Removal of organotin compounds, Cu and Zn from shipyard wastewaters by adsorption – flocculation: A technical and economical analysis

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Abstract

Several commercially available adsorbents were screened for their ability to remove Cu, Zn and organotin compounds from both artificial contaminated and real dockyard wastewater. An adsorption – flocculation process using a mixture of two adsorbents (a clay based adsorbent and a powdered activated carbon) was optimized for an optimal adsorbent and pollutant removal. At the optimal conditions the process was evaluated with both artificial and real shipyard wastewater, and the cost of the adsorption–flocculation process with relation to different influent concentrations and discharge limits was estimated.
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1. Introduction

Effective antifoulants, which prevent the settlement and growth of marine organisms on ship's hulls, are needed to decrease the fuel consumption of ships. For many years, organotin compounds (mainly tributyltin) were the most widely used active ingredients in paint formulations. Their use has been regulated internationally since 1990 because of their severe impact on the aquatic ecosystem. The application of antifouling paint containing organotin compounds on ship surfaces was stopped from 1 January 2003, and organotin containing antifouling paint is supposed to be completely removed by 1 January 2008. Since the alternatives to organotin containing paints are also toxic, their presence in the aquatic environment has been a topic of increasing importance the last years (Yebra et al., 2004).

Because of the toxic effects of antifouling paints on marine organisms, it is important to prevent their introduction into the ecosystem. The main source of tributyltin (TBT) is the release from painted hulls during the lifetime of the paint. However, a major point source of pollution, which is responsible for between 6% and 17% of the total amount of TBT released (Thomas et al., 2002), is high-pressure hosing in shipyards. The majority of biocide released during hosing activities is in the form of paint particles that can become incorporated in sediments. Although the physicochemical properties of antifouling compounds differ significantly and some are rapidly degraded, they will accumulate in marine sediments if introduced as paint particles (Thomas et al., 2003). Treating wastewaters in shipyards will thus prevent a significant part of the introduction of antifouling compounds into the marine ecosystem.

Generally, current shipyard operations do not include wastewater treatment. Also the literature data concerning the treatment of shipyard wastewaters are rare. Ottosen et al., 2005 observed a decrease in TBT concentration from about 40 μg Sn/l to 20 μg Sn/l after coagulation with iron salts (1.4 ml/l of a 1.0 M FeCl$_3$ solution). This significant reduction in TBT is not sufficient to reach strict discharge

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criteria. Song et al. (2005) showed that organotin compounds could be more effectively removed from artificial wastewater by solvent extraction with diesel oil. After 5 h extraction time the level of TBT decreased from 4 mg/l to 0.8 µg/l. Prasad and Schafran (2006) used a full-scale process train consisting of coagulation–flocculation, dissolved air flotation, sand filtration and a series of two granular activated carbon (GAC) filters. About 50% of the TBT was removed after the sand filtration step (initial TBT concentration: 400–500 µg/l). The GAC filters decreased the TBT concentration further to less than 0.1% of the TBT concentration in the influent (final TBT concentration: 0.3–0.4 µg/l).

This paper investigates the removal of dibutyltin (DBT), tributyltin (TBT), Cu and Zn from shipyard wastewaters by a one-step adsorption–flocculation method. This water treatment process, which removes both dissolved pollutants and paint flakes, is evaluated on technical, ecological and economic criteria.

2. Materials and methods

2.1. Materials

Table 1 shows the adsorbents, which were screened for their ability to remove Cu, Zn and organotin compounds from artificially prepared and real shipyard wastewaters. Real shipyard wastewater was obtained from a shipyard in Germany. The characterization of this real wastewater (RWW) (Table 2) reveals that a large amount of TBT is associated with paint flakes. This is not the case for MBT and DBT, which are degradation products of TBT.

The concentrations of the pollutants in the artificial wastewater (AWW) are also given in Table 2 and are comparable to the RWW contents. Apart from the pollutants the AWW also contained inorganic and organic compounds. Their concentration corresponds to the composition of the RWW components and was made up as

follows: 15.092 mmol/l NaCl, 0.442 mmol/l $CaCl_2$, 8 mmol/l $MgCl_2$, 0.925 mmol/l $MgSO_4$, 5.551 mmol/l $NaHCO_3$, 0.019 mmol/l $Fe(NO_3)_3$, 0.691 mmol/l KCl, 0.002 mmol/l $(NH_4)_2$ hydrogen citrate, 0.305 mmol/l Zn acetate and 0.094 mmol/l $CuSO_4$. The pH of the real shipyard wastewater is 7.52 and the conductivity is 787 µS/cm. The pH of the artificial wastewater is 7.45×0.50 and the conductivity is 2.11 ± 0.16 mS/cm.

2.2. Analytical methods

Cu and Zn were analyzed by atomic absorption spectroscopy (Varian SpectrAA-20 plus). The organotin compounds were analyzed by gas chromatography with pulsed flame photometric detection (GC–PFPD). The organotin compounds in the water phase were treated with sodium tetraethyl borate (0.1%) at pH 4.5–5.0. To adjust the pH of the water to this pH an appropriate amount of sodium acetate buffer (2 M) was added. This mixture was shaken for 30 min on an end-over-end shaker. Subsequently the organotin components were extracted in hexane. 2 µl of this hexane phase was injected in a Varian CP-3800 gas chromatograph with a sulfur filter (BG-12) and a pulsed flame photometric detector. The injections were done manually in the splitless mode. The injector and detector temperature was 250 °C. The organotin

Table 2
Composition of artificial wastewater (AWW) and real wastewater (RWW)

Pollutants	Concentration AWW	Concentration RWW
MBT (monobutyltin) (aq.)	0.584 µg Sn/l	0.317 µg Sn/l
DBT (dibutyltin) (aq.)	2.54 µg Sn/l	3.22 µg Sn/l
TBT (tributylttin) (aq.)	23.6 µg Sn/l	25.4 µg Sn/l
TBT associated with paint flakes	0 µg Sn/l	83.0 µg Sn/l
Zn (aq.)	20.0 mg/l	5.88 mg/l
Cu (aq.)	3.80–6.00 mg/l	1.39 mg/l

Table 1
Adsorbents used in the screening experiments

Supplier	Sorbent name	Description	Application
Süd-chemie AG	Südflock P 61	Acid activated bentonite	Suspension
	Südflock P 62	Sorbent based on Ca-bentonite	Suspension
	Südflock P 62 + 1	Sorbent based on Ca-bentonite	Suspension
	Südflock P 63/8	Alkali activated bentonite	Suspension
	Südflock P 290	Bentonite + flocculant	Suspension
	Südflock P 294	Bentonite + flocculant	Suspension
	Südflock P 590	Bentonite + flocculant	Suspension
	Tixosorb	Organically modified bentonite	Suspension
Laviosa Chimica Mineraria	Laviopur LCM 4	Bentonite + flocculant	Suspension
Metapro N.V.	Metasorb bodem	Granulated, modified aluminosilicate	Column
Desotec	Organosorb 10	Granular activated carbon	Column
	Organosorb 100-1	Powdered activated carbon	Suspension
	Organosorb 200-1	Powdered activated carbon	Suspension
Norit	Norit Sae Super	Powdered activated carbon	Suspension
	NRS Carbon	Granular activated carbon	Column
Chemivron carbon	F 400	Granular activated carbon	Column

components were separated by an apolar capillary column of the type WCOT Fused silica (7.5 m × 0.25 mm), covered with CP-Sil 5CB (0.25 μm film thickness) as a stationary phase. The initial column temperature was 60 °C, which was held for 0.5 min. The column was heated until 100 °C at a rate of 25 °C/min. Subsequently the column was heated to 135 °C at a rate of 3 °C/min. Finally the column was heated until 200 °C at a rate of 25 °C/min. This temperature was held for 1 min. The He carrier gas pressure was 5.5 psi, which corresponded to an average gasflow of 1 ml/min through the column.

2.3. Adsorbent screening

To screen the adsorbents for their ability to remove Cu, Zn and organotin compounds from water, 10 or 20 mg adsorbent was added to 40 ml of artificial wastewater in Teflon centrifuge cups. The organotin adsorption onto powdered activated carbon (PAC) was studied by adding 50 mg of PAC to 40 ml of an organotin solution, which contained 10,000 μg Sn/l MBT, DBT and TBT. These suspensions were shaken overnight on an end-over-end shaker. Subsequently the adsorbent was centrifuged off (13,776g for 30 min) and the Zn, Cu and organotin concentrations in the supernatant solution were determined. In the PAC experiment an additional filtration step (0.45 μm Millipore filter) was needed for a complete removal of the PAC sorbent. It was checked that the organotin compounds did not adsorb onto this Millipore filter.

2.4. Combined removal of Cu, Zn and organotin compounds

Combinations of 300–1800 mg/l Südflock P294 and 40–800 mg/l Norit SAE Super were suspended in 500 ml artificial wastewater (aqueous Zn and Cu conc. were, respectively

17.52 and 5.99 mg/l) or real wastewater in a mixing reactor with a volume of 600 ml and a diameter of 8.5 cm. The dimensions of the impeller were 6 cm diameter and 2 cm height. The maximum speed of the impeller was 400 rpm. The mixing reactor contained 4 baffles with a diameter of 1.7 cm. The suspension was stirred for 15 min at 200 rpm. After 15 min settlement time a sample of the upper water layer was taken for Zn, Cu and organotin analysis.

3. Results and discussion

3.1. Adsorbent screening

Fig. 1 shows the percentage Cu and Zn removal from artificial wastewater by various adsorbents. The experiments were made in duplicate and the standard deviation is presented as error bars. The pH in these experiments ranged from 7.3 to 7.9, except for Laviopur (pH 9.1). Südflock P 294 and Laviopur LCM 4 showed the highest percentage Cu and Zn removal (Fig. 1). Both adsorbents contain bentonite, an aluminum coagulant and an organic flocculant. These adsorbents flocculate, and are thus easily separated from the water by flocculation–sedimentation. The powdered activated carbon (Norit SAE Super) has also a large Cu and Zn removal capacity (Fig. 1) The addition of activated carbon to the water (for example, to adsorb organic compounds) will thus also help to reduce the heavy metal concentration in the water.

Figs. 2 and 3 shows the percentage organotin removal from artificial wastewater by various adsorbents, while Fig. 4 shows the percentage MBT, DBT and TBT removal from a solution, which contained 10,000 μg Sn/l MBT, DBT and TBT, by powdered activated carbons. The experiments presented in Figs. 2 and 3 were made in duplicate and the standard deviation is presented as error bars.
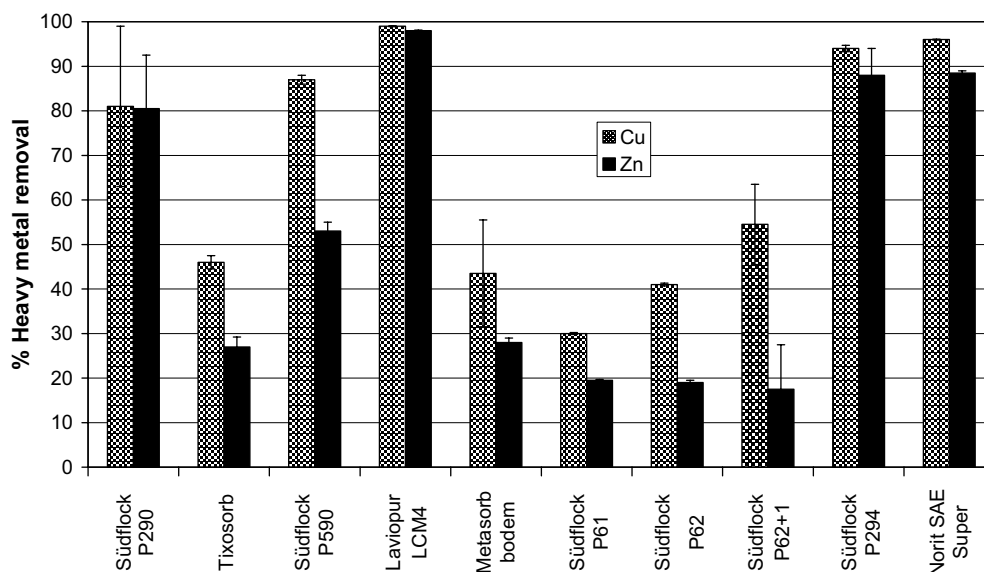

Fig. 1. Percentage Cu and Zn removal from artificial wastewater, adsorbent concentration = 0.5 g/l.
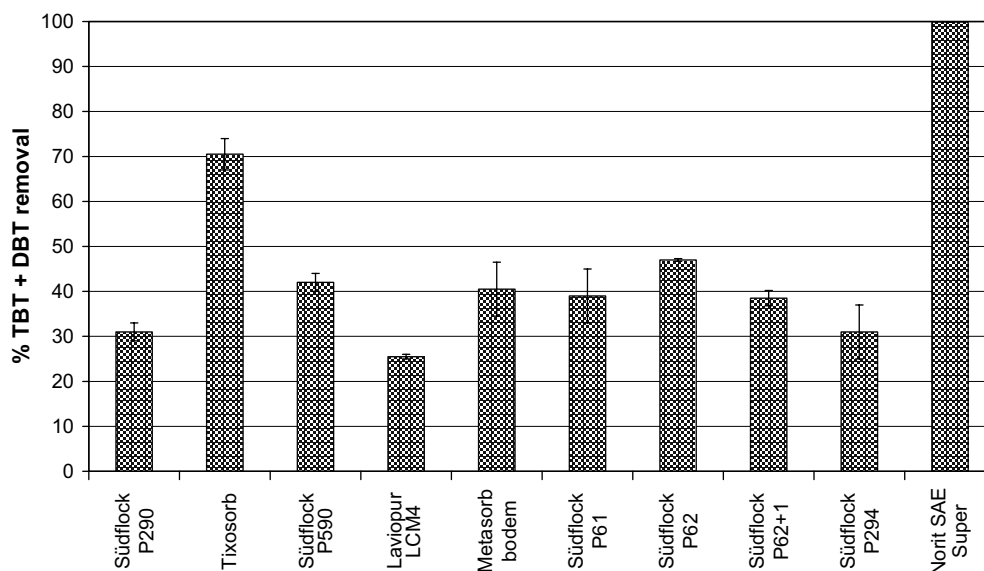
Fig. 2. Percentage Organotin (DBT + TBT) removal from artificial wastewater, adsorbent concentration = 0.5 g/l.
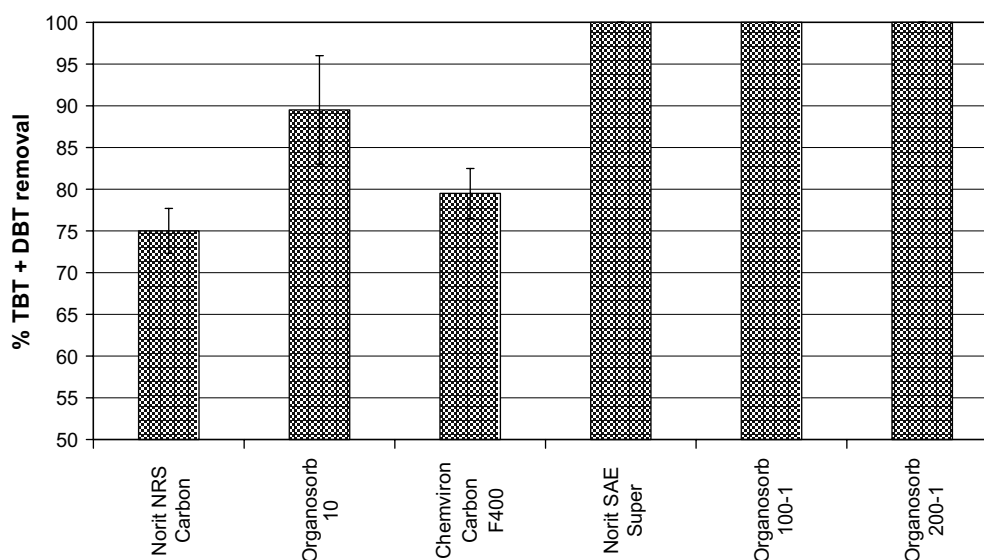

Fig. 3. Percentage Organotin (DBT + TBT) removal from artificial wastewater, adsorbent concentration = 0.25 g/l.

The adsorbents with the largest heavy metal removal capacity (Südflock P294 and Laviopur LCM 4) are not suited for organotin removal form the artificially contaminated wastewater (Fig. 2). Activated carbon adsorbents showed the largest ability to remove organotin compounds from wastewater. This indicates that organotins are mainly removed from the water by hydrophobic adsorption onto the activated carbon. Moreover, the organically modified bentonite adsorbent (Tixosorb) showed the greatest organotin removal ability of all bentonite adsorbents, which also illustrates the importance of the hydrophobic adsorption mechanism. Since the pH of the water (7.3–7.9) is well above the pK_a value of TBT (pK_a = 6.25, Arnold et al., 1998) and the salinity of the water is high, TBT is believed to occur as TBT–Cl, which is indeed

known to adsorb onto natural organic matter by hydrophobic adsorption (Arnold et al., 1998).

The powdered activated carbons showed a larger organotin adsorption ability than the granular activated carbons (Fig. 3), which can be attributed to their larger surface area. Fig. 4 shows that all powdered activated carbons adsorb more than 99.98% of the added organotin compounds. Since Norit SAE Super showed the largest organotin adsorption ability, this adsorbent was used in further experiments.

The screening experiments show that there is no single adsorbent with a large ability to remove both Cu, Zn and organotin compounds from shipyard wastewater. To efficiently remove these pollutants from the wastewaters a mixture of a bentonite based adsorbent and a powdered activated carbon is needed.
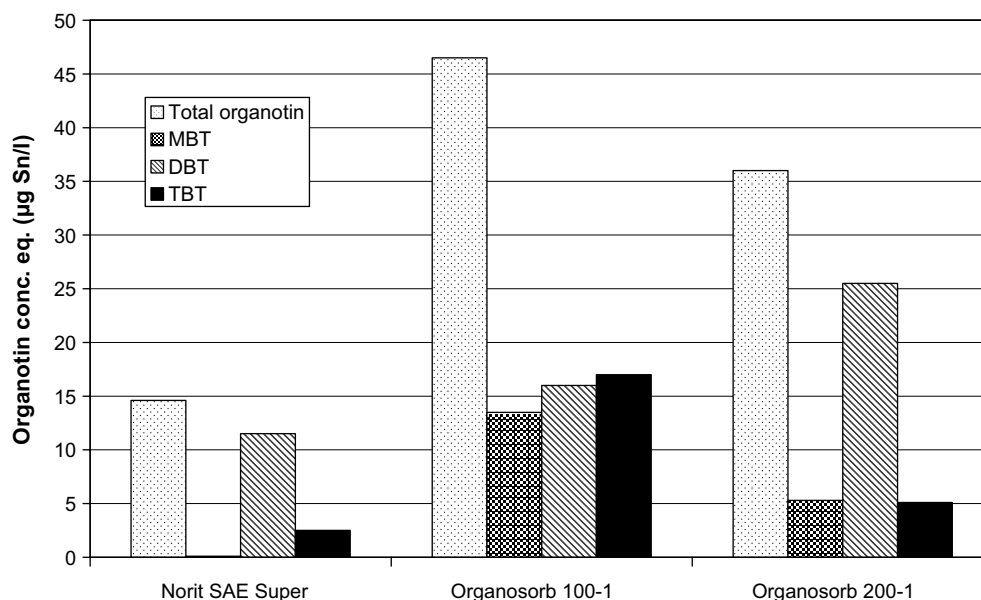
Fig. 4. Organotin (MBT, DBT, TBT and the sum of MBT, DBT and TBT) concentration after PAC sorption. Initial solution contains 10,000 μg Sn/l MBT, DBT and TBT. Adsorbent concentration = 1.25 g/l.

3.2. Process design and optimization

In the one-step adsorption–flocculation process both the adsorbent and the pollutant removal have to be optimized. The selected bentonite adsorbents (Südflock P294 and Laviopur LCM 4) contain an aluminum coagulant and an organic flocculant, which will cause the flocculation of the adsorbent particles. Since preliminary tests showed that Laviopur LCM 4 adhered too much to the baffles and impeller, which would cause serious problems when this adsorbent would be used on an industrial scale; only the

Südflock P294 particle removal is studied in further experiments. In addition the influence of the process conditions (mixing and settlement time) on the Cu and Zn removal by Südflock P294 is investigated.

The adsorbent removal is determined by turbidity measurements. After mixing a Südflock P294 suspension of 300 mg/l for 15 min at various stirring speeds and a settlement time of 15 min the turbidity of the supernatant solution was measured. The flocculation efficiency $\left(100 - \frac{\text{final turbidity}}{\text{initial turbidity}} \times 100\%\right)$ is presented in Fig. 5. Subsequently the Zn and Cu concentrations were determined in
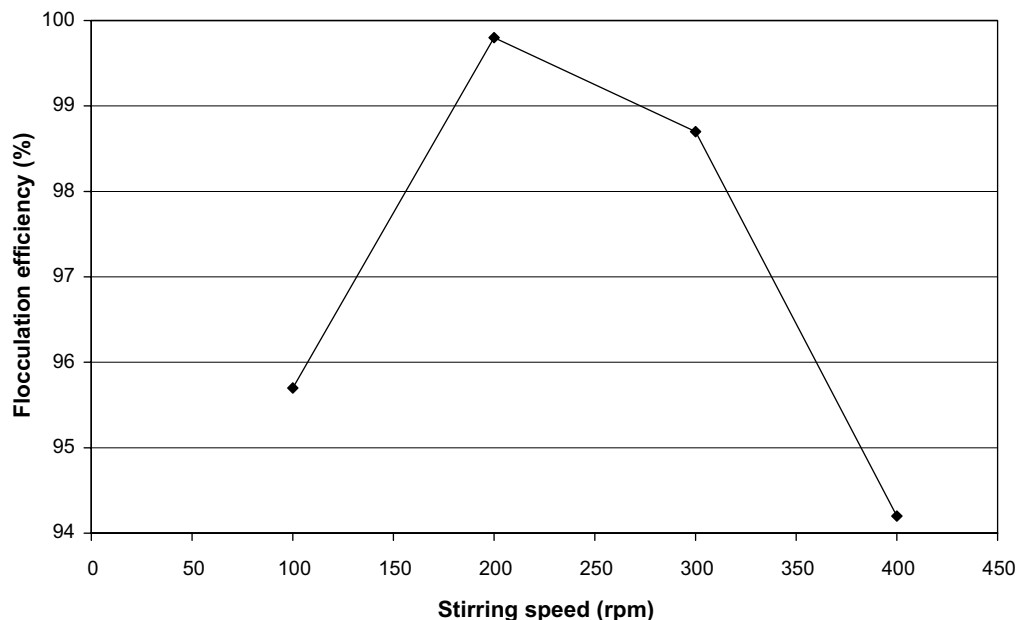

Fig. 5. Flocculation efficiency (%) versus stirring speed. Adsorbent (Südflock P294) concentration = 300 mg/l.

a 40 ml sample, which was withdrawn from the supernatant solution and was centrifuged at 13,776g for 30 min. The Cu/Zn removal efficiency $\left(100 - \frac{\text{final Cu or Zn conc}}{\text{initial Cu or Zn conc}} \times 100\%\right)$ is presented in Fig. 6.

Fig. 5 shows a maximum flocculation efficiency at a stirring speed of 200 rpm. The flocculation efficiency depends on the particle collision frequency (Maes et al., 2003). An increase in the collision frequency, by increasing the agitation speed, leads to an increase in flocculation efficiency. However, if the agitation speed becomes too large, aggregate disruption starts. Therefore, for a given treatment time and adsorbent concentration there exists an optimum agitation speed at which maximum flocculation efficiency is reached, as is illustrated in Fig. 5.

Fig. 6 shows that the Cu or Zn removal generally increases with an increasing stirring speed (except for the Zn removal efficiency at 400 rpm), which is expected since an increased stirring speed enhances the adsorption kinetics. There is no obvious explanation for the low Zn removal efficiency at 400 rpm. In general, an increasing stirring speed enhances the heavy metal removal, but at the same time a very large stirring speed causes aggregate disruption. The stirring speed has to be chosen so that it

ensures fast adsorption kinetics and at the same time good adsorbent flocculation. Since in further experiments adsorbent concentrations above 300 mg/l will be used, optimal stirring speeds for maximal adsorbent flocculation below 200 rpm are expected. On the other hand, sufficient energy has to be added to the suspension to ensure a fast Cu and Zn adsorption. To ensure good adsorbent flocculation and at the same time a fast Cu and Zn adsorption, a mixing speed of 200 rpm ($G = 821 \text{ s}^{-1}$) and a mixing and settlement time of 15 minutes are chosen in further experiments.

3.3. Combined removal of Cu, Zn and organotin compounds

The adsorbent screening tests revealed that mixtures of two adsorbents (Südflock P294 and Norit SAE Super) are needed for the removal of both organotin compounds and heavy metals. After mixing the adsorbent suspension at 200 rpm for 15 min, the bentonite particles and the powdered activated carbon flocculate and settle down fast. The organotin (DBT + TBT), Cu and Zn concentrations remaining in the supernatant solution of an AWW (artificial wastewater) and a RWW (real wastewater) are
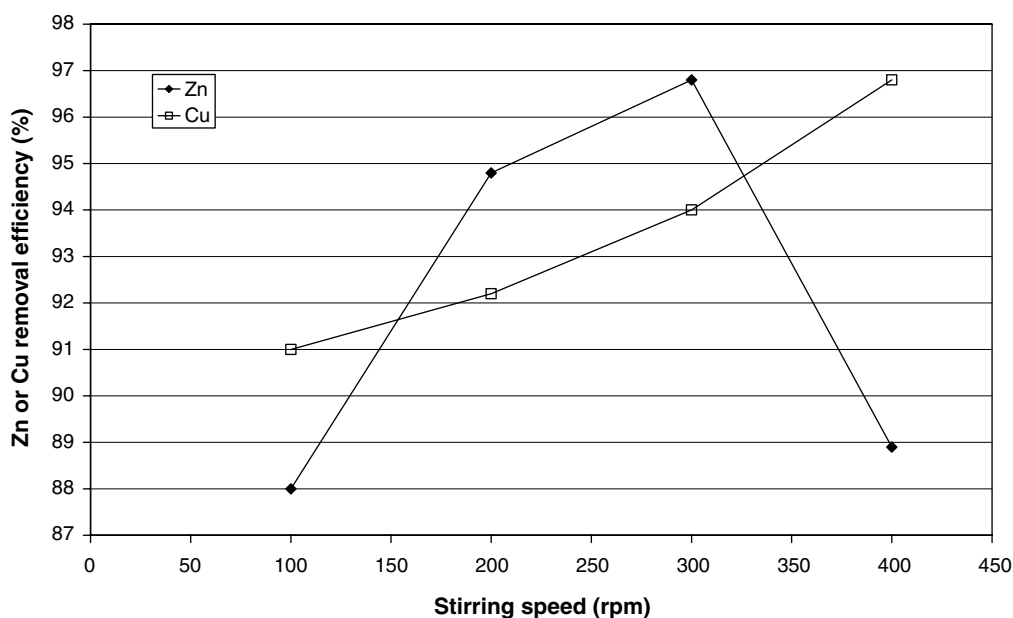

Fig. 6. Cu and Zn removal efficiency (%) versus stirring speed. Adsorbent (Südflock P294) concentration = 300 mg/l.

Table 3
Combined Cu, Zn and organotin removal from artificial wastewater

Sorbent combination	DBT conc. (µg Sn/l)	TBT conc. (µg Sn/l)	Cu conc. (mg/l)	Zn conc. (mg/l)
40 mg/l Norit; 300 mg/l P294	2.14 ± 0.187	2.71 ± 0.382	n.d.	n.d.
60 mg/l Norit; 300 mg/l P294	1.890 ± 0.120	1.12 ± 0.792	n.d.	n.d.
80 mg/lNorit; 300 mg/l P294	1.53 ± 0.212	0.856 ± 0.053	3.77 ± 0.09	7.67 ± 0.01
160 mg/lNorit; 600 mg/l P294	0.052 ± 0.001	0.238 ± 0.016	2.10 ± 0.01	4.34 ± 0.02
700 mg/lNorit; 1600 mg/lP294	0.017 ± 0.008	0.125 ± 0.014	n.d.	n.d.
800 mg/lNorit; 1600 mg/lP294	0.008 ± 0.001	0.031 ± 0.002	0.0315 ± 0.0005	0.438 ± 0.0004

n.d. = not determined.

Table 4
Combined Cu, Zn and organotin removal from real dockyard wastewaters

Sorbent combination	DBT conc. (µg Sn/l)	TBT conc. (µg Sn/l)	Cu conc. (mg/l)	Zn conc. (mg/l)	pH
0 mg/lNorit; 300 mg/lP294	3.77 ± 0.004	7.95 ± 0.838	0.422	1.92	7.89
100 mg/lNorit; 300 mg/l P294	–	3.06	0.520	2.24	8.28
200 mg/lNorit; 600 mg/l P294	0.102	0.981	0.165	0.700	8.12
500 mg/lNorit; 1200 mg/lP294	0.025 ± 0.009	0.528 ± 0.270	0.142	0.464	8.56
600 mg/lNorit; 1200 mg/lP294	0.004 ± 0.001	0.269 ± 0.202	0.037	0.060	8.31
700 mg/lNorit; 1800 mg/lP294	0.006 ± 0.001	0.077 ± 0.050	0.018	0.038	8.47

presented in Tables 3 and 4, which show that an increasing amount of powdered activated carbon (Norit SAE Super) and Südflock P294 decreases, respectively the organotin and the heavy metal concentration in the supernatant solution of the treated artificial and real wastewater.

3.4. Cost calculations

3.4.1. Adsorbent cost

The most important parameter determining the cost of the adsorption–flocculation process is the adsorbent cost. The adsorbent cost is 750 €/ton for Südflock P294 and 1810 €/ton for Norit Sae Super (Süd-chemie and Norit, 2004). The adsorbents cannot be regenerated. The cost for the adsorbent waste treatment consists of the cost of dewatering, transport and treatment by incineration or landfill and is estimated at 100 €/ton. The adsorbent concentration needed to comply with the imposed discharge limits is influenced by the initial concentration of the pollutants in the water and the pollutant removal ability of the adsorbent.

In systems containing only one pollutant and one adsorbent, an adsorption isotherm relates the adsorbents' adsorption capacity to the pollutant concentration in the water at equilibrium conditions. In this paper a mixture of adsorbents and of pollutants (Cu, Zn, organotin compounds and other pollutants which could be present in the RWW) is used. In addition, the adsorption data are collected after only 30 min. Therefore, these data cannot be used to produce adsorption isotherms, which present the theoretical adsorption capacity of the adsorbents for each pollutant at equilibrium conditions.

However, the "adsorption–isotherm approach" can and will be used to estimate the adsorbents dosage needed to reduce the pollutant concentrations to the discharge limits. "Pseudo adsorption isotherms" of Cu and Zn onto Südflock P294 and of organotins (DBT & TBT) onto Norit SAE Super are calculated from the data in Tables 3 and 4 and shows the adsorbed pollutant concentrations versus the pollutant concentration in the supernatant solution after 15 min settlement time (Figs. 7–9).

The screening experiments (Figs. 1–3) shows that the addition of Südflock P294 and Norit SAE Super also influences the removal of organotins and heavy metals, respectively. This (minor) influence was not taken into account for the calculation of the adsorbents dosages.
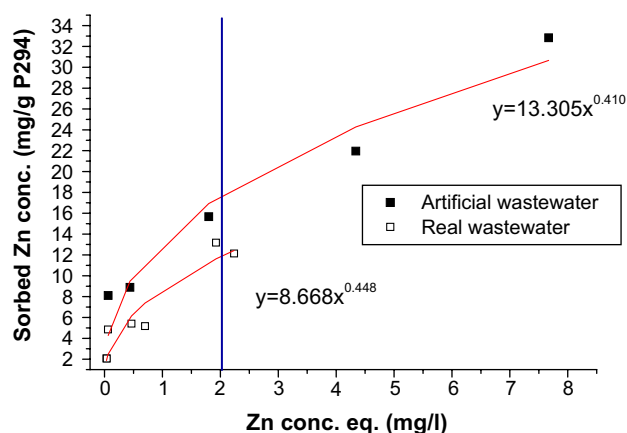

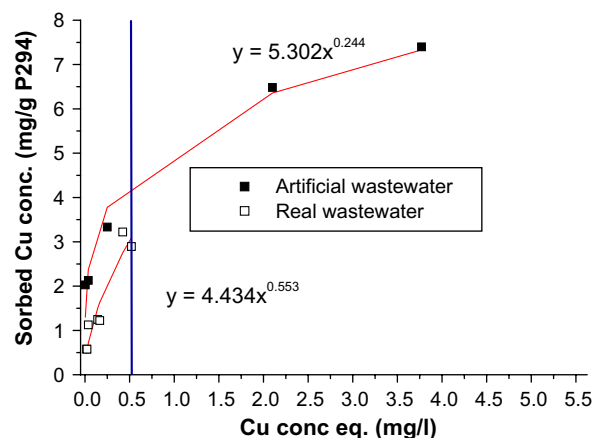Fig. 7. Pseudo adsorption isotherm of Cu onto Südflock P294 in AWW and RWW.

Fig. 8. Pseudo adsorption isotherm of Zn onto Südflock P294 in AWW and RWW.

The pseudo adsorption isotherms of Cu and Zn onto Südflock P 294 (Figs. 7 and 8) can be described by the Freundlich equation $q = KC^{(1/n)}$, where q equals the adsorbed metal concentration and C equals the aqueous metal concentration at equilibrium. The parameters (K and n), and the correlation coefficients of these fits are presented in Table 5.

Figs. 7 and 8 shows that the Cu and Zn removal ability of the Südflock adsorbent is lower in real shipyard wastewater, compared to artificial wastewater. This is probably caused by the presence of complexing agents
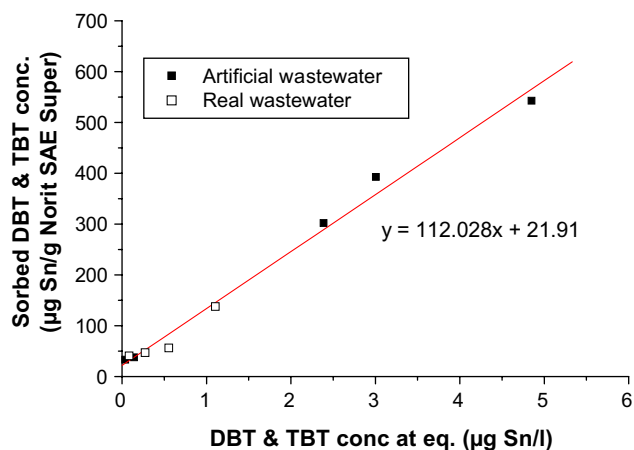
Fig. 9. Pseudo adsorption isotherm of organotin compounds onto Norit SAE super in the AWW and RWW.

Table 5
Freundlich parameters of "pseudo adsorption isotherms"

System	K	n	R^2
Cu – Artificial wastewater	5.302	4.093	0.968
Cu – Real wastewater	4.434	1.807	0.902
Zn – Artificial wastewater	13.305	2.441	0.936
Zn – Real wastewater	8.668	2.234	0.887

(organic matter) or other heavy metals in the real shipyard wastewater.

The pseudo adsorption isotherms of organotin compounds onto Norit SAE Super in the artificial and real wastewater coincide and can be described by the linear equation $q = 112.028C + 21.91$ (Fig. 9). The correlation coefficient (R^2) of this fit is 0.995. This linear sorption isotherm indicates that the adsorption of organotin compounds onto powdered activated carbon occurs mainly by hydrophobic adsorption, which was to be expected from the hydrophobic nature of the organotin compounds and the activated carbon.

Based on the pseudo adsorption isotherms, the adsorbent concentrations (S), which are needed to reduce the initial pollutant concentrations (I) in a *real shipyard wastewater* to the discharge limit (D), can be calculated by Eqs. (1)–(3).

To reduce the Cu-conc. : $S = \dfrac{I - D}{4.434 D^{0.553}}$ (1)

To reduce the Zn-conc. : $S = \dfrac{I - D}{8.668 D^{0.448}}$ (2)

To reduce organotin (DBT TBT) conc. :

$$S = \dfrac{I - D}{112.028 D + 21.91}$$ (3)

In these equations S stands for the amount of sorbent (Südflock P294 for Eqs. (1) and (2) and Norit SAE super for Eq. (3) concentration (mg/l), I = Initial pollutant concentration (mg Cu or Zn/l or µg Sn/l), D = Discharge limit

(mg Cu or Zn/l or µg Sn/l). If both Cu and Zn are present in the wastewater only the largest S value of Eqs. (1) and (2) should be used.

These equations are applicable when the Cu concentration is about one fourth of the Zn concentration. It is not known whether these equations can be used when the Zn/Cu ratio significantly changes (e.g. Cu concentration is larger than Zn concentration). Since this is not expected to occur in real shipyard wastewaters, this aspect was not further investigated.

3.4.2. Electricity cost

In the adsorption–flocculation process, electricity is mainly used for pumping the water and mixing the adsorbent suspension. The suspension is mixed for 15 min at $G = 821\ s^{-1}$. The energy dissipation can be calculated from the formula:

$$G = \sqrt{\dfrac{P}{V\mu}}$$ (4)

where G is the average velocity coefficient, V is the water volume, μ is the dynamic viscosity of water (8.9×10^{-4} Pa s) and P is the power required (Watt). This formula can be rewritten as follows:

$$P = G^2 V \mu$$ (5)

and $V = QT$ (6)

where Q is the flow rate (m³/h) and T is the time (h). Combining Eqs. (5) and (6) results in:

$$P = G^2 Q T \mu\ [\text{W}]$$ (7)

or

$$\dfrac{P}{Q} = \dfrac{G^2 T \mu}{1000}\ [\text{kWh/m}^3]$$ (8)

Since mixing time (T) is constant (0.25 h), the power requirement for mixing is 0.15 kWh/m³. When we assume also 0.15 kWh/m³ for pumping the water, the total power requirement is 0.3 kWh/m³. At an electricity cost of 0.0695 €/kWh (Eurostat, 2005), the energy cost then becomes 0.0209 €/m³. The adsorption–flocculation process is thus a low energy consuming water treatment technology.

The total operating cost consists of the sum of the adsorbent cost (including sludge treatment) and the electricity cost. Fig. 10 shows a total operating cost estimation for 4 polluted wastewaters and 5 different organotin discharge limits. The applied discharge limits for Cu and Zn were taken as 0.5 mg/l Cu and 2 mg/l. Zn in all cases.

3.5. Discharge limits

In Flanders the discharge limits for Cu and Zn are, respectively 0.5 and 2 mg/l (vertical lines shown in Figs. 7 and 8). For organotin compounds no discharge limits exists. Therefore organotin discharge limits are proposed,
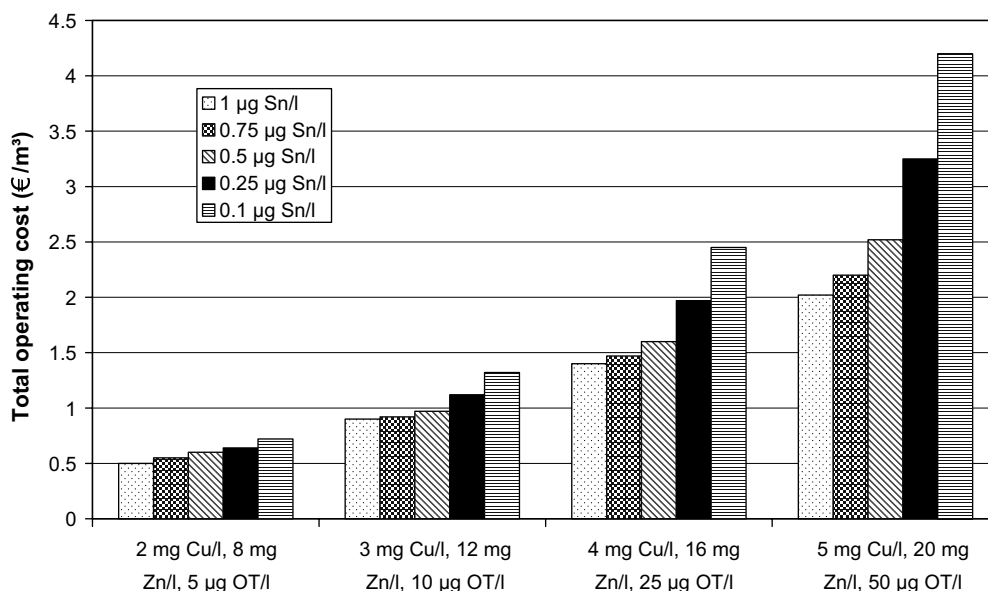
Fig. 10. Total operating costs for 4 different wastewaters for 5 different organotin discharge limits.

which correspond to the BATNEEC (best available technology not entailing excessive costs) principle.

Since organotin removal from shipyards wastewaters can hardly be considered as "state-of-the-art" technology, it is difficult to set a discharge limit for organotin compounds according to this BATNECC principle. Notwithstanding these difficulties we would like to propose a discharge limit, based on the technical and economical evaluation of our own one-step treatment technology for shipyard wastewaters. Therefore the total operating costs for 4 different wastewaters are plotted for various organotin discharge limits (Fig. 10).

Fig. 10 shows that for heavily contaminated waters (50 µg Sn/l) the operating costs exceed 4 €/m³ for an organotin discharge limit of 0.1 µg Sn/l, which is not economically acceptable. For a discharge limit of 0.5 µg Sn/l the total operating cost is about 2.5 €/m³. Increasing the discharge limit beyond this value does not result in a large decrease in operating cost. An organotin discharge limit of 0.5 µg Sn/l is thus economically and technically the best option.

Prasad and Schafran (2006) used a conventional process train of coagulation–clarification, filtration and granular activated carbon adsorption for the combined removal of heavy metals and TBT from shipyard waters with various initial organotin concentrations and found that effluent total TBT concentrations ranged from 0.067 to 1.470 µg/l, while dissolved TBT concentrations ranged from 0.052 to 0.276 µg/l. An organotin discharge limit of 0.5 µg Sn/l can thus also be obtained by this conventional water treatment process, which can be considered as "state-of-the-art".

Since the organotin containing antifouling paint on surfaces is supposed to be completely removed by 1 January 2008, local authorities do not want to impose discharge limits for organotin compounds to shipyards. However, the problem of organotin contaminated sediments will probably last for several decades. The cleaning of these contaminated sediments will also result in organotin contaminated wastewaters. In order to protect the environment around sediment cleaning sites it is needed to set discharge limits for organotin compounds. Based on our lab-scale adsorption–flocculation treatment technology we propose an organotin discharge limit of 0.5 µg Sn/l.

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