
Langmuir	
K_L (ℓ·mg⁻¹)	−0.185
A_{max} (mg·g⁻¹)	−3.64
R^2	0.9168

The adsorption isotherm plots are presented in Fig. 8 and parameters obtained for the models are given in Table 3. Table 3
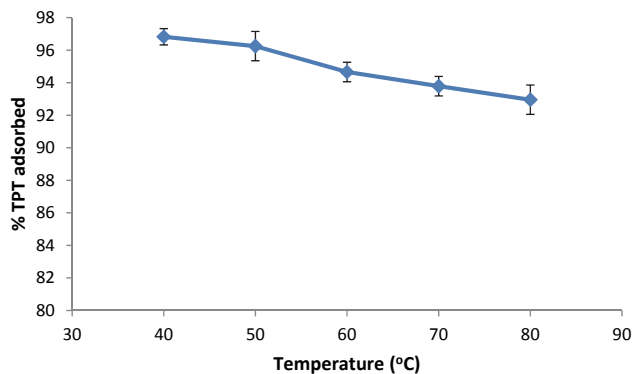
Figure 9

Effect of temperature on TPT adsorption onto nZnO. Experimental conditions: concentration of TPT = 100 mg·ℓ⁻¹; volume of TPT solution = 25 mℓ, mass of nZnO = 0.5 g; contact time = 60 min; pH = 8; stirring speed = 200 r·min⁻¹.

TABLE 4 Thermodynamic parameters for adsorption of TPT onto nZnO				
Temperature (°C)	$\Delta G°$ (kJ·mol⁻¹)	$\Delta S°$ (J·K⁻¹·mol⁻¹)	$\Delta H°$ (kJ·mol⁻¹)	K_c
40	−8.89			30.5
50	−8.71			25.6
60	−7.96	−36.5	−20.3	17.7
70	−7.74			15.1
80	−7.57			13.2

and the figure show that the experimental data is well-fitted to the Freundlich isotherm model. The value of n_F, for the nZnO, falling in the range 1–10, also indicates favourable adsorption (Aksu, 2002).

Effect of temperature

The experimental results show that the adsorption capacity for the adsorption of TPT onto nZnO decreases with increase in solution temperature (Fig. 9). This indicates that the adsorption of TPT onto nZnO is exothermic. From Fig. 9, approx. 92.9% of TPT was removed by nZnO for an initial TPT concentration of 100 mg·ℓ⁻¹, contact time of 60 min, pH 8.0, stirring speed 200 r·min⁻¹ and temperature of 80°C, whereas 96.8% TPT was removed at 40°C under the same conditions.

The thermodynamic parameters were determined from the thermodynamic equilibrium constant, K_c. K_c was calculated using Eq. (6). The standard Gibbs free energy $\Delta G°$ (kJ·mol⁻¹) was obtained using Eq. (7) while the standard enthalpy change $\Delta H°$ (kJ·mol⁻¹) and standard entropy change $\Delta S°$ (J·K⁻¹·mol⁻¹) were calculated from the intercept and slope of the linear plot of $\log K_c$ versus $\frac{1}{T}$ (Eq. (8)).

$$K_c = \frac{C_a}{C_e} \qquad (6)$$

$$\Delta G° = -RT \ln K_c \qquad (7)$$

$$\log K_c = \frac{\Delta S°}{2.303R} - \frac{\Delta H°}{2.303R} \cdot \frac{1}{T} \qquad (8)$$

where:

C_a (mg·ℓ⁻¹) is the amount of TPT (mg) adsorbed per litre of the solution at equilibrium

C_e (mg·ℓ⁻¹) is the equilibrium concentration of TPT in the solution

R is the universal gas constant, 8.314 J·mol⁻¹ K

T is absolute temperature

K_c is the thermodynamic equilibrium constant

Thermodynamic parameters obtained are given in Table 4. As shown in Table 4, K_c decreases with increasing temperature from 40 to 80°C. The negative values of $\Delta G°$ indicate the spontaneous nature of adsorption of TPT by the nZnO. The negative value of $\Delta H°$ (−20.3 kJ·mol⁻¹) for the intervals of temperatures studied (Table 4) also shows the exothermic nature of the

adsorption process. The negative value of $\Delta S°$ (−36.5 J·K⁻¹·mol⁻¹) indicates that the freedom of TPT molecules is restricted in the nZnO as the temperature increases (Sheela et al., 2012). The negative value of $\Delta S°$ obtained is in agreement with other adsorption studies for pesticides adsorbed onto various materials (Varhney et al., 1996; El Bakouri et al., 2009; Li et al., 2009).

Moreover, only one peak was observed on the GC-MS chromatogram of all filtrate samples after adsorption. It shows that the use of nZnO for the remediation of TPT does not result in the degradation of TPT to other derivatives or toxic compounds.

Optimal conditions for the adsorption of TPT from contaminated simulated dockyard wastewater solution were applied to real wastewater obtained from Cape Town dockyard; the wastewater contained 0.643 mg·ℓ⁻¹ TPT. The result showed that 97.0 % TPT was removed from the real contaminated dockyard wastewater by 0.5 g of nZnO at a contact time of 60 min, temperature of 20°C and stirring speed of 200 r·min⁻¹. The value of 97.0% obtained is close to the 97.1% adsorption obtained for the simulated dockyard wastewater solution.

CONCLUSION

In this study, nZnO was selected as an adsorbent for the removal of TPT from contaminated dockyard wastewater. Adsorption of the TPT was studied by batch technique and it was observed that > 95% TPT removal was achieved by using 0.5 g of TPT, for an initial TPT concentration of 100 mg·ℓ⁻¹. The adsorption rate increases with increasing adsorbent dose, contact time, pH, and stirring speed but decreases with an increase in the solution temperature. Adsorption followed pseudo second-order kinetics, and equilibrium data fitted the Freundlich isotherm model well. Thermodynamic parameters indicated that TPT adsorption onto nZnO was exothermic. This study, in comparison with the application of nZnO for the removal of TBT (Ayanda et al., 2013c), showed that approximately 97.0 % organotin compound (TBT or TPT) could be removed with 0.5 g of nZnO at optimal conditions. However, the initial adsorption rate (h_0) and the amount of TPT adsorbed at equilibrium per unit weight of nZnO (q_e) is higher. The thermodynamic studies also showed that TPT and TBT adsorption onto nZnO is exothermic and endothermic, respectively. The results of this study therefore indicate that nZnO can be successfully used for the adsorption of organotin compounds from contaminated dockyard wastewater.

REFERENCES

AKSU Z (2002) Determination of the equilibrium, kinetic and thermodynamic parameters of the batch biosorption of nickel (II) ions onto *Chlorella vulgaris. Proc. Bio.* **38** 89–99.

ÁLVAREZ-AYUSO E and GARCÍA-SÁNCHEZ A (2003) Removal of heavy metals from waste waters by natural and Na-exchanged

bentonites. *Clays Clay Miner.* **51** 475v480.

AYANDA OS, FATOKI OS, ADEKOLA FA and XIMBA BJ (2013a) Removal of tributyltin from shipyard process wastewater by fly ash, activated carbon and fly ash/activated carbon composite: adsorption models and kinetics. *J. Chem. Technol. Biot.* **88** 2201–2208.

AYANDA OS, FATOKI OS, ADEKOLA FA and XIMBA BJ (2013b) Utilization of $nSiO_2$, fly ash and $nSiO_2$/fly ash composite for the remediation of triphenyltin (TPT) from contaminated seawater. *Environ. Sci. Pollut. Res.* **20** 8172–8181.

AYANDA OS, FATOKI OS, ADEKOLA FA and XIMBA BJ (2013c) Kinetics and equilibrium models for the sorption of tributyltin to nZnO, activated carbon and nZnO/activated carbon composite in artificial Seawater. *Mar. Pollut. Bull.* **72** 222–230.

BATZIAS FA and SIDIRAS DK (2004) Dye adsorption by calcium chloride treated beech sawdust in batch and fixed-bed systems. *J. Hazardous Mater.* **B114** 167–174.

COLBORN T and SMOLEN MJ (1996) Epidemiological analysis of persistent organochlorine contaminations in cetaceans. *Rev. Environ. Contam. Toxicol.* **146** 91–172.

DANESHVAR N, ABER S, KHANI A and KHATAEE AR (2007) Study of imidaclopride removal from aqueous solution by adsorption onto granular activated carbon using an on-line spectrophotometric analysis system. *J. Hazardous Mater.* **144** 47–51.

EL BAKOURI H, USER J, MORILLO J, ROJAS R and OUASSINI A (2009) Drin pesticides removal from aqueous solutions using acid-treated date stones. *Bioresour. Technol.* **100** 2676–2684.

EL-NAGGAR NA, EMARA HI, RIFAAT AE, SAID TO, ABOU-SHAHBA RM and SHALTOUT NA (2013) Some anthropogenic driven toxic pollutants in El-Mex Bay and its neighbourhood, Alexandria, Egypt. *World Appl. Sci. J.* **27** 863–871.

EVANS LV (1981) Marine algae and fouling: a review, with particular reference to ship-fouling. *Botanica Mar.* **24** 167–172.

FANG L, BORGGAARD OK, MARCUSSEN H, HOLM PE and HANSEN HCB (2010) The pH-dependent adsorption of tributyltin to charcoals and soot. *Environ. Pollut.* **158** 3642–3649.

FERRERO F (2007) Dye removal by low cost adsorbents: hazelnut shells in comparison with wood sawdust. *J. Colloid Interf. Sci.* **142** 144–152.

FREUNDLICH H (1906) Over the adsorption in solution. *J. Phys. Chem.* **57** 385–470.

GHASEMI Z, SEIF A, AHMADI TS, ZARGAR B, RASHIDI F and ROUZBAHANI GM (2011) Thermodynamic and kinetic studies for the adsorption of Hg(II) by nano-TiO_2 from aqueous solution. *Adv. Powder Technol.* **23** 148–156.

GREGORASZCZUK EL and PTAK A (2013) Endocrine-disrupting chemicals: some actions of POPs on female reproduction. *Int. J. Endocrinol.* **2013** 1–9.

HAMDAOUI O (2006) Batch study of liquid-phase adsorption of methylene blue using cedar sawdust and crushed brick. *J. Hazardous Mater.* **135** 264–273.

HO YS and McKAY G (1998) Sorption of dye fromaqueous solution by peat. *Chem. Eng. J.* **70** 115–124.

KELLER MD, SELVIN RC, CLAUS W and GUILLARD RRL (1987) Media for the culture of oceanic ultraphytoplankton. *J. Phycol.* **23** 633–638.

KHANI A and SOHRABI MR (2012) Simultaneous synthesis-immobilization of nano ZnO on perlite for photocatalytic degradation of an azo dye in semi batch packed bed photoreactor. *Pol. J. Chem. Technol.* **14** 69–76.

KIMBROUGH RD (1976) Toxicity and health effects of selected organotin compounds: a review. *Environ. Health Perspect.* **14** 51–56.

LANGMUIR I (1918) The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* **40** 1361–1403.

LIANG L, LUO L and ZHANG S (2011) Adsorption and desorption of humic and fulvic acids on SiO_2 particles at nano and micro-scales. *Colloids Surf. A* **384** 126–130.

LI K, ZHENG Z, FENG J, ZHANG J and LUO X (2009) Adsorption of p-nitroaniline from aqueous solutions onto activated carbon fiber prepared from cotton stalk. *J. Hazardous Mater.* **166** 1180–1185.

NAJM IN, SNOEYINK VL, LYKINS BW and ADAMS JQ (1991) Using powdered activated carbon: a critical review. *J. Am. Water Works Assoc.* **83** 65–76.

NIGAM P, ARMOUR G, BANAT IM, SINGH D and MARCHANT R (2000) Physical removal of textile dyes from effluents and solid-state fermentation of dye-adsorbed agricultural residues. *Bioresource Technol.* **72** 219–226.

REINDL AR, BOLAŁEK J and FALKOWSKA L (2013) Persistent organic pollutants (POPs) in the marine food web: herrings from the southern Baltic Sea (*Clupea harengus*) — Penguins from the zoo (*Spheniscus demersus*). *Oceanol. Hydrobiol. Stud.* **42** 51–58.

RITTER L, SOLOMON KR, FORGET J, STEMEROFF M and O'LEARY C (2005) Persistent organic pollutants. 43 pp. URL: http://www.chem.unep.ch/pops/ritter/en/ritteren.pdf (Accessed 14 April 2013).

SHEELA T, ARTHOBA NY, VISWANATHA R, BASAVANNA S and VENKATESHA TG (2012) Kinetics and thermodynamics studies on the adsorption of Zn(II), Cd(II) and Hg(II) from aqueous solution using zinc oxide nanoparticles. *Powder Technol.* **217** 163–170.

TANABE S, IWATA H and TATSUKAWA R (1994) Global contamination by persistent organochlorines and their ecotoxicological impact on marine mammals. *Sci. Total Environ.* **154** 163–177.

VARHNEY KG, KHAN AA, GUPTA U and MAHESWARI SM (1996) Kinetics of adsorption on antimony (v) phosphate cation exchanger: evaluation of the order of reaction and some physical parameters. *Colloids Surf. A* **113** 19–23.

VESTED A, GIWERCMAN A, BONDE JP and TOFT G (2014) Persistent organic pollutants and male reproductive health. *Asian J. Androl.* **16** 71–80.

WARANUSANTIGUL P, POKETHITIYOOK P, KRUATRACHUE M and UPATHAM ES (2003) Kinetics of basic dye (methylene blue) biosorption by giant duckweed (*Spirodela polyrrhiza*). *Environ. Pollut.* **125** 385–392.

XU FL, JORGENSEN SE, SHIMIZU Y and SILOW E (2013) Persistent organic pollutants in fresh water ecosystems. *Scientific World J.* **2013** 1–2.

YAMASHITA M, DOZONO M, TAKAHASHI T and HONDA K (2010) Utilization of regenerated iron oxide for treatment of organotin compounds in seawater. *J. Mater. Cycles Waste Manag.* **14** 146–151.

ZHANG F, LAN J, YANG Y, WEI T, TAN R and SONG W (2013) Adsorption behavior and mechanism of methyl blue on zinc oxide nanoparticles. *J. Nanopart. Res.* **15** 2034.