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Original article

Alkaline disinfection of urban wastewater and landfill leachate by wood fly ash

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Wood fly ash is an industrial by-product of the combustion of different wood materials and is mostly disposed of as waste on landfills. In our preliminary experiments, wood ash exhibited antibacterial activity against urban wastewater bacteria and we focused on wood fly ash as a potential substrate for wastewater disinfection. The addition of ash at a concentration of 10 g L^{-1} (1 %) caused an instant increase of pH in urban wastewater and landfill leachate. High pH (10.1–12.7) inactivated bacterial populations in the wastewater and the removal of faecal coliforms and intestinal enterococci after 6 h of contact was 100 % (below the detection limit; <1 CFU per mL) with the most efficient ash sample (ash from combustion of beech) both in urban wastewater and landfill leachate. Properly chosen wood fly ash, i.e. one that tends to increase the pH to the greatest extent, proved to be a very effective disinfection substrate. Considering that water treated with wood ash has a high pH and needs to be neutralised before discharge, ash would be suitable for disinfection of leachates when smaller volumes are treated.

KEY WORDS: *faecal coliforms; intestinal enterococci; pH; waste management*

Wood fly ash is an industrial by-product from the combustion of different wood products in energy or power plants. It is mainly disposed of as waste material on landfills (1, 2). The production of wood ash is likely to increase in the future and finding effective applications for it is vital (2). Most of the proposed applications of wood ash thus far were in agriculture and forestry where it serves as a liming agent and increases the availability of nutrients in acid soils (2-4); as a component in concrete (5), cement, and mortar manufacturing (4, 6, 7); and as a catalyst for biodiesel synthesis (8).

At first, our aim was to test wood fly ash as a substrate for phosphate (P) removal from urban wastewater, since various types of fly ash have been proven to serve as potent P adsorbents (9-11). In addition, we wanted to investigate the potential toxicity of wood fly ash to microorganisms present in the wastewater as, to the best of our knowledge, such a study has not yet been reported. However, preliminary experiments showed that ash exhibited strong antibacterial activity to wastewater bacteria due to the increase of wastewater pH. We therefore shifted our focus and decided to study wood fly ash as a potential substrate for alkaline wastewater disinfection.

Disinfection implies the elimination of pathogenic microorganisms in water treatment systems that facilitate the safe discharge or reuse of wastewater. Alkaline disinfection implies the inactivation of pathogenic bacteria at high pH conditions, usually above 12 (12). We monitored the removal of typical pathogen indicators (faecal coliforms and intestinal enterococci) in effluents of urban wastewater and landfill leachate treatment plants in order to simulate disinfection by using wood fly ash as a potential tertiary treatment method. Nutrient removal (P and Chemical Oxygen Demand) was also monitored.

MATERIALS AND METHODS

Wastewater

The urban wastewater was the effluent of the secondary wastewater treatment plant (50,000 PE) treating the municipal wastewater of the city of Velika Gorica, Croatia. The leachate was collected from an outlet canal after passing the activated sludge treatment plant, treating the leachate from a municipal landfill of the city of Zagreb, Croatia (1 million inhabitants). Both samples were filtered through blue ribbon filter paper (Munktel, Sweden) and used in experiments within 4 h after sampling. Basic chemical parameters of wastewater and leachate are presented in Table 1.

Wood fly ash

Three wood fly ash samples were tested. Samples H and L were obtained from two different heating plants in Sweden (identity not disclosed for reasons of privacy) that combust wood chips and wood dust, respectively. Sample C was obtained from the Croatian cogeneration plant Moderator d.o.o., which combusts beech (*Fagus sylvaticus*) wood chips. Ash samples were sieved and particle size fraction <0.125 mm was used in the experiments.

Table 1 *Physical and chemical parameters of urban wastewater and landfill leachate*

Parameter	Urban wastewater	Landfill leachate
Temperature (°C)	11.5	17.1
pH	7.9	7.7
COD (mg L^{-1})	110	282
Suspended solids (mg L^{-1})	43	73
Total N (mg L^{-1})	42	321
Ammonia-N (mg L^{-1})	38.1	287
P-PO_4 (mg L^{-1})	2.9	< 1

Characterization of wood fly ash

The concentrations of major oxides and selected heavy metals in ash samples were determined by Flame- and Graphite Furnace-Atomic Absorption Spectrometry (AAS, Shimadzu AA-6300, Japan), after the complete digestion of samples with an acid mixture of HCl/H_2SO_4 in a microwave oven (sensitivity/detection limits mg L^{-1}); Cr 0.001/0.0001, Cu 0.002/0.0002, Zn 0.02/0.002).

For the transfer of acidic gaseous components into solution, ash samples have been decomposed in closed microwave vessels (Berghof SPEEDWAVE II, Germany) as described in CEN/TS 15290 (method B) (13). The sulphide concentration in the receiving solution has been determined by applying the principles of ASTM D 516-02 (turbidimetric method; HACH Spectrophotometer DR 2800, USA) (14). The P concentration in the receiving solution has been determined according to the HACH method 8114 and 10127 (HACH Spectrophotometer DR 2800, USA) (15).

The electrophoretic mobility of wood fly ash samples was measured in 0.05 mol L^{-1} NaCl solution at pH values ranging from 2-12. The pH was measured with WTW Germany SenTix 41 electrode. Ash samples at a mass concentration of 0.2 g L^{-1} were dispersed in an ultrasound bath (35 kHz/3 min) and allowed to stand for 5 min to allow larger particles to be settled. An aliquot taken from the supernatant was used to measure the mobility. Measurements were performed on ZetaPlus Zeta Potential Analyser, Brookhaven Instruments Corporation (USA). The instrument uses electrophoretic light scattering and the Laser Doppler Velocimetry method for determination of particle velocity and from this the zeta potential.

The leaching of heavy metals from fly ash into wastewater was determined after 1, 3, and 6 h of contact in the effluent. The effluent was filtered through Sartorius, Germany, 0.2 μm nitrocellulose filters and concentrations of heavy metals were determined by flame atomic absorption spectroscopy (AAS, Shimadzu AA 55B, Japan). At least five measurements were done for each determination. The standard deviation of results was found to be below 2 % (sensitivity/detection limits mg L^{-1}); Cr 0.05/0.005, Cu 0.1/0.01, Zn 0.02/0.002).

Experimental design

The fly ash samples (C, H, and L) were added to Schott bottles containing 100 mL of urban wastewater or leachate at mass concentrations of 1 or 10 g L^{-1}. The control systems were bottles with urban wastewater but without the addition of fly ash. The bottles were incubated (Memmert IPP 400, Germany) at 10 and 30 °C (experiments with urban wastewater) and 22 °C (experiments with leachate) on a mechanical shaker (180 rpm/Biosan OS-10, Latvia) without additional aeration. After 1, 3, and 6 h of incubation physicochemical and bacteriological parameters were determined.

The numbers of bacteria were determined as colony forming units (CFU mL^{-1}) by aseptically taking 1 mL of sample from the bottles, after which serial dilutions (-1 to -6) in sterile saline solution (0.05 mol L^{-1} NaCl) were made, and 0.1 mL of samples were plated onto suitable media. The numbers of faecal coliforms (Fc) were determined by incubating the samples on m-Faecal coliform agar plates (Biolife, Italy) at 44.5 °C for 24 h. After the incubation blue colonies were counted and designated as faecal coliforms. The numbers of intestinal enterococci (Ie), bacteria of the genus *Enterococcus*, were determined by incubating the samples on Slanetz-Bartley agar plates (Biolife, Italy) at 35 °C for 72 h. After the incubation, the confirmation of intestinal enterococci was done by development of black colonies on Kanamycin aesculin azide agar (Oxoid, UK). In addition, the numbers of total heterotrophs (He) were determined by incubating the samples on Tryptic glucose yeast agar plates (Biolife, Italy) at 22 °C for 72 h.

The P concentration in the effluent samples was measured using HACH spectrophotometer DR2500, USA (method 8114 and 10127) (15). Prior to measurements the pH of effluent was set to 6-8 with 1 mol L^{-1} HCl using the SenTix 41 (WTW, Germany) electrode and filtered through Sartorius nitrocellulose filters of 0.2 μm pore diameter. The chemical oxygen demand (COD) concentration was measured by HACH method 8000 (15).

Data analysis

The survival of bacteria was determined as the percentage of viable cells after the designated time of incubation compared to the number of cells at the start of the experiment (t_0). The CFUs were logarithmically transformed to normalise distribution and equalize the variances of the measured parameters. Statistical analysis was done using Statistica Software 10.0 (StatSoft, Tulsa, USA). The results were compared using one-way ANOVA with *post hoc* Duncan's new multiple range test. Correlation between variables was done using Pearson's linear correlation. Significant differences were considered at level of $p<0.05$.

RESULTS AND DISCUSSION

Characterization of wood fly ash

Oxide composition and heavy metal concentrations in the examined fly ash samples are shown in Table 2. In general, the examined samples seemed to possess a typical wood chip ash composition. Samples C and H were strongly calcareous while sample L was basically siliceous with an elevated alumina presence. As in the case of most biogenic ash types, all three samples were rich in alkali elements, with potassium accounting for over 10 wt.% in samples C and H and over 4 wt.% in sample L. Sodium concentrations exceeded 3 wt.% in all of the three samples.

Wood fly ash is generally rich in magnesium, a tendency also displayed in the currently examined samples (mainly the calcareous ones, which could be expected), some of which demonstrate percentages as high as >4.5 wt.% (Sample C). As for iron, unlike sample C, its presence was strong in samples H and L, reaching a level of 5.31 %, which is significantly

Table 2 *Chemical composition of the wood fly ash samples. Major oxides (in wt.%); heavy metals (in mg kg^{-1})*

Major oxides	**Sample C**	**Sample H**	**Sample L**
SiO_2	29.06	27.7	38.41
Al_2O_3	4.02	3.79	13.29
Fe_2O_3	0.99	4.09	5.31
CaO	41.66	33.42	20.93
Na_2O	6.45	3.35	4.14
K_2O	10.58	15.12	4.73
MgO	4.62	4.02	2.95
P_2O_5	2.31	5.86	7.80
SO_3	0.10	0.10	0.40
Heavy metals			
Cd	6	64	55
Cr	46	62	945
Cu	106	192	1,485
Mn	1,818	16,789	2,365
Ni	<15	<15	163
Zn	121	8,245	15,416

higher than normally in typical wood chip ash samples (16, 17). The phosphorus concentration was noticeably higher in sample L than in samples C and H and the same could be said for the concentration of heavy metals, with the exception of manganese. Zinc in sample L appeared to occur in concentrations significantly higher than in the others.

Disinfection of urban wastewater

Without the addition of fly ash (Control 1), the numbers of heterotrophic bacteria (He), faecal coliforms (Fc), and intestinal enterococci (Ie) in the wastewater remained constant during 6 h of incubation at 10 or 30 °C (Table 3). Ash at 1 g L^{-1} caused a slight increase in pH (8.2-9.8), which had no significant antibacterial effect on the monitored bacterial populations. The only exception was the reduction of Fc (30 %) after 6 h of contact with ash sample C at 30 °C (Table 3). The reduction in Fc was the result of the increased pH and high incubation temperature.

When ash was added at 10 g L^{-1}, the pH of the wastewater immediately increased to 10.1-12.7 (depending on the ash sample) and remained high during the entire 6 h of incubation, which had a strong antibacterial or bactericidal effect on the monitored bacterial populations (Figure 1). The pH values correlated significantly ($p<0.05$; R=0.813) with a reduction in bacterial numbers. It can be concluded that the increase of pH caused the inactivation of bacteria in the wastewater. A similar conclusion was reported by Blinova et al. (18), where the high alkalinity of oil shale combustion fly ash solutions was the key factor of its toxicity to bacterium *vibrio fischeri*, crustacean *Daphnia magna*, and microalga *Pseudokirchneriella subcapitata.*

The reduction of bacteria correlated positively ($p<0.05$; R=0.252) with the time of incubation and did not correlate significantly ($p>0.05$; R=0.119) with the incubation temperature (10 or 30 °C).

Most bacteria can live and multiply within the range of pH 5-8 and have an optimum-near neutral pH (19). Very few bacteria can grow at pH values above 10 and the highest proven pH limit for bacterial growth was 11.3-11.4, reported for *Bacillus firmus* and *Nitrosomonas halophila* (20, 21). *Escherichia coli*, a typical representative of faecal coliforms, can grow within the pH range of 5.5-8.0 (22), while bacteria from the genus *Enterococcus* tolerate highly alkaline environments; growth occurs at pH 9.6. A pH of 10.5-11.0 was shown to impede the growth of *Enterococcus faecalis*, and no growth was observed at pH 11.5 or higher (23). Our results showed that the Fc were the most susceptible to high pH values while the Ie and He were more tolerant (Figure 1). At pH above 12 (experiments with ash C), the Fc and Ie populations were completely inactivated to below detection limit (<1 CFU mL^{-1}) (Figure 1). This is in agreement with the available literature on alkaline disinfection of biosolids. Meckes and Rhodes (24) found that Fc and *E. coli* populations were more susceptible to lime

Table 3 *Survival of faecal coliforms (Fc), intestinal enterococci (Ie), and total heterotrophs (He) in the urban wastewater with addition of 1 g L^{-1} of wood ash samples C, H or L after 1, 3, and 6 h of contact at 10 and 30 °C.*
Control 1-wastewater without ash; t_0 pH = 7.9±0.1; t_0 faecal coliforms (log CFU mL^{-1})=4.45±0.55; t_0 intestinal enterococci (log CFU mL^{-1})=3.76±0.25; t_0 total heterotrophs (log CFU mL^{-1})=5.83±0.38

Experiment		**Survival (%)**					
		10 °C			**30 °C**		
		1 h	**3 h**	**6 h**	**1 h**	**3 h**	**6 h**
Control 1	**pH**	8.2	8.5	8.7	8.2	8.3	8.5
	Fc	99±1	100±1	104±1	99±1	107±1	104±1
	Ie	100±3	98±4	100±4	101±2	96±2	100±3
	He	99±6	95±12	93±3	108±5	101±7	104±9
C	**pH**	9.4	9.7	9.8	9.6	9.7	9.8
	Fc	98±14	93±4	91±5	95±4	85±4	**69±1**
	Ie	96±1	101±9	101±10	95±9	98±17	104±5
	He	95±6	94±5	97±6	96±5	96±5	98±5
H	**pH**	8.7	8.8	8.8	8.5	8.5	8.6
	Fc	88±13	90±14	96±12	92±22	87±14	92±14
	Ie	92±7	94±5	96±13	87±2	91±1	91±6
	He	98±6	98±5	107±5	97±5	100±3	108±6
L	**pH**	8.7	8.9	8.9	8.6	8.5	8.7
	Fc	98±22	94±18	101±16	89±16	102±25	92±7
	Ie	89±1	79±3	98±10	91±2	93±7	93±5
	He	93±4	93±4	97±5	97±6	97±6	102±2

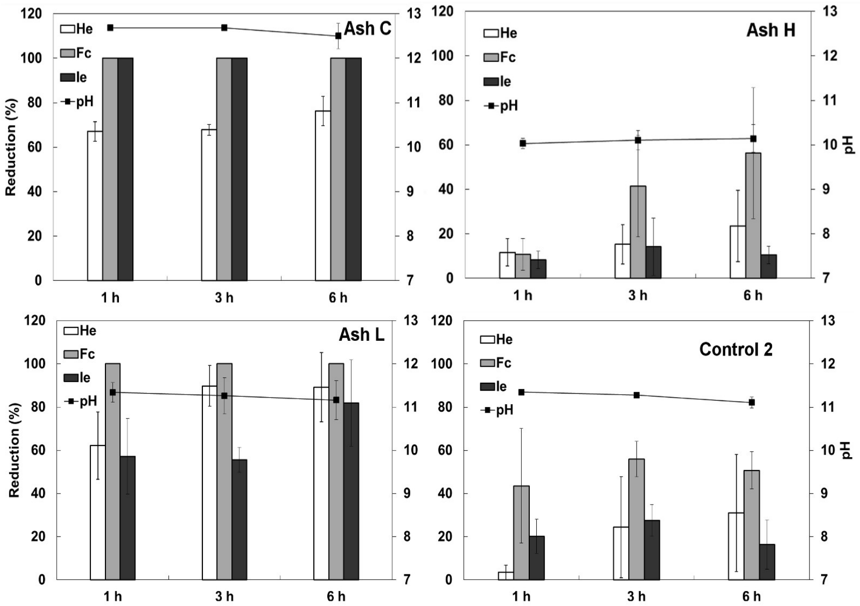

Figure 1 *Reduction of faecal coliforms (Fc), intestinal enterococci (Ie), and total heterotrophs (He) in urban wastewater with addition of 10 g L^{-1} of wood ash samples C, H or L after 1, 3, and 6 h of incubation. Control wastewater without ash and with pH initially set to 11.5; t_0 pH=7.9±0.1; t_0 faecal coliforms (log CFU mL^{-1})=4.8±0.5; t_0 intestinal enterococci (log CFU mL^{-1})=3.75±0.3; t_0 total heterotrophs (log CFU mL^{-1})=5.7±0.4.*
**measurements from experiments conducted at 10 and 30 °C are presented collectively*

treatment than other heterotrophic bacteria and Brewster et al. (25) reported complete inactivation of Fc and 4-log reduction of *Clostridium perfringens* also during lime treatment.

Leaching of heavy metals from wood fly ash

The leaching of heavy metals from fly ash to water solutions has been covered by a substantial number of studies (26, 27). The leaching of Cr and Zn from coal fly ash was responsible for toxic effects of ash/sewage sludge mixtures toward bacterium *Vibrio fischeri* (28) and heavy metals leached from oil shale combustion ash showed toxic effect in standardised tests with bacterium, crustacean, and microalgae (18). In general, the leachability from coal fly ash is relatively low and depends on the conditions in the water system. However, the leaching of heavy metals in laboratory conditions may noticeably differ from the leaching in natural conditions. It was thus suggested that the leaching behaviour test for the investigated water system should be performed before the use of fly ash as a substrate in water treatment (27).

Our results have indeed shown substantial leaching of Cr, Cu, and Zn to the tested effluent wastewater from one of the tested samples (sample L), while samples C and H leached only Zn (Table 4). The leaching enhanced the antibacterial effect of sample L, which is visible from the comparison with the control system depicted in Figure 1; the Control 2 was effluent wastewater with pH set to 11.5 at the start of

Table 4 *Concentrations of heavy metals leached into effluent water and its weight percent contained in wood ash samples C, H or L in experiments with 10 g L^{-1} of ash after 1, 3, and 6 h of contact at 10 and 30 °C. Leaching of Cd, Co, Mn, and Ni was not detected*

Heavy metal		**Leaching (mg L^{-1})/wt.%**					
		10 °C			**30 °C**		
		1 h	**3 h**	**6 h**	**1 h**	**3 h**	**6 h**
Cr	**C**	0.00/0	0.00/0	0.00/0	0.00/0	0.00/0	0.00/0
	H	0.00/0	0.00/0	0.00/0	0.00/0	0.00/0	0.00/0
	L	0.26/3	0.32/3	0.31/3	0.28/3	0.23/2	0.31/3
Cu	**C**	0.00/0	0.00/0	0.00/0	0.00/0	0.00/0	0.00/0
	H	0.00/0	0.00/0	0.00/0	0.00/0	0.00/0	0.00/0
	L	0.04/0.3	0.05/0.3	0.05/0.3	0.05/0.3	0.05/0.3	0.05/0.3
Zn	**C**	0.01/1	0.11/18	0.09/7	0.19/16	0.30/25	0.19/16
	H	0.04/0.05	0.03/0.04	0.02/0.02	0.05/0.06	0.08/0.10	0.27/0.33
	L	0.06/0.04	0.10/0.06	0.61/0.40	0.23/0.15	0.47/0.30	0.31/0.20

the experiment. After 1, 3, and 6 h of incubation, the pH values were the same, but the reduction in bacterial numbers in the system with ash L (70-100 %) was significantly higher when compared to the reduction in bacterial numbers in the Control 2 (10-60 %). The pronounced antibacterial activity of sample L was therefore ascribed to the synergistic effect of high pH and leached Cr, Cu, and Zn. Results confirmed that a proper leaching test should be mandatory for each wood fly ash sample and water sample prior to usage in treatment systems, since the discharge of wastewater with elevated concentrations of heavy metals poses an environmental hazard.

Disinfection of leachate wastewater

Guided by the results obtained in the experiments with urban wastewater, ash sample C, which showed the strongest antibacterial activity, was chosen for further experiments with leachate wastewater and the experiment was conducted at room temperature (22 °C). The monitored bacterial populations remained the same since Fc and Ie are commonly used as indicators of pathogenic bacteria for landfill leachate (29, 30).

The initial values of Fc and Ie in leachate effluent were respectively $7.1\pm3.6\times10^3$ CFU 100 mL^{-1} and $1.1\pm0.7\times10^4$ CFU 100 mL^{-1}, which is comparable to results from Grisey et al. (29) and Umar et al. (30). As in the experiments with urban wastewater, the addition of ash sample C exhibited strong antibacterial effect due to pH increase and inactivated the Fc and Ie in leachate after 1 h of contact to below the detection limit (<1 CFU mL^{-1}) (Figure 2). The number of total heterotrophs was also significantly reduced (38-45 %).

Successful disinfection of leachate can be achieved by using hydrogen peroxide and chlorine (30, 31). However, recent regulatory trends have turned to alternative disinfectants, such as UV, due to the production of hazardous disinfection by-products during chlorination (32). The problem with UV disinfection is its strong quenching of UV light owing to the unique characteristics of the leachate, which diminishes the disinfection effectiveness (32). Our results suggest that, compared to the abovementioned methods, wood fly ash is very effective and has no negative side effects apart from increasing pH in the leachate.

Nutrient removal from urban and leachate wastewater

Fly ash has been suggested as a potent substrate for phosphate (P) adsorption by many studies (9-11, 33, 34). All of these studies were conducted in systems with aqueous solutions of P salts and none used real wastewater. Urban wastewater, especially from combined sewage systems as in this study, is a complex biological and chemical system containing many different anions and emerging pollutants, such as aromatic organic compounds, chlorine, detergents, dyes, heavy metals, medicals, pesticides, surfactants, and other xenobiotics (35). These components can also adsorb on fly ash and competitively diminish the P sorption (36).

We monitored P removal from urban wastewater and showed that wood fly ash is indeed a promising substrate for its removal. At an ash concentration of 10 g L^{-1}, all three ash samples removed over 90 % of the initial P (2.3–3.2 mg L^{-1}) during 6 h of incubation

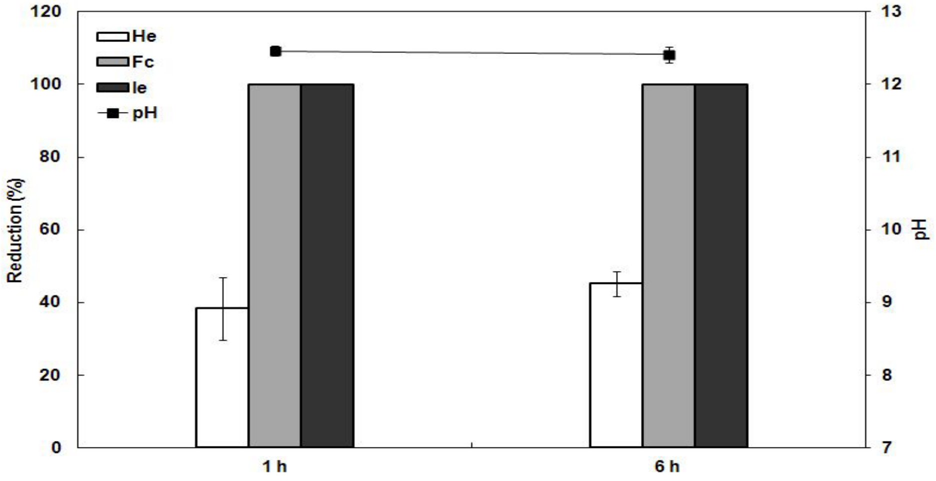

Figure 2 *Reduction of faecal coliforms (Fc), intestinal enterococci (Ie), and total heterotrophs (He) in leachate with addition of 10 g L^{-1} of wood ash sample C, after 1, and 6 h of incubation at 22 °C. t_0 pH=7.9±0.1; t_0 faecal coliforms (log CFU mL^{-1})=1.8±0.2; t_0 intestinal enterococci (log CFU mL^{-1})=1.9±0.2; t_0 total heterotrophs (log CFU mL^{-1})=4.3±0.3*

at 10 or 30 °C (Figure 3). At an ash concentration of 1 g L^{-1}, the removal percentage was lower and varied depending on the sample. The P was removed from wastewater by sorption on fly ash, rather than spontaneous precipitation due to high pH. This was confirmed by monitoring P concentrations in the control system, where the pH of wastewater was initially set to 11.5. There was no significant removal (0-14 %) during 6 h of incubation at 10 or 30 °C. Since the ash samples were positively charged at very low pH values and negatively charged at neutral and alkaline pH (Table 5), the proposed mechanism of P removal by fly ash is P adsorption onto calcite surfaces and the formation of amorphous calcium phosphate precipitates (9, 33).

Zeta potential values could be related to the isoelectric points (pHiep) of various metal oxides. The wood fly ash samples are a mixture of various oxides and their isoelectric point could be influenced by their composition. Since the isoelectric point of silica (pHiep≤4) is lower than the isoelectric points of iron oxides (pHiep=6-8) and aluminium oxides (pHiep≈5), it is not surprising that, e.g. in the case of sample L (which contained the highest amount of silica), the isoelectric point seemed to be lower than in the case of sample C.

The removal of COD was monitored in leachate since P concentrations were below 1 mg L^{-1}. After addition of wood ash C, the COD reduced by 25±9 % after 1 h and 73±2 % after 6 h of incubation (starting COD=282±14 mg L^{-1}). There was also an obvious reduction in colour; after 1 h of incubation, the leachate treated with ash sample C was transparent, while the control reactor without ash remained as yellow/brownish as it was at the start of the experiment. The pH of the leachate was 7.7±0.4 at the start, 12.5±0.1 after 1 h, and 12.4±0.1 after 6 h of incubation. A removal of COD from real industrial wastewater (detergent company) by 39 % (starting COD was 560 mg L^{-1}) after 2 h of contact with coal fly ash has been reported by Ragheb (37).

Comparison of wood ash to other disinfection substrates

In the field of wastewater disinfection, recent research has focused on novel inorganic antibacterial media such as modified zeolites and activated carbon. Activated carbon loaded with Ag (38, 39), Cu^{2+}-treated zeolite (40-42), CuO/Cu_2O-coated carbon (43), Zn-treated zeolite (44), have all been shown to exhibit a satisfactory removal of bacteria. The prominent negative sides of all of the mentioned materials are its stability, high dependency on exogenous factors (salinity of wastewater, flow velocity, etc.), questionable cost-effectiveness, and leaching of metals from substrate into wastewater. Our results suggest that, compared to the mentioned substrates, along with chlorination and UV disinfection methods, wood fly ash is extremely effective for alkaline disinfection and has no negative side effects apart from increase in wastewater pH. The alkaline disinfection in closed

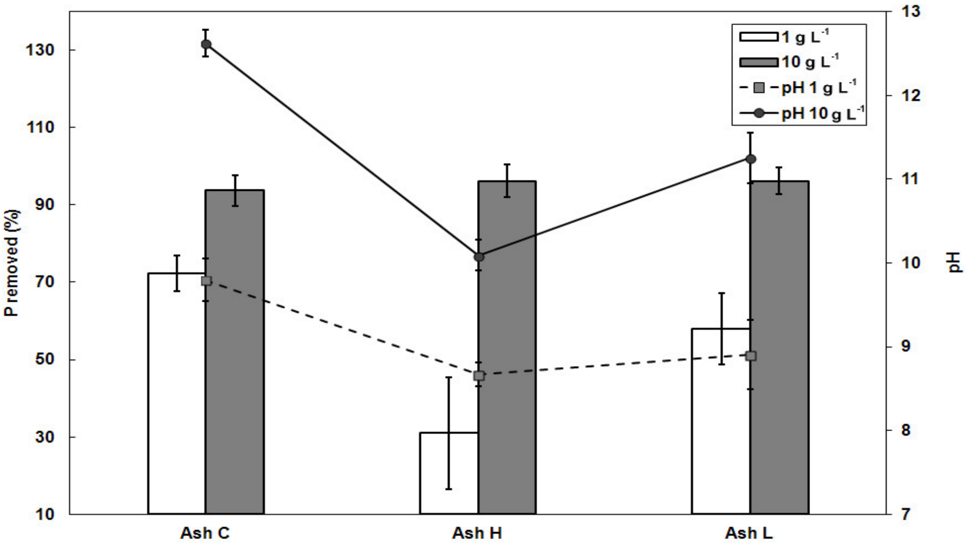

Figure 3 *The amount of P (%) removed from urban wastewater incubated* with 1 and 10 g L^{-1} of wood fly ash samples C, H, and L.*
**measurements obtained at 1, 3, and 6 h of incubation are presented collectively; measurements from experiments conducted at 10 and 30 °C are presented collectively; t_0 ($P\text{-}PO_4$)=2.3±0.2 mg L^{-1} (in experiments with samples H and L); 3.2±0.1 mg L^{-1} (in experiments with sample C)*

Table 5 *Zeta potential of the wood fly ash samples C, H, and L in 0.05 mol L^{-1} NaCl. Mean values of 10 measurements with corresponding standard deviation are presented.*
pH start-pH value of 0.05 mol L^{-1} NaCl solution measured before addition of fly ash; pH final-pH value of 0.05 mol L^{-1} NaCl solution measured 2 h after addition of 0.2 g L^{-1} of fly ash

Sample C			
pH start	1.34	3.15	11.83
pH final	1.45	10.45	11.90
Zeta potential (mV)	17.44±3.15	-12.72±1.73	-13.63±3.30
Sample H			
pH start	1.96	2.99	8.44
pH final	2.05	5.03	10.35
Zeta potential (mV)	3.52±2.01	-27.78±1.63	-23.59±2.38
Sample L			
pH start	1.02	2.99	8.44
pH final	0.88	8.72	10.61
Zeta potential (mV)	18.20±3.81	-14.37±1.71	-17.13±2.39

systems has been shown to depend on pH, exposure time, temperature, total solids content, and ammonia concentration (12, 45). In our case, the disinfection was effective in both urban (low ammonia) and leachate wastewater (high ammonia), depending on exposure time (1-6 h) and irrespective of the temperature (10 or 30 °C).

The antibacterial activity of the modified zeolites and activated carbon relies on bacteria/substrate contact at solid/liquid interface (40), meaning that the physicochemical surface properties of the substrate (charge, adsorption sites, ion-exchange) play a vital role in antibacterial activity. This also means that efficiency is reduced as flow velocity (40) and the bacteria concentration in the wastewater increase. The antibacterial activity of fly ash is completely independent of the bacteria/substrate contact, as the ash increases the pH of the entire wastewater – the effectiveness is the same in all parts of the vessel, extensive mixing is not required, the form of the filter is irrelevant, and effectiveness is the same regardless of the bacterial concentration in the wastewater.

The antibacterial effectiveness of the modified zeolites and activated carbon depends not only on the type of wastewater, but also on the seasonal changes in the same type of wastewater (40). Wood fly ash has shown the same level of effectiveness in two very different types of wastewater (urban, leachate) and it could be reasoned that its antibacterial activity should be the same in other types of wastewater, as well.

The modified zeolites and activated carbon exhibit significant leaching of metals from substrate into outflow wastewater; up to 35 mg L^{-1} of Cu from the Cu-zeolite (40), up to 2 mg L^{-1} of Ag from the Ag-zeolite (46), and 2.36 mg L^{-1} of Zn from the Zn-zeolite (42). At the proposed wood ash concentration (10 g L^{-1}), leaching of heavy metals from the ash into urban wastewater was negligible compared to the above mentioned substrates (Table 4).

Along with antibacterial properties, wood fly ash showed nutrient (P and COD) and colour removal from urban wastewater and leachate. The main drawback of using wood ash is the increase in pH of wastewater, which should be neutralised prior to discharge into a natural recipient.

CONCLUSION

Properly chosen wood fly ash, in our case ash from the combustion of beech wood chips, proved to be a very effective disinfection substrate for urban wastewater and landfill leachate. The inactivation of bacteria resulted from increased wastewater pH, caused by the addition of ash. The fly ashes that tend to increase the pH to the greatest extent should therefore be considered the best disinfectant substrates. Wood fly ash was also capable of nutrient and colour removal to a certain extent.

Considering that water treated with wood ash has a high pH and needs to be neutralised before discharge, the ash would be suitable for leachate disinfection, when smaller volumes are treated.

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Sažetak

Dezinfekcija komunalne i procjedne otpadne vode s odlagališta otpada korištenjem letećeg pepela iz drvne industrije

Leteći pepeo iz drvne industrije je nusproizvod koji nastaje spaljivanjem različitog drvnog materijala i većinom završi na odlagalištima otpada. Budući da je u preliminarnim ispitivanjima leteći pepeo pokazao antibakterijsko djelovanje prema bakterijama iz otpadne vode, pokusi su usmjereni istraživanju pepela kao potencijalnog supstrata za dezinfekciju otpadne vode. Dodatak pepela u koncentraciji od 10 g L^{-1} (1 %) uzrokovao je trenutno povećanje vrijednosti pH komunalne i procjedne otpadne vode s odlagališta otpada. Visoki pH (10,1–12,7) uništio je bakterije u otpadnoj vodi te je korištenjem najučinkovitijega pepela (dobivenog spaljivanjem bukve) postignuto 100-postotno uklanjanje (odnosno manje od mogućnosti detekcije; <1 CFU mL^{-1}) fekalnih koliforma i crijevnih enterokoka iz komunalne i procjedne otpadne vode nakon šest sati kontakta. Odgovarajući pepeo, odnosno onaj koji uzrokuje najveće povećanje vrijednosti pH, pokazao se kao vrlo učinkovit supstrat za dezinfekciju. Uzimajući u obzir činjenicu da otpadna voda tretirana pepelom ima povišen pH, te da je vrijednost pH potrebno neutralizirati prije ispuštanja u prirodni prijemnik, leteći drvni pepeo bio bi pogodan za dezinfekciju procjedne otpadne vode zbog manjih volumena koji zahtijevaju obradu.

KLJUČNE RIJEČI: *fekalni koliformi; crijevni enterokoki; pH; zbrinjavanje otpada*

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