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Scientific Paper

BOAT PRESSURE WASHING WASTEWATER TREATMENT WITH CALCIUM OXIDE AND/OR FERRIC CHLORIDE

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The aim of this study was to investigate the efficiency of (1) chemical precipitation by calcium oxide, (2) coagulation/flocculation by ferric chloride (FC), and (3) the combination these two methods in reducing the toxicity of wastewater generated by boat pressure washing. All three methods gave satisfactory results in the removal of colour, turbidity, Cr, Fe, Cu, Zn, and Pb. The concentrations of heavy metals were lowered below national limits with 1 g of CaO, 2.54 mg of Fe^{3+} in the form of $FeCl_3 \times 6H_2O$, and the combination of 0.25 g of CaO and 5.08 mg of Fe^{3+} per 50 mL of wastewater. Both CaO (1.50 g per 50 mL of wastewater) and FC proved efficient, but their combination yielded a significantly better performance: 99.41 %, 100.00 %, 97.87 %, 99.09 %, 99.90 %, 99.46 % and 98.33 % for colour, turbidity, Cr, Fe, Cu, Zn, and Pb respectively. For colour, Cr, Cu, Zn, and Pb removal efficiencies increased in the following order: FC<CaO<CaO+FC, while this order for turbidity and Fe was as follows: CaO<FC<CaO+FC. As expected, all three methods increased the concentration of total dissolved solids in the final effluent. Our results suggest that the combined treatment of marina wastewaters with calcium oxide followed by ferric chloride is efficient, cost-effective, and user-friendly.

KEY WORDS: *antifouling paints, CaO, chromium, colour, copper, lead, heavy metals, turbidity, zinc*

The major source of heavy metals in the sediments around shipyards and marinas are the antifouling paints (1) that have been extensively used for boat protection for over the last 100 years (2). Antifouling paints contain strong agents that kill algae and other organisms and prevent them from attaching to the hull (2). Efficient protection usually requires that the hull be treated once a year (1). Old paint is removed by pressure washing that generates 100 L to 150 L of wastewater per boat. This amount of wastewater contains about four kilograms of paint distributed over particles of different size (3). The major biocide present in all paints is copper (Cu). Other metals like zinc (Zn), chromium (Cr), titanium (Ti), and lead (Pb) can also be present, but their concentration varies with the brand and the type of paint (1). A number of studies (reviewed in ref. 1) have determined their genotoxic effects on marine environment, including extinction of local species.

There are over a hundred marinas along the Croatian Adriatic coast and most still release boat pressure washing wastewater directly into the sea.

Our group has been testing several physico-chemical methods of wastewater treatment with red mud as coagulant, first in the laboratory (4, 5) and then full-scale (1). The average removal efficiency of the full-scale treatment was 99.6 % for Pb and Cu and 99.9 % for Zn. In a pilot-scale trial, Walker et al. (2) managed to remove over 98 % of chemical oxygen demand (COD) from shipyard wastewaters using dolomite and dolomitic sorbents. Ottosen et al. (3) efficiently lowered Cu, Zn, and Sn levels in dockyard wastewaters to below regulatory limits using the coagulation/flocculation method with ferric chloride.

Coagulation/flocculation with alum and ferric sulphate was also efficient (99.8 %) in removing tributyltin from shipyard wastewaters in a laboratory and a full-scale system (6). In another study (7), organotin species was successfully removed from shipyard wastewaters by electrochemical oxidation using niobium coated with boron-doped diamond and titanium coated with iridium dioxide anodes (7). Vreysen et al. (8) combined adsorption with a bentonite-type adsorbent and coagulation/flocculation with activated carbon in powder and removed up to 98.7 % of Cu and 99.4 % of Zn from shipyard wastewaters.

The aim of this study was to develop and test a cost-effective and user-friendly laboratory-scale method combining precipitation with calcium oxide (CaO) followed by neutralisation and coagulation/flocculation with ferric chloride (FC) for the removal of inorganic/organic contaminants from wastewaters generated in marinas by boat pressure washing

MATERIALS AND METHODS

Wastewater sampling and storage

Wastewater generated from boat pressure washing was collected in the Marina Kaštela, Kaštel Gomilica, Croatia. The effluent was collected in a channel with fine grate at the end. To obtain representative samples, eight boats with different paint coatings (different colour and brand) were washed. One hundred litres of wastewater was sampled. Before purification, wastewater was homogenised as described in our previous research (9).

Purification experiments

All purification experiments were conducted at 22 °C. The treatment with CaO was performed as follows; aliquots of wastewater (50 mL) were mixed with 0.25 g, 0.50 g, 1.00 g, or 1.50 g of CaO (Lička tvornica vapna, Ličko Lešće, Croatia) (12). After adding 1.50 g of calcium oxide, we lowered the pH to 9 by adding 4 mol L^{-1} of hydrochloric acid (Kemika, Zagreb, Croatia). The suspension was mixed for 10 minutes on a magnetic stirrer (30 MAG 12, Labline Stock Centre, Mumbai, India; 200 rpm) and left to settle for 30 minutes. After floc sedimentation, clear water was decanted and analysed.

Treatment with ferric chloride (FC), $FeCl_3 \times 6H_2O$ (Kemika, Zagreb, Croatia), was performed as follows; aliquots of wastewater (50 mL) were mixed with the 1.27 mg, 2.54 mg, 3.81 mg, or 5.08 mg of Fe^{3+} added in the form of ferric chloride. Due to the drop in pH caused by Fe^{3+} hydrolysis, we had to adjust it to 8 by adding ammonium hydroxide (Kemika, Zagreb, Croatia). The suspension was mixed on a magnetic stirrer for 15 minutes and left to settle for 30 minutes.

For the combined treatment, we mixed wastewater aliquots (50 mL) with 0.25 g, 0.50 g, 1.00 g, or 1.50 g of CaO on a magnetic stirrer without pH adjustment. After 10 minutes, we added 5.08 mg of Fe^{3+} into each beaker and mixed on a magnetic stirrer for another 15 minutes, and let it settle for 30 minutes.

All experiments were done in triplicate. In all cases, the relative standard deviation (RSD) was less than 10 %.

Sample preparation and analysis

Untreated and treated wastewater was prepared for the analysis as follows: 5 mL of untreated effluent and 100 mL of purified effluent were adjusted to pH 3 by adding hydrochloric acid (Kemika) or ammonium hydroxide (Kemika) preconcentrated (9) with ammonium-pyrolidinedithiocarbamate (APDC) (Merck, Schuchardt, Germany). Wastewater was filtered through Millipore micro filters and analysed using a MINIPAL4 X-ray spectrometer (PANalytical, Almelo, Nederland) (10-12). Colour and turbidity were determined using a HACH DR890 colorimeter (Hach Company, Loveland, Colorado, USA) (9, 12), while the pH and total dissolved solids (TDS) were determined using a PHT-027 water quality multi-parameter monitor (Kelilong Electron, Fuan Fujian, China) (9, 12).

Statistical analysis

For statistical analysis we used the STATISTICA 7.0 software package. The level of significance in all tests was set to $P<0.05$. Differences between treatment methods were tested using the analysis of variance and the Student-Newman-Keuls test.

RESULTS AND DISCUSSION

Chemical precipitation with CaO

Table 1 shows the results of the analysis of boat pressure washing wastewater. The baseline colour and turbidity and the respective concentrations of Fe, Cu, and Zn were 1.98, 16.23, and 5.58 times higher than the limit values for wastewaters to be discharged into a natural recipient.

Adding 0.25 g of CaO into 50 mL of wastewater resulted in 98.71 %, 98.31 %, 62.84 %, 81.60 %, 90.60 %, 95.42 %, and 59.36 % removal of colour, turbidity, Cr, Fe, Cu, Zn, and Pb, respectively (Figure 1). In spite of good removal efficiencies obtained for all seven parameters, the concentration of Cu in the final effluent was still 1.5 times higher than the maximum allowed level. The concentrations of all metals were lowered below the limit after adding 1 g of CaO. A further increase to 1.50 g of CaO improved the final removal efficiency for colour and turbidity to 99.07 % and 99.54 %, respectively. Removal efficiency of heavy metals increased linearly with the amount of CaO. It increased the most for Fe, followed by Cu and Zn. The highest removal efficiencies for Cr, Fe, Cu, Zn, and Pb were 86.97 %, 96.77 %, 97.81 %, 98.76 %, and 84.10 %, respectively.

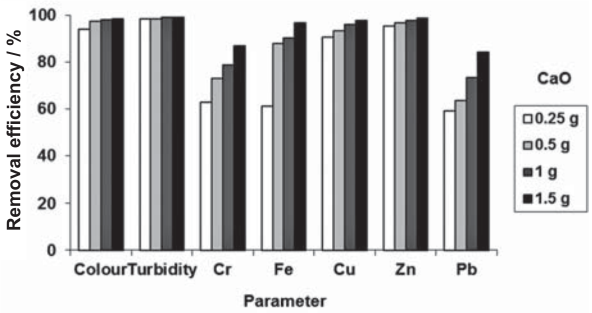

Figure 1 *CaO treatment removal efficiency. CaO amount expressed per 50 mL of wastewater.*

Coagulation/flocculation with ferric chloride

With ferric chloride (Figure 2) we obtained better removal efficiencies for colour and turbidity than for heavy metals. Acceptable levels of heavy metals were obtained after adding 2.54 mg of Fe^{3+}. Removal efficiency increased linearly with further increases in the amount of coagulant for all seven parameters, and the final was as follows: 98.76 % for colour, 99.85 % for turbidity, 78.99 % for Cr, 97.35 % for Fe, 96.77 % for Cu, 98.53 % for Zn, and 78.99 % for Pb. All measured parameters in the treated effluent below the maximum allowed level for wastewater suitable for discharge into the environment (Table 1).

Table 1 *The values of the measured parameters, at baseline (before treatment) and after the treatment of 50 mL of wastewater with 1.50 g calcium oxide, 5.08 mg Fe^{3+} in the form of $FeCl_3 \times 6H_2O$ and their combination against maximum allowed levels that can be released into a natural recipient (13).*

Measured parameter	**Untreated effluent**	**Treated effluent**			**Maximum allowed levels (13)**
		1.50 g CaO per 50 mL of wastewater	**5.08 mg Fe^{3+} per 50 mL of wastewater**	**(1.50 g CaO+5.08 mg Fe^{3+}) per 50 mL of wastewater**	
Colour / PtCo	8370	78	104	49	colourless on visual inspection
Turbidity / NTU	1300	6	2	0	clear on visual inspection
Cr / mg L^{-1}	0.890	0.116	0.187	0.019	0.5
Fe / mg L^{-1}	3.968	0.128	0.105	0.036	2
Cu / mg L^{-1}	8.118	0.178	0.262	0.008	0.5
Zn / mg L^{-1}	11.162	0.138	0.164	0.060	2
Pb / mg L^{-1}	0.790	0.124	0.187	0.013	0.5
TDS / mg L^{-1}	4850	8340	6540	7500	-
pH	7.84	8.25	7.93	7.43	6.5-9
Sludge volume / mL	-	6.4	12.8	15	-

PtCo-platinum cobalt units; NTU - nephelometric turbidity units; TDS-total dissolved solids

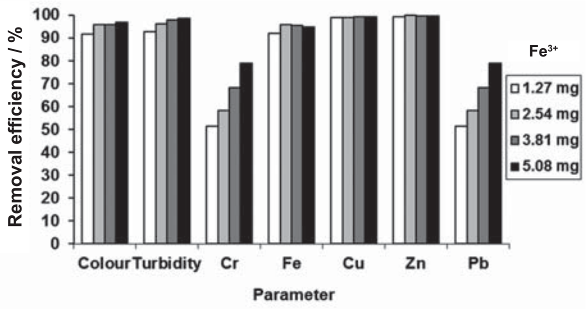

Figure 2 *$FeCl_3 \times 6H_2O$ treatment removal efficiency. Fe^{3+} amount expressed per 50 mL of wastewater.*

Combined treatment with CaO and ferric chloride

In combination with 5.08 mg of Fe^{3+} CaO lowered the concentrations of all heavy metals below the discharge limit as early as 0.25 g per 50 mL (Figure 3). Any further increase in the amount of CaO was followed by a significant linear increase in the removal efficiency for Fe, Cr, and Pb, while the removal efficiency for the other four parameters increased slightly. The final removal efficiencies with the highest doses of CaO (1.50 g per 50 mL) were 99.41 %, 100.00 %, 97.87 %, 99.09 %, 99.90 %, 99.46 %, and 98.33 % for colour, turbidity, Cr, Fe, Cu, Zn, and Pb, respectively.

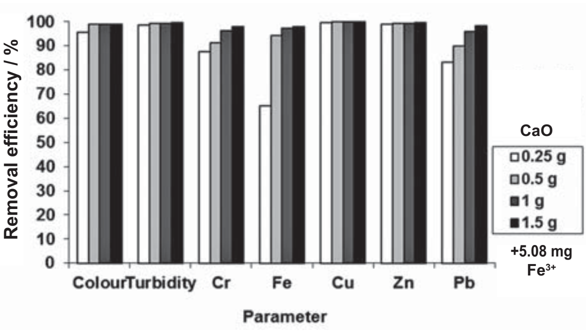

Figure 3 *Combined treatment removal efficiency. CaO and Fe^{3+} added in the form of $FeCl_3 \times 6H_2O$.*

Figure 4 compares the best removal efficiencies of the three treatment methods. The analysis of variance showed a statistically significant difference ($P<0.05$) in mean removal efficiencies between the treatment methods for all parameters. Significant differences were confirmed by the Student-Newman-Keuls test. The most efficient method in removing all seven parameters was the combined treatment. For colour, Cr, Cu, Zn, and Pb, the removal efficiencies increased in the following order: FC<CaO<CaO+FC, while for turbidity and Fe this order was as follows: CaO<FC<CaO+FC. Better performance of CaO than FC in the removal of Cu and Pb is probably related to the heat released by hydration of CaO that destroyed Cu and Pb organic complexes (10). Consequently, elements liberated from the organic ligands into the solution could be removed easily by hydroxide precipitation and coagulation/flocculation. The destruction of organic matter during the hydration of CaO could also explain better removal performance of colour by CaO compared to FC (12).

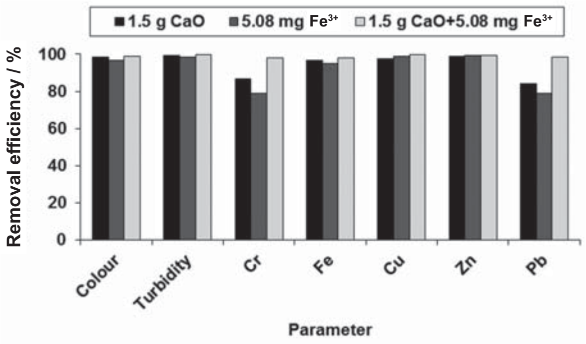

Figure 4 *Comparison of the best removal efficiencies between the three treatment methods (treatment of 50 mL of wastewater with 1.50 g CaO, 5.08 mg Fe^{3+} in the form of $FeCl_3 \times 6H_2O$ and their combination).*

Taking into account the cost of CaO and FC and their consumption per m^3 of treated water, the approximate cost of the combined treatment is 10.3 € per m^3. From what we learn, this is at the lower half of the price range for this kind of wastewater treatment, but we have no data to support it.

With the combined treatment Cr, Fe, Cu, Zn, and Pb levels were 26, 56, 63, 33, and 38 times lower than the maximum allowed level set by the Croatian regulations (13), respectively.

Our earlier toxicological study (14) showed that the treated effluent with similar Cr, Fe, Cu, Zn, and Pb levels did not cause any significant toxic effect on HEp2 and HeLa human cell lines or on human white blood cells. Similarly, treated wastewater in our earlier studies produced no significant toxic effects on either bacterial cell lines (TA98 and TA100) or HEp2 and HeLa human cell lines (15) or on duckweed (16). Gajski et al. (17) found that the leachate of solidified sewage sludge containing 0.110 mg L^{-1} of Cr, 0.240 mg L^{-1} of Fe, 0.066 mg L^{-1} of Cu, 0.080 mg L^{-1} of Zn, and 0.060 mg L^{-1} of Pb did not cause significant toxic effects on human blood lymphocytes determined by the DNA diffusion assay, micronucleus test, and the comet assay. Medley and Clements (18) found no significant toxic effect of Zn concentrations lower than 0.200 mg L^{-1} on diatom communities. Zinc at values similar to ours also did not have a toxic effect on a benthic macroinvertebrate community studied by Clements and Kiffney (19).

In addition, our concentrations in the treated wastewater are significantly lower than the LC_{50} values for Cu, Zn, Pb, and Cr obtained by Calabrese et al. (20). All this suggests that a discharge of effluents treated by a combination of CaO and FC in the final concentrations described in our study will not have a toxic effect on local marine life.

Sludge treatment

The sludge formed during the purification must be dewatered by filtration on filter presses, stored in a pool, and handed over to the authorised waste collection service for further disposal.

CONCLUSION

Combined treatment yielded the best performance in the removal of organic (colour, turbidity) constituents and heavy metals from boat pressure washing wastewater. However, CaO treatment alone yielded the highest TDS increase and generated the lowest volume of sludge. The remaining concentrations of heavy metals in the effluent following the combined treatment are lower than or comparable with previously published data (14-17), and we do not expect any toxic effects on the environment and humans. All in all, the combined treatment of marine wastewater with CaO and FC has turned out to be efficient, cost-effective, and user-friendly.

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Sažetak

OBRADA OTPADNIH VODA OD PRANJA BRODOVA KOMBINACIJOM FIZIČKO-KEMIJSKIH METODA

Radi smanjenja toksičnosti otpadnih voda koje nastaju pranjem brodova premazanih bojama protiv obraštaja primijenjene su tri metode obrade: (1) kemijsko taloženje s pomoću kalcijeva oksida, koagulacija/flokulacija s pomoću željezova klorida (FC) i (3) kombinacija ovih dviju metoda. Sve tri metode dale su zadovoljavajuće rezultate u uklanjanju boje, mutnoće, kroma, željeza, bakra, cinka i olova. Koncentracije teških metala niže od graničnih vrijednosti postignute su nakon tretmana s 1 g CaO ili 2,54 mg Fe^{3+} dodanog u obliku $FeCl_3 \times 6H_2O$ ili kombinacijom od 0,25 g CaO i 5,08 mg Fe^{3+} na 50 mL otpadne vode. Optimalne vrijednosti uklanjanja boje, mutnoće, Cr, Fe, Cu, Zn odnosno Pb s pomoću CaO (1,50 g na 50 mL) bile su 99,07 %, 99,54 %, 86,97 %, 96,77 %, 97,81 %, 98,76 % odnosno 84,10 %, dok su u slučaju željezova klorida te vrijednosti iznosile 98,76 %, 99,85 %, 78,99 %, 97,35 %, 96,77 %, 98,53 % odnosno 78,99 %. Značajno viši stupanj uklanjanja postignut je kombinacijom navedenih dvaju pristupa čime je postignuta maksimalna učinkovitost uklanjanja i to 99,41 % boje, 100,00 % mutnoće, 97,87 % kroma, 99,09 % željeza, 99,90 % bakra, 99,46 % cinka i 98,33 % olova. Za boju, krom, bakar, cink i olovo učinkovitost uklanjanja raste ovim redoslijedom: FC <CaO <CaO + FC dok za mutnoću i željezo raste u ovom nizu: CaO <FC <CaO + FC. Sukladno očekivanju, sve tri metode povećavaju koncentraciju ukupne otopljene tvari u konačnom ispustu.

Naši rezultati pokazuju da je primijenjeni način pročišćavanja otpadnih voda iz marina kombinacijom kalcijeva oksida i željezova klorida učinkovit s obzirom na stupanj uklanjanja, s povoljnim odnosom stupnja pročišćavanja i cijene te jednostavan za primjenu.

KLJUČNE RIJEČI: *boja, boje protiv obraštaja, CaO, mutnoća, teški metali, željezo(III) klorid*

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