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REMOVAL OF CADMIUM FROM AQUEOUS SOLUTION BY NATURAL AND THERMALLY ACTIVATED DOLOMITE

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SUMMARY

Removal of Cd(II) from aqueous solution by natural and thermally activated dolomite was investigated. Maximum activation temperature and maximum adsorption capacities were determined as 700 °C for 2 hours and 1.02 mg g⁻¹ for natural dolomite, but 64.93 mg g⁻¹ for thermally activated dolomite at 25 °C, respectively. Equilibrium contact time of cadmium was determined as 1 hour. Adsorption of Cd(II) on dolomite conforms to Langmuir's isotherm.

KEYWORDS:

Cadmium, dolomite, removal, sorption.

INTRODUCTION

Water pollution due to heavy metals such as cadmium is a serious global problem. Toxicological effects of acute cadmium poisoning are manifested in a variety of symptoms including high blood pressure, kidney damage, and destruction of red blood cells. Cadmium is used in different branches of industry such as electroplating, nickel-cadmium batteries, pigments, plastics, pesticides, dyes and textiles.

Therefore, a systematic study of the removal of Cd from wastewater is of considerable significance from an environmental point of view. There exist several methods to treat metal-contaminated wastewaters such as precipitation, ion exchange or adsorption, but the selection is based on concentration of waste and costs of treatment. Adsorption is one of the more popular methods but low-cost alternative technologies or sorbents, which are available in large quantities for treatment of waste streams, are still needed. Possible alternatives as sorbents are bark, fly ash, chitosan, clays, dead biomass, modified wool, moss, peat, seaweed, zeolite, humic acid, sesquioxides (iron, alu-

minium or manganese oxides). Several materials have been suggested in the literature as suitable heavy metal sorbents [1-9]. Highest adsorption capacities have been reported for: 48.78 mg Cd/g hydroxyapatite [10]; 1587 mg Pb/g lignin, 1123 mg Hg/g chitosan, 92 mg Cr(III)/g chitosan, 76 mg Cr(III)/g peat, 558 mg Cd/g chitosan, 215 mg Cd/g seaweed [11]; 6.52 mg Ni/g wollastonite, 6 mg Pb/g and 55 mg Cr(VI)/g natural bentonite [11]; 4.11 mg Cd/g acid treated bentonite, 16.50 mg Cd/g heat treated bentonite [12]; 0.57 mmol (64 mg) Cd/g bone char [13], 7.5 mg Cd/g activated carbon at pH 8 [14].

In this paper, systematic laboratory investigations on the removal of Cd(II) from aqueous solutions using natural and thermally activated dolomite by a batch operation technique have been reported.

MATERIALS AND METHODS

Adsorbate: Cd(NO₃)₂ · 4H₂O, used as adsorbate in this study, was obtained from Merck RA. A stock solution of Cd²⁺ (1029 ppm) was prepared by dissolving Cd(NO₃)₂ · 4H₂O in distilled water.

Adsorbent: A natural dolomite from Izmir-Turkey was sieved to 100 mesh size, dried at 110 °C, kept in bottles and used as adsorbent.

Activation of Dolomite: The temperature of activation was chosen according to thermal gravimetric analysis data (presented in Figure 5). Natural dolomite was heated in a furnace to 700 °C for 2 hours.

Reagents: All the chemicals used were of analytical grade.

Apparatus: A flame atomic absorption spectrometer was used for determination of cadmium and magnesium concentrations. A single channel flame photometer was used for determination of calcium concentrations.

The equilibrium concentrations of cadmium were calculated by a calibration curve. Conditions for the spectrophotometric analysis: acetylene-air under oxidising conditions at 228.8 nm for 0.02 to 3 mg L⁻¹ and 326.1 nm for 20 to 1000 mg L⁻¹.

Procedure: Aliquots of an aqueous Cd²⁺ solution of known concentration were introduced into stoppered glass bottles (100 ml) containing accurately weighed amounts (1 g) of the adsorbent. The bottles were shaken at 25 °C using an immersed water bath until equilibrium pH was measured. The adsorbent was then removed by centrifugation at 3500 rpm.

RESULTS AND DISCUSSION

Chemical analysis data of the material from Izmir, Turkey used as adsorbent for this series of experiments are given in Table 1.

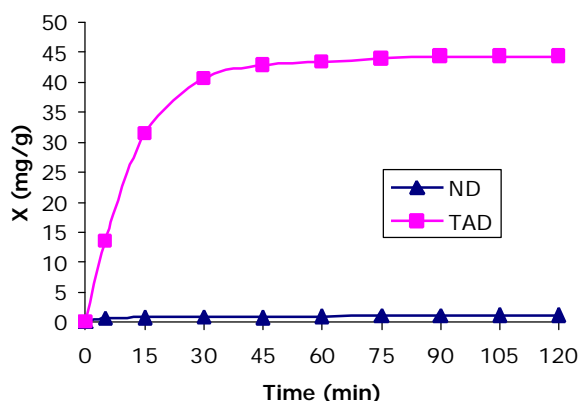
TABLE 1 - The chemical analysis of dolomite.

Compounds	Composition (%)
SiO ₂	1.83
Al ₂ O ₃	0.06
Fe ₂ O ₃	0.04
MgO	20.07
CaO	29.03
Na ₂ O	0.19
K ₂ O	0.017
MnO	0.01
Loss of Mass (%)	45.94

Influence of contact time on adsorption

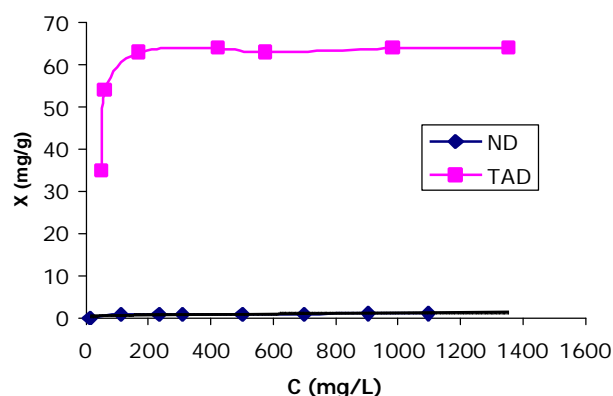
Fig. 1 shows the experimental results of adsorption of cadmium ions on natural and thermally activated dolomite samples from an aqueous solution containing 600 mg Cd L⁻¹.

FIGURE 1 - Influence of contact time on cadmium adsorption (ND: natural dolomite; TAD: thermally activated dolomite; X: amount of Cd adsorbed per g of dolomite).



The equilibrium was attained after shaking for 60 min in both natural and thermally activated dolomite. Therefore, in all experiments the shaking period was 60 min and kept constant. Then experiments of adsorption isotherms were carried out (Fig. 2).

FIGURE 2 - Adsorption isotherms of CD(II) on natural and thermally activated dolomite (explanations see Fig. 1).



To quantify the adsorption capacity of natural and thermally activated dolomite samples in relation to the cadmium ions, the experimental data points were fitted to the Langmuir adsorption equation:

$$C/X = 1/(bX_m) + C/X_m \quad (1)$$

where C is concentration of Cd in the equilibrium solution, X is the amount of cadmium adsorbed per g dolomite, X_m is the maximum amount of Cd that can be adsorbed in a monolayer (adsorption capacity), and b is a constant related to the energy of adsorption.

Figs. 3 and 4 show the straight lines obtained plotting C/X versus C for Cd on natural and thermally activated dolomite samples studied. The correlation coefficients were >0.99 in both cases (all correlations significant at the 0.001 level). The values of X_m and b are summarized in Table 2 and were calculated from the Least Squares Method applied to the straight lines in Figs. 3 and 4.

FIGURE 3
The Langmuir isotherms of Cd(II) for natural dolomite.

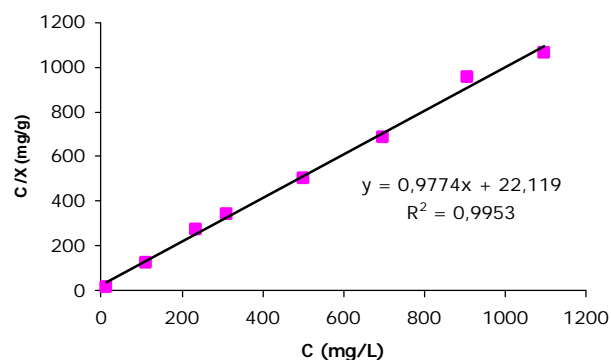


FIGURE 4

The Langmuir isotherms of Cd(II) for thermally activated dolomite.

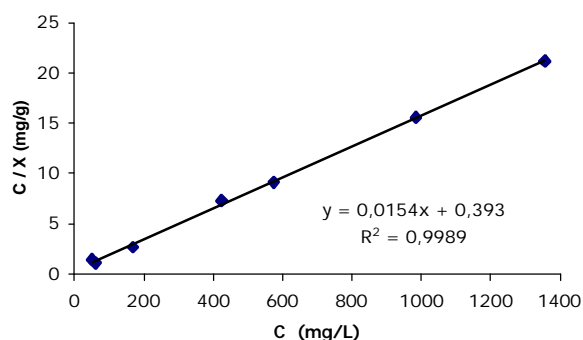


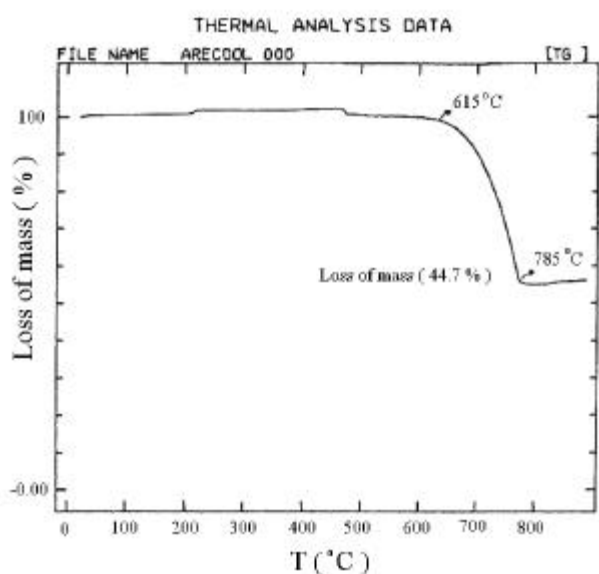
TABLE 2
Values of constants of Langmuir equation.

Sample	X_m (mg/g)	b (L/mg)	r
Natural Dolomite (ND)	1.02	0.044	0.99
Thermally Activated Dolomite(TAD)	64.93	0.039	0.99

The heat treatment of natural dolomite from 110 up to 700 °C increased the adsorption capacity for Cd ions. This might be explained by considering the thermal gravimetric diagram (TGA) of natural dolomite (Fig. 5). The TGA curve shows a decrease of mass (up to 44.7 %) between 615-785 °C. Decomposition of dolomite $[MgCa(CO_3)_2]$ starts at 615 °C and completes at about 785 °C, mainly due to the following reactions (conversion of dolomite to MgO and CaO).



FIGURE 5 - TGA curve corresponding to natural dolomite.



CONCLUSION

Experiments have shown that thermally activated dolomite (heating to 700 °C) adsorbed cadmium ions about sixty five-fold compared to untreated natural dolomite (maximum adsorption capacities: 1.02 mg/g for natural dolomite, 64.93 mg/g for thermally activated dolomite at 25 °C, respectively). Both may be used for removal of trace amounts of Cd in aqueous solutions.

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ACUTE TOXICITY AND ACCUMULATION OF LEAD IN POST-LARVA OF TIGER PRAWNS, *PENAEUS MONODON*, MALAYSIA

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SUMMARY

The acute toxicity test was conducted on the postlarvae of tiger prawns, *Penaeus monodon*, to determine the 96-h LC₅₀ values for Pb. The 96-h LC₅₀ values using static and semistatic methods were 5.88 ± 1.39 mg/l and 5.73 ± 0.94 mg/l, respectively. Accumulation of Pb in the postlarvae reached steady state in 10 days with an accumulation factor of 139. Irreversible sublethal effects observed were growth retardation, black tail and muscular atrophy. Acute toxicity and accumulation of Pb were antagonized by the presence of Ni and Cd.

KEYWORDS:

Prawns, lead, toxicity, accumulation, elimination.

INTRODUCTION

Prawn culture is carried out quite extensively in Malaysia and it is amongst the country's seven largest export [1]. Suitable geography and climate enable large areas of mangrove swamp in Malaysia to be converted into prawn aquaculture ponds, including the tiger prawns, *Penaeus monodon*. Malaysia's climate makes it possible to harvest two to three times per year. However, its production is still not satisfactory due to poor pond management [2]. In Sabah (Malaysia) a substantial number of tiger prawn aquaculture farms are managed by the Cooperative for Advancement of Fishery and Fishermen, known for short as Ko-Nelayan.

Mokhtar *et al.* [3] have conducted a water quality survey of the Inanam Estuary and the nearby *P. monodon* aquaculture ponds of Ko-Nelayan. They monitored the pH, temperature, salinity, conductivity, suspended solids, dissolved oxygen and some heavy metals of the estuary and the ponds. Concentrations of cobalt (Co) and lead (Pb)

were found to be higher than the maximum recommended values for fishery and agriculture [4, 5]. Research on the effects of heavy metals upon *P. monodon* are still very scarce. Chen [6] has suggested maximum safety levels for a number of metals for the optimum growth of *P. monodon* such as 0.0025 mg/l for Hg, 0.1 mg/l for Cu, 0.15 mg/l for Cd and 0.25 mg/l for Zn. Knowledge on toxicity of other metals is still not available [2] and hence this study was carried out. In this study the postlarvae stage was selected because at this stage the *P. monodon* is being released into the Ko-Nelayan ponds. Water for these ponds was drawn directly from the Inanam River, which was found to contain a high level of Pb.

The objectives of this study were:

- (i) to determine the 96-h LC₅₀ values of Pb,
- (ii) to estimate the maximum safety level of Pb for the *P. monodon* postlarvae,
- (iii) to estimate the bioaccumulation factor (BCF) of Pb in *P. monodon* postlarvae and to observe its sublethal effects,
- (iv) to observe the elimination trend of Pb out of the postlarvae, and
- (v) to investigate the interactive effects of Ni and Cd with Pb.

MATERIALS AND METHODS

The methods used in this study were as recommended by APHA [7], FAO [8], Ward and Parrish [9] and Reish and Oshida [10]. The lead solution used for the toxicity tests was prepared by diluting a 1000 mg/l stock solution of Pb (Merck, Titrisol) with triply distilled water. Testing solutions were made up from artificial sea water salts (Marinemix + Bioelement). The salinity of the solution

was made to 20-25 ‰, a range suitable for tiger prawns. The solution was aerated and its temperature (20 °C) was found not to have varied by more than 2 °C.

Tests Organisms

The *P. monodon* postlarvae were obtained from the Ko-Nelayan Hatchery, Likas, Sabah. They were 17 to 25 days old hence called PL17 or PL25. They were acclimatised in aquaria for seven days before toxicity tests were conducted. During acclimatisation period these postlarvae were fed with *Artemia nauplii* three times for 24 hours before toxicity tests were conducted.

Toxicity Tests

Test aquaria were made of glass with a dimension of 600 x 180 x 150 mm. Each aquarium was divided lengthwise into three subsections, each sub-section representing one replicate. Each of these three sub-sections was further divided into ten smaller sections by using movable glass pieces to prevent cannibalism. Static & semistatic methods were used with water not being renewed in the static method whereas 50% of the water was renewed every two days in the semistatic method. Measurements of pH, temperature, dissolved oxygen, salinity and conductivity were performed *in situ* using portable meters. Dissolved lead concentrations were measured at the beginning and end of each test.

Accumulation Study

In the accumulation study, about 2000 postlarvae of the *P. monodon* were placed in an aquarium containing 120 liters of Pb solution with a concentration of 0.71 ± 0.02 mg/l. This Pb concentration was equal to that normally found in water at the Ko-Nelayan hatchery. The aquarium solution was aerated continuously and its temperature and salinity were monitored closely so that variation was not more than 2 °C and 2 ‰, respectively. About 50% of the solution was renewed every two days. A control tank with a similar number of postlarvae was also set up. They were sampled (2 g each time) every two days. After recording the wet weight, the sample was digested in concentrated nitric acid, then diluted with distilled water and the Pb content measured by atomic absorption spectrophotometry (AAS) with a Perkin-Elmer model 2350 using the graphite method. Sampling was stopped when concentration of Pb in postlarvae reached a steady state (plateau). Besides the Pb-alone study, accumulation studies involving combinations of Pb with Ni, and Pb with Cd were also conducted.

Elimination Study

When the measured Pb in the postlarvae reached a steady state all the remaining postlarvae in the aquarium

were transferred into another aquarium containing clean artificial sea water for a day to eliminate their gut content. Then they were transferred into an aquarium containing 120 l of clean artificial sea water and hence the elimination process began. The postlarvae were sampled every 3-4 days, or at shorter intervals, if elimination processes occurred at a faster rate.

RESULTS AND DISCUSSION

The 96-h LC₅₀ values were calculated using the arithmetic graph and logarithm plot methods. In the arithmetic graph method the percentage survived was plotted against Pb concentration. The average value obtained from this method for the static toxicity tests was 5.88 ± 1.39 mg/l with a 95% confidence interval of 4.49-7.27 mg/l. The logarithm plot gave an average 96-h LC₅₀ value of 5.73 ± 1.00 mg/l Pb for the three replicates. Its 95% confidence interval is 4.73-6.73 mg/l and was not significantly different from the value obtained from the arithmetic method. For the semi-static tests the 96-h LC₅₀ value obtained was 5.73 ± 0.94 mg/l Pb using either the arithmetic or logarithmic method. Information on Pb toxicity towards other crustaceans are still scarce. The 48-h LC₅₀ for the prawns *Pandalus montagui* and juveniles of *Penaeus merguensis* are 375 mg Pb/l and 51.0 mg Pb/l, respectively at 20 °C and salinity of 20.0 ‰ [11]. For *Macrobrachium rosenbergii* the 96-h LC₅₀ value was estimated to be < 0.1 mg/l [12]. Direct comparison of Pb toxicity upon crustaceans is difficult to make due to abiotic factors such as pH, temperature, salinity, hardness and presence of complexing agents, and biotic factors such as the organism's physiology, life stage and specificity of species which affect the bioavailability of metals [13]. Denton and Burdon-Jones [11] reported a toxicity trend for *Penaeus merguensis* as follows, Hg > (Cu, Cd, Zn), > Ni > Pb. The toxicity trend for *M. rosenbergii* is Cu > Cd > Zn > Pb [12]. According to Connell and Miller [14] the toxicity mechanism for metal ions could be categorised as follows: (i) blocking the activity of functional groups attached to biomolecules, such as enzymes and proteins; (ii) substitution of metal ions bound to biomolecules and (iii) changing the active conformation of biomolecules. Pb is a toxic metal with a wide spectrum of mechanisms. It is effective when bonded to the SH group donors such as cysteine and to nitrogen groups such as imidazole, lysine and histidine, at the active catalytic centre of enzymes. Pb also could substitute other metal ions like Zn²⁺ from metalloenzymes, hence deactivating these enzymes by changes in conformation. Pb also could form ionic organo-metals which are lipid soluble and permeable through biological membranes and could be accumulated in cells and organelles [14]. In this study it was found that high Pb concentration could cause hyperactivity of the *P. monodon* postlarvae. Other effects include muscle stress, respiratory disorder and loss of balance.

These symptoms show its effects on the nervous system. Pb was reported to be interactive with Ca located on certain sites during neurotransmission [15]. It could also cause damage to the nervous tissues by inhibiting the biosynthesis of hemoglobin and reducing the survival of red blood cells. The dead postlarvae were noticed to have white gills which were covered with mucous. This could be related to the coagulation film anoxia theory [15, 16], whereby at high concentrations of Pb a layer of coagulated mucous will cover the whole body, especially the gills, thus affecting the respiration. This was also observed in *Micropterus dolomieu* [17]. Using the application factor of 0.02 for Pb, as suggested by the National Academy of Sciences and Engineering, USA in 1974 [11], the safety level of Pb for the *P. monodon* postlarvae was calculated to be 0.1176 mg/l, which was obtained by multiplying 0.02 with 5.88. This is higher than the Pb

concentration in normal aquatic marine environment, which is 0.005-0.4 ug/l [15]. In the accumulation study, it was found that the postlarvae took 10 days to achieve the steady state (Table 1). The Accumulation Factor (BCF) calculated was 139. Other aquatic species were reported to have BCF values in the range of 102 - 106 [14]. Crustaceans such as *Pandalus jordanii* have a BCF of 440, *Paguristers sericeus* 11 300 and *Xiphopenaeus krogeri* 3 700 [16]. The growth rate for the postlarvae exposed to the Pb and the control were similar up to the tenth day, after which the exposed postlarvae show a decrease in growth rate. This coincided with the day at which steady state of Pb in them was achieved. Continuous uptake is expected to further decrease their growth rate. The elimination of Pb with time is consistent with the two phase elimination theory [18] with estimated half lives at Day 1 and Day 8 for the two phases, respectively (Table 2).

TABLE 1 - Concentration of Pb in postlarvae of *P. monodon* during accumulation study.

Day No.	Pb in postlarvae ($\mu\text{g/g}$ wet wt) Replicate 1 (control values are shown in parentheses)	Pb in postlarvae ($\mu\text{g/g}$ wet wt) Replicate 2 (control values are shown in parentheses)	Mean of Pb in postlarvae ($\mu\text{g/g}$ wet wt) \pm standard deviation (control values are shown in parentheses)
0	5.90 (4.68)	5.94 (4.73)	5.92 \pm 0.03 (4.70 \pm 0.04)
2	51.52 (4.36)	51.78 (4.46)	51.65 \pm 0.18 (4.41 \pm 0.07)
4	55.03 (4.20)	53.87 (4.57)	54.45 \pm 0.82 (4.38 \pm 0.26)
6	69.45 (4.32)	68.04 (4.36)	68.75 \pm 1.00 (4.34 \pm 0.03)
8	87.21 (5.14)	87.03 (4.83)	87.12 \pm 0.13 (4.98 \pm 0.22)
10	100.71 (4.44)	97.84 (4.29)	99.28 \pm 2.03 (4.36 \pm 0.11)
11	99.21 (4.07)	97.64 (4.09)	98.43 \pm 1.11 (4.08 \pm 0.01)
12	98.20 (3.73)	97.80 (3.84)	98.00 \pm 0.28 (3.78 \pm 0.08)
13	97.03 (2.97)	97.66 (3.17)	97.35 \pm 0.45 (3.07 \pm 0.14)
14	99.59 (3.22)	100.77 (3.16)	100.18 \pm 0.83 (3.19 \pm 0.04)
15	98.36 (4.17)	98.71 (3.74)	98.54 \pm 0.25 (3.95 \pm 0.31)
17	99.82 (3.74)	99.62 (3.55)	99.72 \pm 0.14 (3.64 \pm 0.13)

TABLE 2 - Concentration of Pb in postlarvae of *P. monodon* during elimination study.

Day No.	Pb in postlarvae ($\mu\text{g/g}$ wet wt) Replicate 1 (control values are shown in parentheses)	Pb in postlarvae ($\mu\text{g/g}$ wet wt) Replicate 2 (control values are shown in parentheses)	Mean of Pb in postlarvae ($\mu\text{g/g}$ wet wt) \pm standard deviation (control values are shown in parentheses)
0	99.82 (3.74)	99.62 (3.55)	99.72 \pm 0.14 (3.64 \pm 0.13)
1 (Estimated half life of phase one)	50.66 (3.21)	51.41 (3.08)	51.04 \pm 0.53 (3.14 \pm 0.09)
5	28.76 (2.99)	30.04 (3.09)	29.40 \pm 0.91 (3.04 \pm 0.07)
8 (Estimated half life of phase two)	22.88 (3.08)	24.54 (3.69)	23.71 \pm 1.17 (3.39 \pm 0.43)
12	15.14 (3.44)	14.66 (3.25)	14.90 \pm 0.34 (3.35 \pm 0.13)
15	12.69 (3.59)	14.33 (3.16)	13.51 \pm 1.16 (3.38 \pm 0.30)
16	10.54 (3.07)	10.07 (3.47)	10.31 \pm 0.33 (3.27 \pm 0.28)
18	9.87 (3.25)	10.08 (3.29)	9.98 \pm 0.15 (3.27 \pm 0.03)
21	8.63 (2.88)	9.15 (2.96)	8.89 \pm 0.37 (2.92 \pm 0.06)
24	8.43 (3.15)	8.67 (3.13)	8.55 \pm 0.17 (3.14 \pm 0.01)
26	8.47 (2.99)	8.53 (2.88)	8.50 \pm 0.04 (2.94 \pm 0.08)

The postlarvae were seen to shed their skin almost immediately after being transferred into the clean water and this explains the fast rate of elimination if the Pb was mostly bound onto the exo-skeleton of the postlarvae. The elimination study performed is useful in determining whether the toxic effect is reversible. The sublethal toxicity observed in the postlarvae include black tail, muscle atrophy and growth retardation. The growth rate of them exposed to Pb was found to be slower than the control. The black tail phenomenon could not be remedied even though after more than 90% of the total body-Pb had been eliminated in about 26 days. In the combined toxicity study, it was found that the 96-h LC_{50} values for Pb in the presence of Cd and Ni were 1.5 mg/l (equivalent to 8.82 mg Pb/l) and 1.64 mg/l (equivalent to 9.65 mg Pb/l), respectively. This shows that the toxicity effects of Pb were reduced by the presence of Cd and Ni. This effect is known as the antagonistic interaction, which refers to the masking ef-

fect caused by one metal towards the other due to the reduced uptake of both metals by the cells on the surface of certain tissues [19]. Similarly, the presence of Cd and Ni decreased the BCF value of Pb from 139 to 106 in the postlarva.

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COPPER, NICKEL, LEAD AND CHROMIUM DETERMINATION BY ATOMIC ABSORPTION SPECTROMETRY IN URINE AFTER ENRICHMENT/ SEPARATION ON AMBERLITE XAD-2000

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SUMMARY

A simple and rapid enrichment/separation procedure for the determination of copper, nickel, lead and chromium in urine samples has been proposed. The analyte ions were preconcentrated on Amberlite XAD-2000 as 1-(2-pyridylazo) 2-naphtol (PAN) chelates. The influences of the main components of urine as interferents were investigated. The present method was applied for the determination of Cu, Ni, Pb and Cr in urine samples of six people randomly selected in Kayseri and Nigde-Turkey with satisfactory results (recovery >95% and relative standard deviation <10%).

KEYWORDS:

Amberlite XAD-2000, Separation, Enrichment, Trace Metal, Urine.

INTRODUCTION

Accurate, sensitive and simple analysis of environmental samples including natural waters, soils, dusts and body fluids such as serum, plasma, for their trace metal contents is an important field of analytical chemistry [1-7]. For this purpose, modern analytical techniques like atomic absorption spectrometry (AAS), inductively coupled plasma-mass spectrometry (ICP-MS) or neutron activation analysis (NAA) have been used regularly. The two main determination problems of heavy metal ions by these techniques are matrix and low metal concentration. For example, urine is a very complex matrix containing only trace levels of metal ions and also interferents for AAS determinations [8-9].

Prior to the determination of trace metals by AAS or ICP-MS in urine, a precise preconcentration and sensitive separation method is required. Methods including coprecipitation, ion exchange, and liquid-liquid extraction can be easily used for the separation and enrichment of heavy metals. Because of simplicity, also the sorbent extraction procedures have been widely used in this field. The use of various types of sorbents for enrichment and separation of heavy metal ions by sorbent extraction has gained increasing popularity. The supports used for this purpose include active carbon [10-12], cellulose [13-14], chelating resins [15-16], sephiolite [17], Diaion HP-20 [18-19], and micro-crystalline benzophenone [20]. Also Amberlite XAD adsorption resin has been continuously used for preconcentration and separation of heavy metals from various media [21-29].

To the best of our knowledge, hitherto, Amberlite XAD-2000/1-(2-pyridylazo) 2-naphtol (PAN) preconcentration system has not been applied to the analysis of urine samples. In this work, the determinations of copper, nickel, lead and chromium in urine were performed by atomic absorption spectrometry after enrichment/ separation procedure on Amberlite XAD-2000.

MATERIALS AND METHODS

Reagents

All chemicals were of suprapure grade and all solutions were prepared in distilled-de-ionized water. Metal standard stock solutions were prepared from respective nitrates as 1000 mg/L solutions in 0.01 M nitric acid and appropriately diluted as reference solutions.

TABLE 1 - Instrument settings and conditions of GFAAS analysis.

		Elements			
Parameter		Cu	Ni	Cr	Pb
Wavelength (nm)		324.8	232.0	357.9	283.3
Slit width (nm)		1.3	0.2	0.7	1.3
Lamp current (mA)		7.5	15.0	12.0	7.5
Step	Condition				
Dry	time (s)	15	15	15	15
	temp (°C)	120	120	120	120
Ash	time (s)	30	30	30	30
	temp (°C)	600	700	1200	400
Atomize	time (s)	10	10	10	10
	temp (°C)	2700	2700	2300	2400

TABLE 2 - Effect of interferent species present in urine on metal ion recovery (n=3)

Ion	added as	Concentration (g/l)	Recovery, %			
			Cu	Ni	Pb	Cr
Control			96	98	99	96
Na ⁺	NaCl	10.0	98	97	99	99
		50.0	96	101	97	96
K ⁺	KCl	0.5	98	98	95	98
		1.0	95	94	96	93
Ca ²⁺	CaCl ₂	0.5	97	98	96	96
		1.0	96	94	96	97
Mg ²⁺	MgCl ₂	0.5	99	101	96	98
		1.0	89	96	93	93
Cl ⁻	NaCl	10.0	97	99	96	95
		50.0	96	98	97	99
(SO ₄) ²⁻	Na ₂ SO ₄	1.0	97	97	96	99
		2.0	96	98	97	99
Urea		5.0	100	98	97	96
		10.0	99	98	100	99
Uric Acid		2.0	96	98	95	96
		5.0	96	97	96	97
Creatine		2.0	96	101	100	96
		5.0	100	95	101	97

Amberlite XAD-2000/20-40 mesh (Sigma, St Louis) was washed successively with methanol, water, 1 M HNO₃, water, 1 M NaOH and water, respectively, to remove organic and inorganic contaminants. The chelating agent was PAN [1-(2-pyridylazo) 2-naphthol] (E. Merck, Darmstadt), which was dissolved in a water-ethanol (75/25, v/v) mixture.

Apparatus

A Perkin-Elmer Analyst 100 atomic absorption spectrometer equipped with a Deuterium background corrector and a graphite furnace was used in the determinations. 20 µl of sample was introduced into the graphite tube using an Eppendorf pipette. The operating parameters for working elements were set as recommended by the manufacturer (Table 1). A pH meter, Delta 320 Mettler, was employed for measuring pH values in the aqueous phase.

Preconcentration procedure of metal reference solutions

To 50 and 100 ml portions of reference solutions containing 2.5-5 µg of the metal ions 10 ml each of ammonium chloride buffer (pH 10) and PAN (0.75 x 10⁻³ mol L⁻¹) solution were added. The XAD-2000 column was preconditioned with buffer solution. After 5 min the metal/PAN solution was passed through the column at a flow rate of 10 ml/min. Then the column was rinsed twice with 10 ml of water. The metal chelates retained on the column were eluted with 10 ml of 1 M HNO₃ in acetone. The eluent was concentrated by heating over a hot plate to 1.0 ml and redissolved to 5 ml with 1.0 M HNO₃ before AAS analysis.

Procedure for enrichment of Cu, Ni, Cd and Pb in urine samples

The urine samples were collected from randomly selected six healthy people living in Nigde City-Turkey on May 2001. The samples were collected in pre-washed (with detergent, doubly de-ionised distilled water, dilute HNO₃ and doubly de-ionised distilled water, respectively) polyethylene bottles and stored in refrigerator until analysis within one week.

Prior to separation/preconcentration of trace metal ions from urine the digestion procedure was applied [30]. 25 ml of urine was digested in a quartz vessel with 5 ml of concentrated sulfuric acid and 20 ml of hydrogen peroxide 30% at 110 °C for 3 h. The sample was evaporated and diluted with 25 ml distilled water.

The digested urine samples were buffered and treated on a XAD-2000 column as described above for reference solutions of metal ions GFAAS analysis.

RESULTS AND DISCUSSION

The effects of various analytical parameters, such as 1-(2-pyridylazo) 2-naphthol concentrations, eluent type, amounts of XAD-2000, on the recovery of metal ions investigated in urine samples were examined. All experiments were carried out at pH 10 adjusted by addition of 10 ml ammonium chloride buffer solution and a PAN concentration of 0.75 x 10⁻³ M. This had not any effect on recovery rates and was used in all subsequent experiments. Variation of sample volume (50-1000 ml) does not affect quantitative recoveries on Amberlite XAD-2000 (500 mg) for the investigated metal ions except chromium. For chromium, the recoveries were quantitative till 500 ml. The highest preconcentration factor used was 250. Analytes were quantitatively retained up to a sample flow rate of 10 ml/min. Different elution flow rates (1.0-10.0 ml/min), comparable to those described in literature [31], had no effect on elution efficiency.

Desorption studies

Pre-experiments using organic solvents like acetone and ethanol etc. or inorganic acids at various concentrations (1M HNO₃, 2 M HNO₃, 1M HCl and 2M HCl etc.) for elution of metal ions retained on Amberlite XAD-2000 column, resulted in recovery rates less than 50 %. Therefore, desorption of metal ions from XAD-2000 was studied by using 10 ml of different organic eluents mixed with inorganic acids, such as 1 M HCl in acetone, 2M HNO₃ in acetone, 1 M HNO₃ in ethanol and 1 M HCl in ethanol.

Quantitative recoveries for the analytes from urine samples were obtained by using minimum volumes of 7.0 – 11.0 ml 1M HNO₃ in acetone as eluent.

Effects of urine matrix

The effects of matrix ions of urine on the recovery of analyte ions Cu, Ni, Pb and Cr were also investigated. For this purpose, 50 ml of model solutions containing 2.5-5 µg of each analyte and other matrix components (Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻, urea, uric acid and creatine) were prepared. Preconcentrated and analysed as described in Materials & Methods. The results are given in Table 2. The recovery rates were not influenced by large amounts of matrix ions which are not complexed with PAN. Therefore, they are not retained on the resin as the analytes, prior to elution from Amberlite XAD-2000 column. They can be easily washed out with 10 ml of distilled water.

Application to urine samples

The separation and enrichment procedure described under experimental section was applied to determine Cu, Pb, Ni and Cd in urine samples collected from randomly

selected six people living in Nigde and Kayseri-Turkey. The results are given in Table 3. The relative standard deviations (RSD's) of the preconcentration procedure were found to be below 10%.

TABLE 3
Cu, Pb, Ni and Cr contents in 25 ml urine samples (n=5).

Sample	Concentration ($\mu\text{g l}^{-1}$)*			
	Cu	Pb	Ni	Cr
D1550	BDL	3.1 \pm 0.3	6.3 \pm 0.2	4.1 \pm 0.1
D1551	1.4 \pm 0.2	BDL	7.5 \pm 0.5	BDL
E1650	BDL	4.7 \pm 1.2	5.4 \pm 0.5	5.7 \pm 0.3
E1651	BDL	BDL	BDL	BDL
E1750	BDL	BDL	1.9 \pm 0.2	BDL
E1751	1.8 \pm 0.2	3.0 \pm 0.1	1.3 \pm 0.2	3.6 \pm 0.1

* mean value \pm standard deviation, BDL: below detection limit; elution: 1 M HNO₃ in acetone

Accuracy of results

The accuracy of results was verified by analyzing the concentration after addition of known amounts (2.5 μg) of analytes into urine samples. The recovery values varied from 96 to 102%, thus confirming the accuracy of the analytical procedure and the absence of matrix effects (Table 4).

TABLE 4 - Recovery of analytes added to 50 ml urine (n=4).

Analyte	Added (μg)	Found (μg)	Recovery (%)
Cu	2.5	2.5	100
Cr	2.5	2.5	100
Pb	2.5	2.6	102
Ni	2.5	2.4	96

Comparison with other preconcentration methods

The method presented in this study is most promising for Cu, Ni, Pb and Cr enrichment as the preconcentration factor is 100 and superior to those of techniques including solvent extraction, ion exchange, coprecipitation etc. [2-6, 10-12]. The matrix effects were reasonably tolerable. Additionally, the method is easily adaptable to the enrichment and determination of trace metal ions by flow injection analysis (FIA) techniques.

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TRACE ELEMENTS IN VEGETABLES GROWN IN AN AREA EXPOSED TO THE EMISSIONS OF GEOTHERMAL POWER PLANTS

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SUMMARY

Concentrations of three trace elements were determined in the edible portions of lettuce plants, other vegetable plants and in forages from a geothermal area in Tuscany (Central Italy). No phytotoxicity evidence was observed. When compared to samples collected from the market and in fields far from the geothermal fields, increase in As, Hg and Sb was found, but levels reported did not seem to pose either phytopathological implications or health risks for consumers. A relevant fraction of the metal load was simply deposited onto the leaf surfaces.

KEYWORDS:

Antimony, arsenic, lettuce, mercury, trace elements

INTRODUCTION

In the context of alternative and renewable energy sources, in Italy a relevant role in power generation is played by geothermal plants. Since the beginning of the 20th century, electricity has been generated from geothermal fields and, nowadays, this represents 1.7% of the total national production, with a production of $4.4 \cdot 10^9$ kWh. Tuscany is the region where this activity was first developed and is far more concentrated, with some 25 power plants in activity; in the last ten years production has grown by 37%. Other countries like Iceland, Japan, Mexico, New Zealand, and U.S.A. are profitably involved in the field.

Pressure for intensified geothermal exploration should not allow us to overlook long-term environmental hazards associated with the exploitation of geothermal power. It was considered in the past that geothermal energy produc-

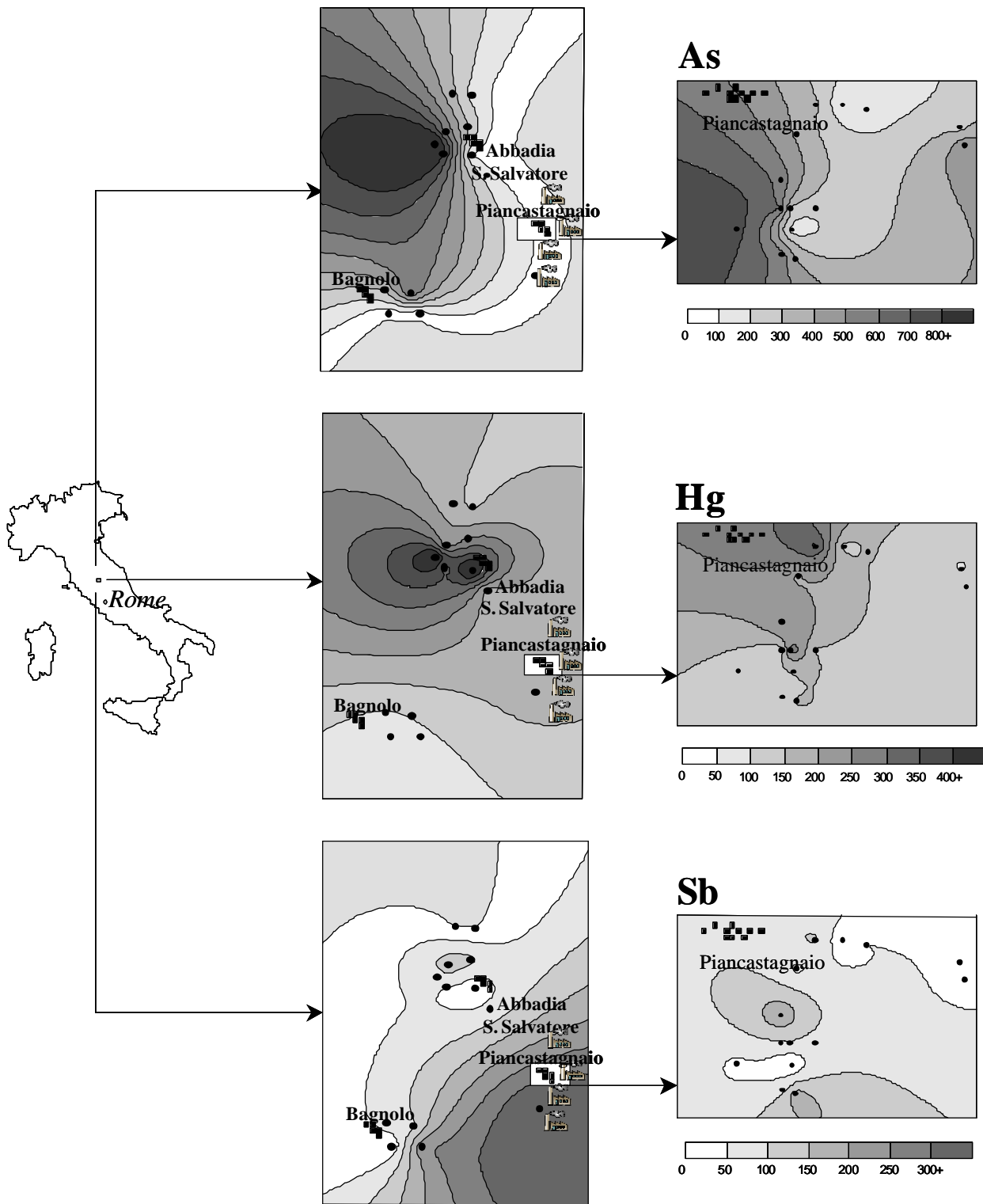
tion had practically no detectable environmental impact, and actually ambient interactions of geothermal activities are not easy to study. Apart from accidental releases, direct and acute phytotoxicity does not seem to be a major problem [1], boron being in these cases indicated as the main culprit. On the contrary, the exposure to low levels of trace elements in the uncondensable fraction of geothermal vapours released by cooling towers may be responsible for the dangerous enrichment in edible portions of plants. The association of high atmospheric Hg levels with geothermal activity has long since been established [2]; other trace elements of geothermal origin worthy of interest are As and Sb [3].

The aim of this study was to investigate the presence of selected trace elements in/on the edible portions of vegetables growing in the geothermal area of Mt Amiata, in Tuscany, Central Italy, to evaluate the potential risks for humans and for plant health.

MATERIALS AND METHODS

The study area: The geothermal area of Piancastagnaio is on the southeastern slope of Mt Amiata (1738 m a.s.l.), in southern Tuscany (the area is shown in the left part of Fig. 1). The study area is about 30 km², and ranges in altitude from 350 to 900 m a.s.l. Intensive agriculture is scarce and concentrated in small allotments, the prevailing vegetation being conifer woods and meadows. Mt Amiata is an important part of the geological anomaly of the Mediterranean Basin, an area which comprises several cinnabar deposits; until 1980, this area was important for Hg mining and smelting activities. Four geothermal power plants were active at the time of this study: PC2 (8 MW), Bellavista (20 MW), PC3 (20 MW) and PC4 (20 MW). During the warm season prevailing winds are breezes and those coming from the west.

FIGURE 1
 Map of Italy, localization of the study area (*left*) and maps of the distribution of mean values of the trace elements As, Hg and Sb in washed lettuce plants in the study area. (Black squares indicate the urban areas. The location of the four geothermal power plants is shown. Dotted areas refer to a low density of sampling points. Data are in ng g^{-1} dry weight).



Sampling: During the growing season 1995, a series of 166 samples of vegetable species (lettuce, Swiss chard, garden cabbage) and fodder crops (whose common and Latin names are listed in Table 2) were harvested during 11 sampling campaigns in the area of Piancastagnaio, at different distances from active power plants. Special attention was devoted to lettuce, due not only to its large presence, but also to its peculiar prone architecture, which makes it very fit to intercept fall-out from aerodisperse materials. Routine phytosanitary inspections were made prior to collecting samples, in order to evaluate the presence of symptoms related to toxicity of aerodisperse factors. Composite samples were taken from allotments grown under normal agronomic conditions. In addition, four samples of lettuce were taken from a reference 'clean' area and from the market. The collected material was kept in polythene bags at 4 °C.

Sample preparation: The edible portions of vegetable material were prepared for analysis as is normally done in the kitchen within the same day of collection. Dead or yellow leaves, as well as leaves showing visible marks of parasites were discarded. One half of each plant sample was processed without any further manipulation ('unwashed'), the other half was 'washed' in order to remove the material on the surface. Washing was performed after the samples were carefully rinsed with tap water to remove surface dust. 100 g of fresh material were then put in 3 L distilled water acidified to 3% with conc. HCl and vigorously stirred. The sample was dripped and treated twice in the same way. Finally the material was gently centrifuged by means of a domestic hand-centrifuge. The material was put in an oven at 45 °C until constant weight and then ground (42 mesh) in a food processor with a stainless steel cutter.

Analysis: Dried vegetables (300 mg samples) were digested with a mixture of HNO₃ (5 ml) + H₂O₂ (2 ml) + H₂O (2 ml) and mineralised in a microwave oven throughout one cycle. Diluted subsamples were analysed for Hg by Graphite Furnace-Cold Vapour Atomic-Absorbance Spectrometry and, for As and Sb, by Graphite Furnace-Hydride Generation Atomic Absorbance Spectrometry [4]. Element concentrations were expressed on a dry weight basis in ng g⁻¹. Instrumental detection limits

were 1 ng g⁻¹ for As, 1 ng g⁻¹ for Hg, and 0.1 ng g⁻¹ for Sb. Quality control was assured by duplicate samples, blanks and the method of standard additions. Accuracy was checked by concurrent analysis of standard reference material (CRM062, BCR, Brussels). The relative standard deviation in concentration was <10% for the three elements.

Data processing: Data were elaborated in order to obtain their distribution and correlation. The factor 'sampling time' was not considered, to better simulate the human consumption of metals with the diet during the year. A spatial interpolation of data was performed with a kriging gridding method and a linear variogram model (Surfer 6.04 for Windows). Orographic effects were not considered here, as altitude differences in the study area were relatively small.

RESULTS AND DISCUSSION

Phytopathological investigations never evidenced visible marks attributable to phytotoxicity of chemical stressors.

Figure 2, Table 1 and Table 2 summarize the results of analytical determinations on unwashed and washed samples of lettuce and other matrices. Element content was highly variable, especially in unwashed samples. In lettuce As reached the peak value of 2,680 ng g⁻¹, Hg 1,705 ng g⁻¹ and Sb 1,180 ng g⁻¹. Washing the fresh samples played a relevant role in reducing the presence of trace elements in the edible fractions, the ratio between washed and unwashed samples being 1 : 1.47-1.80 in lettuce (Table 1). Similar values were obtained for the other plant species (Table 2). This means that a relevant fraction of the metal load - especially the highest values - was simply deposited onto the leaf surfaces. Washing certainly removed both airborne dust and soil particles deposited on the plant probably via 'splash' during periods of precipitation [5]. It is interesting to observe how the most frequent classes of values (the *modes*) for lettuce (Table 1) are quite low, being below the instrumental detection limit for Sb and in the ranges 101-200 ng g⁻¹ for Hg and 0-100 ng g⁻¹ for As.

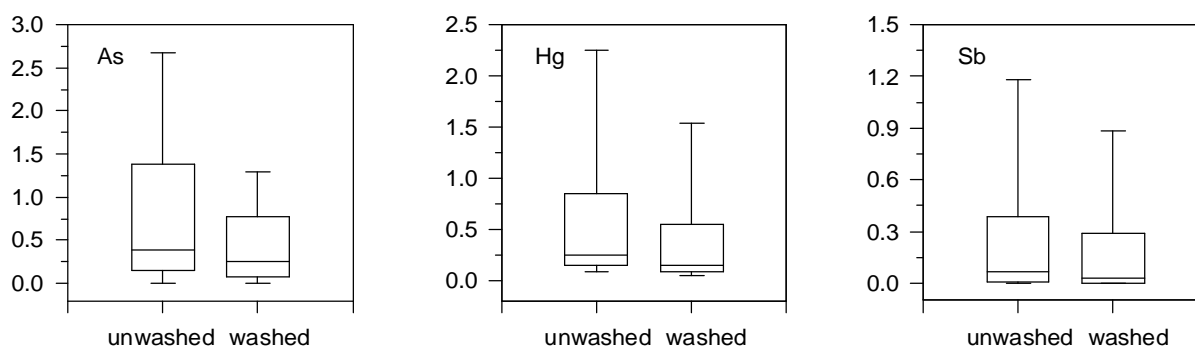
TABLE 1
Elemental composition of lettuce (*Lactuca sativa*) samples collected from the study area. Modal classes of values are reported.

Element	No. of samples analysed	Unwashed (ng g ⁻¹)		Washed (ng g ⁻¹)		Mean ratio
		Mean	Mode	Mean	Mode	
As	74	571	0-100	389	0-100	1.47
Hg	68	352	101-200	196	101-200	1.80
Sb	78	118	<0.1	72	<0.1	1.64

TABLE 2
Elemental mean composition of plant samples other than lettuce collected from the study area.
Modal classes of values are not reported, due to the poor number of samples.

Matrix	Element	No. of samples analysed	Unwashed (ng g ⁻¹)	Washed (ng g ⁻¹)	Mean ratio
Garden cabbage (<i>Brassica oleracea</i>)	As	2	251	86	2.92
	Hg	2	292	267	1.09
	Sb	2	85	70	1.21
Swiss chard (<i>Beta vulgaris</i>)	As	7	1063	546	1.95
	Hg	7	339	233	1.45
	Sb	8	327	212	1.54
Clover (<i>Trifolium</i> sp.)	As	10	182	168	1.08
	Hg	6	147	119	1.24
	Sb	10	40	21	1.91
Sulla sweetvetch (<i>Hedysarum coronarium</i>)	As	12	276	245	1.13
	Hg	10	242	140	1.73
	Sb	15	111	103	1.08
Alfalfa (<i>Medicago sativa</i>)	As	26	286	262	1.09
	Hg	19	154	95	1.62
	Sb	27	46	37	1.24
Mixed meadow	As	22	98	81	1.21
	Hg	17	182	119	1.53
	Sb	22	37	26	1.42
Common vetch (<i>Vicia sativa</i>)	As	4	65	35	1.86
	Sb	4	22	14	1.57

FIGURE 2
Box and whiskers representation of the data referred to the unwashed and washed lettuce samples (all figures $\mu\text{g g}^{-1}$).
For each sample, the top line represents the maximum value, the bottom line the minimum value and the box the 75th percentile (upper side), the 25th percentile (lower side) and the median (50th percentile, central line), respectively.



The concentrations of the same elements in lettuce samples taken from uncontaminated areas or from the market are shown in Table 3. Figures are comparable to the elemental composition of the 'reference plant'; according to Markert [6] normal or background levels of As, Hg and Sb in the 'reference plant' are of the order of 100 ng g⁻¹. It may be worthy of interest to observe that in these samples, as well, a relevant fraction of the trace elements is simply deposited on the leaf surface, as demonstrated by the ratios between unwashed and washed subsamples.

There are few reference standards available in the literature to indicate the background values for the presence of trace elements such as Hg, As and Sb in lettuce. For instance, Voutsas *et al.* [7] report in washed lettuce samples collected in the industrial area of Thessaloniki (Greece) the following values (ng g⁻¹; d.w., min-max): As: 40-290; Hg: 10-80; Sb: 40-6,150; for cabbage, figures are: As: 10-370; Hg: 20-160; Sb: 20-7,370.

TABLE 3
Elemental composition of four lettuce samples (ng g⁻¹ dry weight) collected from a reference 'clean' area (unwashed) and from the market (washed).

Element	Unwashed			Washed			Mean ratio
	min	max	mean	min	max	mean	
As	281	392	356	9	344	121	2.9
Hg	77	128	90	49	86	63	1.4
Sb	59	184	120	1	96	64	1.9

Although comparisons with data from literature are hindered by differences in sample preparation and analytical procedures, the metal contents in plant samples were similar to those previously measured in higher plants from the same district. For instance, Bargagli *et al.* [8] found in unwashed leaf samples of sulla (*Hedysarum coronarium*) average concentrations (dry wt of 420 ng g⁻¹ for As and 190 ng g⁻¹ for Hg, while the content of Sb ranged from 90 to 4,500 ng g⁻¹, with a mean of 1,200 ng g⁻¹. These authors as well did not find any correlation between the element pairs considered in the present study. For unwashed lettuce, they found an average concentration (ng g⁻¹, dry wt) of 770 for As, 170 for Hg and 490 for Sb. Barghigiani and Ristori [9] found in unwashed dry samples Hg levels of 24-1,503 ng g⁻¹ (min-max of sample averages) in lettuce, 124-508 ng g⁻¹ in beet, and a mean of 33 ng g⁻¹ in cabbage.

The distribution patterns in washed lettuce samples of the elements investigated are depicted in the right portion of Fig. 1 showing how the three metals present heterogeneous and different spatial distribution. This is confirmed by data reported in Table 4, which demonstrate that no statistically significant correlation exists among data referred to the three elements from both washed and un-

washed samples. This likely implies that the sources of these elements are different. Indeed, in addition to the emissions from geothermal power plants, other routes of introduction of these elements may be listed. Special attention should be paid to the large distribution of roasted cinnabar slag discharged in the past ('*rosticci*'). A further source of Hg is the air which is still released by the ventilation systems of mine shafts [10]. In addition, airborne soil particulates may be a significant source of trace elements in/on plant foliage.

TABLE 4
Coefficient of determination (R²) referred to the correlation analysis of trace element contents in/ on lettuce and other plant matrices (Data refer to all the samplings; Details for 'other matrices' are reported in Table 2).

Lettuce	Unwashed	Washed
As vs Hg (n = 62)	0.056	0.008
As vs Sb (n = 71)	0.261	0.084
Hg vs Sb (n = 65)	0.050	0.047

Other matrices	Unwashed	Washed
As vs Hg (n = 57)	0.145	0.031
As vs Sb (n = 84)	0.372	0.317
Hg vs Sb (n = 61)	0.490	0.369

A better understanding of the behaviour of trace elements in the air-soil-plant system seems to be particularly significant in geothermal areas where horticulture is present. It is not possible to establish whether the uptake of these elements involves active or passive mechanisms nor to assess the relative contribution of root and leaf route.

CONCLUSIONS

The evaluation of the environmental impact of geothermal power plants is a complex affair, and also implies aspects like landscape, smell and noise [11]. However, toxicological evaluations related to trace element transfer in the food chain due to the presence of toxic elements in edible portions of plants are crucial. The public's perception of the biological effects of persistent pollutions is high. This survey gives, in relative terms, a general idea of the state of the atmosphere with reference to the pollutants As, Hg and Sb, in the geothermal area of Mt Amiata.

It is not easy to evaluate the toxicological implications of the presence of trace elements in lettuce. Parameters such as 'acceptable daily intake' (ADI) should be elaborated on the basis of what has been done for pesticides. Derived parameters, such as 'maximum residue limit' (MRL), take into account the ordinary hu-

man diet [12]. On these bases, it can be provisionally considered for vegetables an MRL of 1,000 ng g⁻¹ (dry wt) for As, 500 ng g⁻¹ (dry wt) for Hg, and 1,000 ng g⁻¹ (dry wt) for Sb. Consequently, on the basis of the results here reported, the intake of population from vegetables in the studied area does not seem to pose toxicological risks, also for people whose dietary consumption of local products is relevant. In the same way, elemental composition of agricultural plants was well below the phytotoxicity thresholds [13].

ACKNOWLEDGEMENTS

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PREPARATION OF ACTIVE SORBENT FROM PETROLEUM COKE AND ITS APPLICATION FOR PHENOL AND 4-NITROPHENOL REDUCTION FROM AQUEOUS SOLUTION

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SUMMARY

Active sorbents from green petroleum coke were produced using a modified method. The ground coke was impregnated with pulverized KOH and the activation product was washed with 15%-HCl solution for 4 h after thermal treatment. The sorbents were evaluated using an aqueous solution of phenol and 4-nitrophenol at concentration of 100 mg/L. It was observed that the uptake of phenol and 4-nitrophenol increased with an increase of the KOH dosage. The combination of the factors, namely KOH dosage, pulverization and the HCl-washing, enhanced significantly the sorbent activity. Removal of 86.4% and 99.3%, for phenol and 4-nitro-phenol, respectively, were achieved by the use of the modified technique with a KOH/coke weight ratio of 1.

KEYWORDS: Green petroleum coke, activation, adsorption, phenol, 4-nitrophenol, waste water treatment.

INTRODUCTION

Although the process technology in the field of petroleum refinery has been developing most rapidly, the production of cokes - a byproduct - is unavoidable. On the world average, 3.1% by volume of the crude processed is converted to petroleum coke [1]. Since 1992 world petroleum coke production capacity has increased by more than 40% to reach a peak of 141,814 t/d in 1999. This expansion is expected to continue with at least fifteen new coking units coming into production between 1998 and 2003 [2].

Petroleum coke is utilized for a variety of purposes, e.g., green petroleum cokes are mostly used as utility fuels (about 73% for fuel-grade) in power generation and cement kilns and as feedstock (about 27%) for further upgrading calcination [3]. The consumption of this material in the cement industry has increased steadily, and is likely to increase at around 5% per year until 2005. The coal burning electric power plants also turn to petroleum coke as a cheaper alternative. Among cokes there are those that can be processed into electrodes for metallurgical processes.

In the future, petroleum coke may become an alternative raw material for active carbon production instead of coal, peat, wood, coconut shell and other carbonaceous precursors because of its low ash content and generally higher yields of active carbon [4] as well as its abundant, cheaper and ready availability. As previously reported by Shawwa et al. [5], the activated carbons from petroleum coke prepared by activating at 850 °C in a steam medium were effective for the color and chlorinated organics reduction from pulp mill wastewater. A type of high-surface area active carbon, MAXSORB, prepared from petroleum coke has been developed and commercialized by employing a continuous process as described by Otowa et al. [6]. This product has been successfully applied for purification of drinking water. Such type was originally developed by the AMOCO Corporation [7] and commercialized by the Anderson Development Company [6]. The KOH activation was found to be an effective technique in preparing active carbon from petroleum coke. However, this method has a disadvantage associated with the excessive activator requirement, bringing about a high production cost. For example, the high-surface area active carbon can only be produced from petroleum coke by employing a fourfold amount of KOH [4,6-8].

The major interests of this investigation were to generate an activated sorbent by applying a developed method at a minimum quantity of the activator and to evaluate the products for phenol and 4-nitrophenol reduction from an aqueous solution. These compounds were chosen as models of the organic pollutant, which are very commonly encountered in wastewater. Phenol and substituted phenols take the 11th place under the 129 chemicals which have been designated as priority pollutants by the US EPA [9].

MATERIALS AND METHODS

a) Characterization of the applied green coke

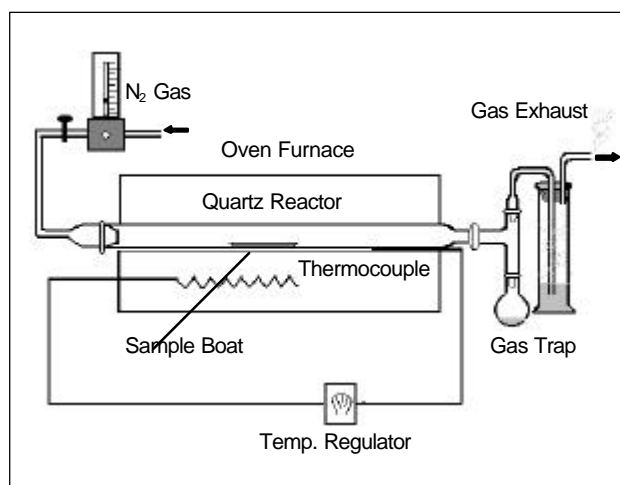
Green petroleum coke utilized as a precursor of adsorbent was obtained from Pertamina UP II Dumai, Indonesia. The material was dried overnight in an oven at 40 °C, then ground and sieved through standard sieve with appropriate numbers to obtain particles having geometrical diameters ranging from 0.63 to 2.00 mm.

The coke characterization involved element analysis of acidic microwave-digested sample, carried out using ICP-OES spectrometer JY 70 Plus (JOBIN YVON) and, organic (PAH) analysis after soxhlet extraction with GC-MS (HP 5890 Series II-MSD series 5970 B). Work-up of toluene extract was done according to the procedure described by Richter et al. [10]. The ash content and the volatile matter were determined using procedures described in references [11] and [12].

b) Activation process

Petroleum coke (0.63-2.00 mm) was dried in an oven at 110 °C for 2 h prior to activation. The activation processes evaluated were carried out in a horizontal quartz tube reactor 34 mm inner diameter setup in an oven furnace, Heraeus type ND1-30755, as shown in Fig. 1. A sample boat was placed at the center of the reactor.

FIGURE 1 - Equipment setup for coke activation process



In this study two activation methods were compared:

Method A: Dried sample was mixed with KOH pellet in the range of KOH/Coke weight ratios of 0.5 to 2 to produce the sorbents (A1-A3). The mixture was dehydrated at 450 °C under N₂ (130 cm³/min.) for 2 h and then subjected to thermal treatment at 850 ± 20 °C, and held at this temperature for 2 h. The remaining KOH and the salts formed during activation were removed by washing thoroughly with distilled water at pH 6-7 and dried in an oven at 120 °C for 2 h. This procedure has been described by previous researchers [4, 6, 8].

Method B: Sorbents B4-B7 were prepared by impregnating 10 g of raw coke with 5-15 g of pulverized KOH at 450 °C for 2 h followed by carbonization at 850 °C for 1.5 h. The cooled product was washed with a 15% (v/v) HCl solution for 4 h followed by washing with distilled water. For comparison a KOH-untreated coke was prepared by the same heat-treatment procedure.

c) Adsorption experiments

All adsorption experiments for evaluating equilibrium of sorbates adsorption by activated coke were carried out using batch technique. The reaction vessels were 100 mL glass stoppered-Erlenmeyer flasks placed in a 100 mL glass beaker containing water in order to maintain constantly 20 °C. Each glass used was pre-washed with 10% HNO₃ solution, rinsed in distilled water and dried at 110 °C for 2 hours prior to usage. A magnetic stirrer was used to mix the reaction mixtures.

Adsorption experiment was performed by adding 0.02-0.30 g of coke into 100 mL of phenolic solution (100 mg/L). The flask was put in a constant-temperature water-bath and stirred continuously with a speed of 500 rpm for 0-180 min. The pH of the system was adjusted with phosphate buffer solution prepared according to procedure in reference [13]. After equilibrium, the mixture was filtered through blue ribbon filter paper (S & S, Germany).

The concentrations of the adsorbates in the residual solution were determined spectro-photometrically using UV-visible Model HP-UV 8254A Diode Array Spectrometer at wavelengths 270 and 320 nm for phenol and 4-nitrophenol, respectively. For comparison some experiments were performed using a commercial activated carbon (AC). Activated carbon of the following specifications was used: particle size: 0.3-0.5 mm, surface area (BET): 1000 m²/g for GC (E. Merck, Germany).

The amount adsorbed (Q_e) at any time was determined according to mass balance on adsorbate [14]:

$$Q_e = (C_i - C_e) V/m \quad (1)$$

where C_i is initial concentration (mg/L), C_e is the residual or equilibrium concentration (mg/L), V is the

volume of the liquid phase (L), and m is the mass of the active sorbent (g).

The modelling of adsorption equilibria is usually achieved by applying either the Freundlich or the Langmuir isotherm represented mathematically by equations (2) and (3) [15]:

$$Q_e = K_F C_e^{1/n} \quad (2)$$

$$Q_e = \frac{Q^{\circ} b C_e}{1 + b C_e} \quad (3)$$

where Q_e is the amount of solute adsorbed per unit weight of adsorbent, K_F , $1/n$ and b are the characteristic constants, C_e is the solute phase and Q° is the solid phase concentration corresponding to complete coverage of available adsorption sites. A linear graph of $\ln Q_e$ against $\ln C_e$ in eq. (2) would give the Freundlich parameter values, n from the slope and K_F from the intercept. The Langmuir constants, b and Q° , were obtained from the slope and the intercept of plotting of C_e/Q_e against C_e .

RESULTS AND DISCUSSIONS

a) Characterization

As shown in Tab. 1 the ash content of coke sample is only 0.1%. This low value of the ash content is one of several advantages of petroleum coke as an activated carbon precursor compared with other carbonaceous materials. For example the ash content of coal is between 5.10 to 15.07%. The volatile matter of 15.4% is also below the value of coal (ca. 26.17%) [16].

TABLE 1 - Chemical analysis of petroleum coke sample

Elements	Conc. mg/kg	PAH compounds	Conc. mg/kg
Al	28	Naphthalene	5.34
As	< 5	Fluorene	1.34
B	20	Phenanthrene	15.9
Ca	40	Anthracene	5.55
Fe	43	Fluoranthene	3.83
K	19	Pyrene	21.6
Mg	< 9	Benzo[a]anthracene	48.0
Ni	172	Chrysene	50.5
S	4,310	Benzo[b]fluoranthene	31.6
V	5	Benzo[k]fluoranthene	4.21
Zn	< 5	Benzo[a]pyrene	< 1
Ash content, %			0.10
Volatile matter, %			15.4

The organic analysis data shows that the total PAH content of coke sample of about 189 mg/kg. This value is below the critical level of 1,000 mg/kg [17]. Also, the content of the key component benzo[a]pyrene was not detectable. On the other hand, some elements were found in coke sample in various concentrations as shown in Tab. 1. Among the heavy metals, only Ni and V were detectable within limit of detection.

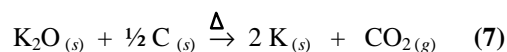
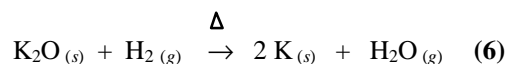
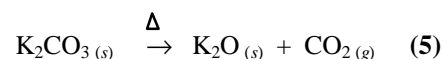
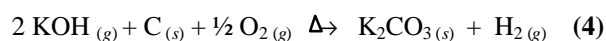
Moreover, the preliminary examination of the raw material, i.e. phytotoxicity tests of coke water eluate using an aquatic (duckweed, *Lemna minor*) and a terrestrial plant (garden cress, *Levidium sativum*) performed in our laboratory according to the methods of reference [18], showed that the coke material used in this study was not toxic to these plants. This is an important aspect especially when viewed from the environmental perspective.

b) Effect of KOH dosage

In order to assess the effect of KOH on the adsorption capacity, one sample obtained by the same heat treatment procedure, but without impregnating with KOH, was primarily examined. The measurable removal seems to be very small, i.e. only 3.9 and 5.1 mg/g for phenol and 4-nitrophenol, resp. adsorbed.

It can be seen from Fig. 2 that the uptake of phenol and 4-nitrophenol by the active sorbents increases when a larger quantity of KOH was used. In case of phenol, the adsorption capacity rises from about 55.6 mg/g to 69.9 mg/g, when the KOH/coke weight ratio used is increased from 1/2 to 2/3, and further enhances to about 86 mg/g when an equal amount of KOH and coke was used. On increasing the ratio further to 3/2, this removal goes up to be 93.2 mg/g. A similar trend was shown for the 4-nitrophenol reduction. A removal of more than 90% was achieved by the use of the activator equal to the raw material (1:1). 4-Nitrophenol was found to be almost completely adsorbed from the bulk solution when the KOH to coke ratio used was 3/2. The enhancement of these adsorption capacities indicates clearly that the chemical activator played an important role in the activation process.

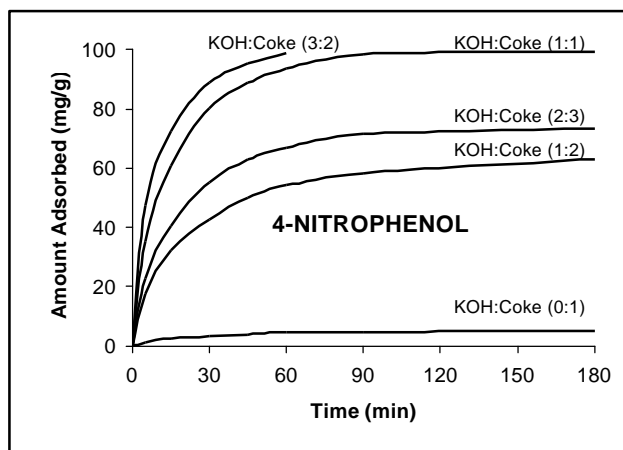
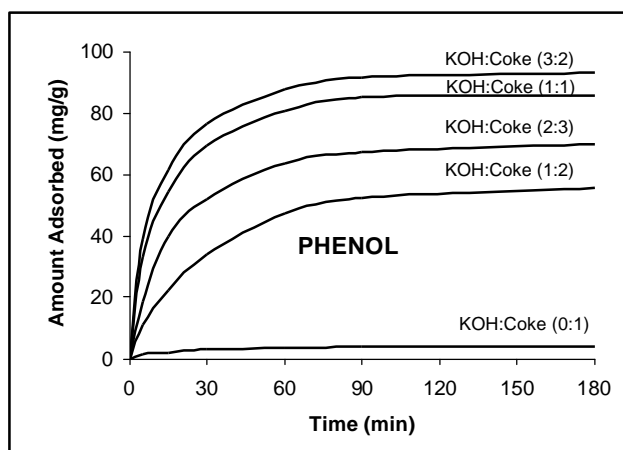
A series of chemical reactions is supposed to occur during the activation process:



This expectation is based on the facts that the gas generated during the activation is predominantly H_2 , as measured thermo-gravimetrically with effluent gas analysis by Otowa et al. [19]. This indicates that the KOH-activation proceeded with the transformation of KOH to K_2CO_3 .

FIGURE 2

Effect of variation of the KOH dosage on the adsorption activity of sorbent. (Activation: method B. Adsorption condition: weight of sorbent: 0.1 g. Initial concentration of phenolics: 100 mg/L, pH = 6, temperature: 20 °C).



A qualitative analysis of the trapped exhaust gas from the activation reactor proved that CO_2 was released. The analysis was performed by trapping the gas with a calcium hydroxide solution resulting in a precipitate of calcium carbonate.

In this closed system, reaction (4) should be facilitated by oxygen from the KOH activator and/or oxygen contained in the coke precursor itself. According to a CONCAWE's Report [20] the oxygen content of an uncalcined coke is about 1.10 – 2.56 mg/g. At a higher temperature, K_2CO_3 is likely converted to form K_2O and CO_2 (reaction 5) which is reduced further by carbon or

hydrogen through reaction (6) and/or (7) to K. This metallic potassium metal was observed visually when activation temperature exceeded 700 °C. This was also regarded to contribute to the activation [6]. Moreover, the water drops were released into a water trapping-flask during the activation and this can also be used for the sake of the argument.

(c) Comparison of activation methods

The sorbents produced with the two activation methods showed a very significant difference in their adsorption capacity towards phenol and 4-nitrophenol, as shown in Tab. 2.

TABLE 2
Equilibrium adsorption capacity of active sorbents prepared with different methods towards phenol (P) and 4-nitrophenol (4-NP)

Sorbent	KOH Coke	Me- thod	P adsorbed		4-NP adsorbed	
			mg/g	%	mg/g	%
Raw	0 : 1	-	2.3	2.3	2.9	2.9
A1	1 : 2	A	22.2	22.2	25.6	25.6
A2	1 : 1	A	53.1	53.1	60.3	60.3
A3	2 : 1	A	76.3	76.3	89.8	89.8
B4	1 : 2	B	55.6	55.6	63.1	63.1
B5	2 : 3	B	69.9	69.9	73.6	73.6
B6	1 : 1	B	86.4	86.4	99.3	99.3
B7	3 : 2	B	93.2	93.2	99.6	99.6

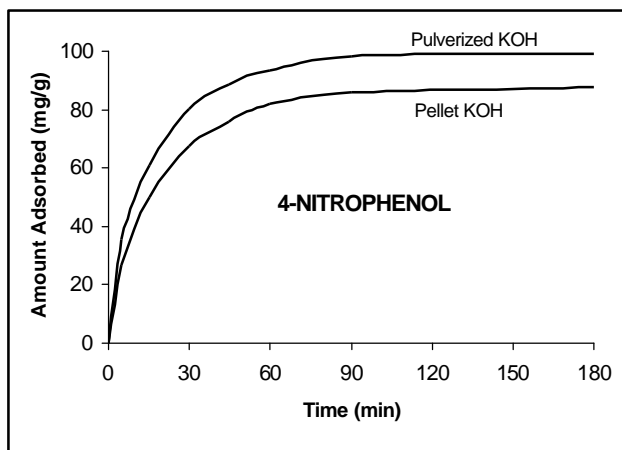
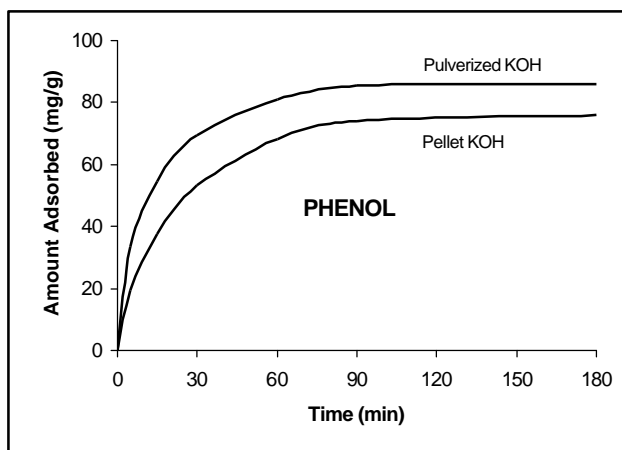
(Conditions: weight of sorbent 0.1 g, initial concentration of sorbate 100 mg/L, volume of solution 100 mL, contact time 180 min, pH = 6, temperature 20 °C)

The equilibrium removals of the phenolic compounds by sorbents **B4**, **B6** and **B7** prepared according to the modified procedure (method B) were higher than those produced with another method (**A1**, **A2** and **A3**) at the same KOH dosages and activation temperature. As seen in Tab. 2, the use of the developed procedure with the KOH/coke weight ratio, only 1/2, enhanced the amount adsorbed from 22.2 to 55.6 mg/g and from 25.6 to 60.3 mg/g for phenol and 4-nitrophenol, respectively. The use of an equal amount of KOH-precursor (1:1) by this method produced a sorbent having a higher adsorptive capacity. Maximum removal obtained with 0.1 g of the sorbent was 86.4% for phenol and more than 99% for 4-nitrophenol. These values are 62-65% greater than those obtained according to the previous technique.

The low activity of samples **A1** and **A2**, in this case, indicates their inferior quality. This is presumably due to their small surface area. From the previous investigation, as reported elsewhere [8] it is known that the surface area of the activated coke generated from green coke with the procedure A with the KOH/coke ratio, 1, was 177 m²/g.

On the other hand, the more highly activated sorbents prepared with method B, in comparison with the other, suggests that the combination of pulverized KOH and acid washing is the important factor. To verify that these factors influence the sorbent activity, some experiments were performed by applying the KOH activator in different particle sizes (pulverized and pellet) as well as a variation of treatments of the activation product, i.e., water-washing or HCl-washing. It was observed that pulverization of KOH before use increases the adsorption activity of the product to some extent.

FIGURE 3 - Effect of impregnation of pulverized KOH on the adsorption activity of the sorbent. (Conditions: weight of sorbent (B6): 0.1 g. Initial concentrations of adsorbates: 100 mg/L, pH = 6, temperature: 20 °C).

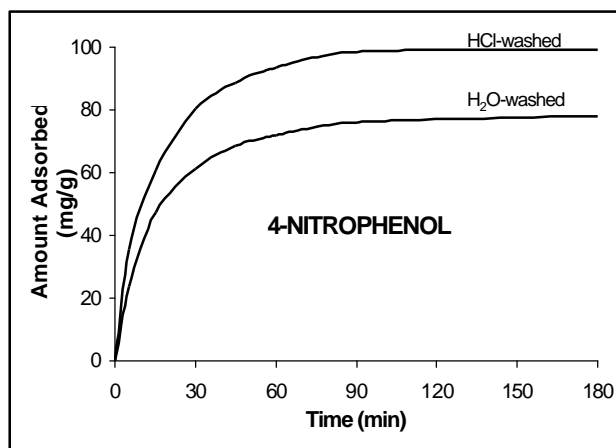
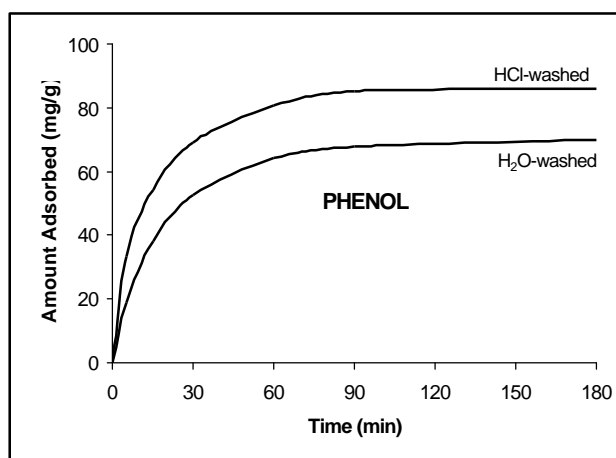


As shown in Fig. 3 the activity of sorbent towards phenol and 4-nitrophenol is clearly higher when pulverized KOH was used. The enhancement to maximum uptake of phenol and 4-nitrophenol by the pulverized KOH, i.e. 13%, was observed when the amounts of KOH and coke used were equal, namely, the amounts adsorbed of phenol and 4-nitrophenol increases from 75.8 to 86.4 mg/g and 87.8 to 99.3 mg/g, respectively. This may be easily explained from a chemical reaction approach where the reactions between the activator and precursor should

more effectively take place in a pulverized form than in a pellet one because in the former the particles come closely and completely into contact. Moreover, the effect of the HCl-washing is seen, as shown in Fig. 4. Therein, the sorbent prepared by washing the activation product in a 15%-HCl solution for at least 4 h adsorbed both phenol and 4-nitrophenol more than any other. Compared with the water-washed coke, the uptake enhancements by the HCl-washed coke are 24 and 26% for phenol and 4-nitrophenol, respectively.

It is presumed that the acid solution, in this case, acts as a good solvent, which is effective to remove impurities from the product, namely, the remaining KOH and salts [6]. These residues might adhere to the surface, or fill and block the interstices of the resulting active coke, leading to a lower adsorption activity of the product. According to McKay [21], in a bath system, besides adsorption on the outer surface, the sorbate molecules diffuse from the bulk solution into the pores of the sorbent. The diffusivity is delayed by the adhering impurities in the carbon pores, leading to a decrease in the activity of the sorbent.

FIGURE 4 - Effect of the HCl-washing on the adsorption activity of the sorbent. (Conditions: weight of sorbent (B6): 0.1 g. Initial concentrations of adsorbates: 100 mg/L, pH = 6, temperature: 20 °C).



(d) Comparison with commercial product

As mentioned before, a commercial activated carbon (AC) was examined for comparison. In the Tables 3 and 4 the comparative test results of Freundlich and Langmuir parameters for the sorbents generated from green petroleum coke and the commercial activated carbon are shown. There it can be seen that two samples, sorbents **A2-A3**, obtained according to the procedure A seem to have lower adsorption capacities Q° and K_F than the commercial one, even when the KOH used was doubled to precursor in quantity. On the other hand, the adsorption capacities for two samples prepared with method B (**B4 and B5**) were smaller than those of the commercial active carbon. However, the Q° and K_F values of sample **B6** impregnated with only equal amount of KOH/coke (1:1) appear to be comparable. And, on increasing the KOH/coke weight ratio further to 3/2, the adsorption capacities increase to a higher level than of the commercial sample. In addition to these facts, the values of the sorption intensity factor $1/n$ for sorbents B are higher than those for sorbents A on the same KOH dosage, indicating the better sorption capacities. In brief, the activation technique indicates an improvement in the adsorption activity of the sorbents.

CONCLUSIONS

From the experimental data it can be concluded that active sorbents can be produced by impregnating petroleum coke with an equal amount of pulverized KOH. The mixture was activated at 450 °C for 2 h, then subjected to thermal treatment at 850 °C for 1.5 h and followed by washing with a HCl solution. The effect of some variables of activation on the activity of the sorbent towards phenol and 4-nitrophenol was studied. It was observed that the combination of KOH pulverized before treatment and HCl-washing of the activation product significantly increases the adsorption capacity of coke sorbent. It is worth noting that the percent removals by the coke sorbent prepared by this modified method, 86.4 for phenol and 99.3 for 4-nitrophenol, were achieved by the use of pulverized KOH with a KOH/coke weight ratio of 1, whereas these achievements can be possibly reached by another method only when an excess amount of the activator is used. In other words, this developed procedure can improve the adsorption activity of sorbents from petroleum coke which are effective to remove phenol and 4-nitrophenol from aqueous solutions.

TABLE 3 - Freundlich and Langmuir parameters of the phenol adsorption on the sorbents

Sorbent	Particle Size (mm)	Freundlich			Langmuir		
		K_F	n	R^2	Q°	b	R^2
AC	0.3 - 0.5	66.9	5.03	0.938	155	0.332	0.989
A2	0.63-2.0	10.1	2.34	0.917	73.5	0.0489	0.989
A3	0.63-2.0	24.3	3.00	0.917	106	0.0978	0.996
B4	0.63-2.0	10.8	2.26	0.918	96.2	0.0294	0.976
B5	0.63-2.0	23.0	3.25	0.860	105	0.0599	0.989
B6	0.63-2.0	56.9	4.47	0.878	149	0.316	0.975
B7	0.63-2.0	73.9	5.48	0.943	158	0.391	0.989

AC = commercial activated carbon (Particle size: 0.3-0.5 mm. Surface area: 1000 m²/g)

TABLE 4 - Freundlich and Langmuir parameters of the 4-nitrophenol adsorption on the sorbents

Sorbent	Particle Size (mm)	Freundlich			Langmuir		
		K_F	n	R^2	Q°	b	R^2
AC	0.3 - 0.5	115	5.65	0.953	222	0.618	0.999
A2	0.63-2.0	10.9	2.23	0.945	101	0.0342	0.988
A3	0.63-2.0	51.3	4.34	0.981	137	0.214	0.999
B4	0.63-2.0	12.2	2.29	0.924	102	0.0401	0.998
B5	0.63-2.0	16.1	2.26	0.958	125	0.0512	0.996
B6	0.63-2.0	108	5.55	0.967	213	0.610	0.999
B7	0.63-2.0	122	6.41	0.974	227	0.620	0.999

AC = commercial activated carbon (Particle size: 0.3-0.5 mm. Surface area: 1000 m²/g)

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PARAMETER DEPENDENT ECNI-MS FRAGMENTATION OF C10, C11, C12, AND C13 POLYCHLORINATED ALKANES

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SUMMARY

ECNI mass spectrometric fragmentation of chloroalkanes depends mainly on the degree of chlorination, but also on the chain length and ion source temperature. The interpretation of mass spectra is further complicated by the abundance of spectra of different mixtures obtained with the conventional HRGC-MS, which to compare is tedious and time-consuming. The recently developed short-column GC-MS method, which leads to the elution of all chloroalkanes of the mixture as one peak, can be used to obtain one single MS spectrum, which then may be more conveniently interpreted in comparison with the spectra of mixtures of defined chain length and chlorination degree. To obtain reliable results, the variability of the spectra in dependence on different parameters has to be taken into account. In this work, the MS fragmentation of several C10-C13 polychloroalkanes in dependence on chlorination degree, alkane chain length, and ion source temperature was investigated. The most intensive ion registered under ECNI conditions was either $[M-HCl]^-$ or $[M-Cl]^-$ depending on the chlorination degree or ion source temperature. It was also found that the low boiling compounds cannot completely be detected even at an ion source temperature of 250 °C.

KEYWORDS:

chlorinated paraffins, polychloroalkanes, ECNI-MS fragmentation.

INTRODUCTION

Chlorinated paraffins (CPs) are industrially produced from n-alkane mixtures by addition of molecular chlorine and heating or irradiating with light [1]. CPs are classified according to their chain length as short chain (C10-C13), middle chain (C14-C17), and long chain (C20-C30) CPs. The short chain CPs are the most important group with respect to their toxicological effects [2,3]. Especially after the ban of polychlorinated biphenyls (PCBs), for which CPs are good substitutes in some application fields, the production of CPs amounted to about 300,000 t per year.

Nevertheless, reports on the occurrence of chlorinated paraffines in the environment are rare. Because of the unspecific nature of the radical chlorination reaction, a great number of isomers are formed, together with possibly thousands of compounds. For the determination of CPs, mostly HRGC/ECNI-MS methods are used, although gas chromatographical separation brought no satisfactory results [4-8]. All attempts to separate these very complex mixtures by column chromatography or distillation methods were unsuccessful [9, 10]. Nevertheless, a mass spectrometric discrimination of CPs, especially in the case of incomplete separation from other groups of chlorinated xenobiotics, is indispensable. For this, more knowledge about the mass spectrometric behaviour of CPs is essential.

Up to now, only one investigation on ECNI-MS fragmentation of CPs has been published [11]. The study was executed with one mixture of polychlorodecanes and one of polychlorododecanes, each with 60 % chlorination degree obtained by the reaction with sulfuryl chloride. The authors reported on the formation of $[M+Cl]^-$, $[M-HCl]^-$, and $[M-Cl]^-$ as the main fragment ions in the case of polychlorodecanes. With polychlorododecanes, they could also detect $[M-Cl-HCl]^-$, $[M-2Cl]^-$, and $[M-2HCl]^-$ fragments. But, besides the problem that only two mixtures do not allow for a systematic study, the interpretation of the mass spectra was hampered by the repeated shift in the spectra, because, as a result of the HRGC separation used and the poor solution, the successive scans represented different masses. For the mass spectrometric discrimination of CPs it should be sufficient to characterize the unseparated mixtures; the resulting spectrum should contain all relevant fragments, which then may be interpreted. Dispensing with the separation, brings the additional advantage of improving the sensitivity [12]. The assignment of the clusters should not be more difficult than with the pre-separated, yet more complicated mixtures provided enough data on the fragmentation behavior of this substance class in dependence on the relevant parameters, such as chlorination degree, chain length, and ion source temperature, are available. There-

fore, the short column GC/ECNI-MS method for the determination of short chain CPs, which has recently been described [12, 13], has now been applied for a more comprehensive ECNI-MS study of typical fragmentation patterns of several polychloroalkane mixtures of different chain lengths (C10-C13) and chlorination degrees (45-50, 55-60, and 65-70 %).

EXPERIMENTAL

Materials

The synthesis of the polychloroalkanes has been described elsewhere [12]. Their exact chlorination degrees are listed in Table 1. For short column GC/ECNI-MS measurements, polychloroalkane solutions of 20 ng/ μ l in cyclohexane was used. For the measurements with the 30 m column (see below), the concentrations were 1000 ng/ μ l.

TABLE 1 - Polychlorinated alkanes and their chlorine contents investigated in the study.

Alkane chain	Low chlorinated (Cl %)	Middle chlorinated (Cl %)	High chlorinated (Cl %)
C10	49.6	59.1	65.6
C11	48.5	57.1	66.4
C12	46.6	59.8	69.3
C13	47.8	57.7	66.6

GC/MS System

The GC/MS measurements were performed with an HP 5890/5988A GC/MS equipment with HP-5MS column (30m \times 0.25 mm i.d., film thickness 0.25 μ m) for

HRGC studies and a DB 5 column (65 cm, 42 μ m in the interface; 0.25 mm i.d., film thickness 0.2 μ m) or a fused glass capillary column with the same dimensions, but without stationary phase (isotherm at 290 $^{\circ}$ C, injector 290 $^{\circ}$ C splitless 0.5 min, interface 290 $^{\circ}$ C, ion source 100 $^{\circ}$ C, methane as reactand gas, injection volume 2 μ l) for direct introduction of the substances into the system. In short column measurements, injections were performed 20 sec after the start of scan. Some measurements were performed in the EI mode at 70 eV and 200 $^{\circ}$ C ion source temperature. Peak intensity was calculated as sum of all scans. The methane pressure was $2 \cdot 10^{-3}$ atm.

RESULTS AND DISCUSSION

The results discussed were obtained by short column measurements, unless stated otherwise. For each mixture one spectrum was obtained, and for each spectrum recorded and each mass range in this spectrum, the total intensities of the peak clusters were split between the possible contributing fragments of the congeners. Only the contribution from ^{13}C and ^2H isotops has been neglected. The calculation procedure is explained below using, as an example, the two clusters of one mass range of the mass spectrum of CP10:59.1 (a polychlorinated decane with 59.1 % chlorine content) measured at an ion source temperature of 100 $^{\circ}$ C. The mass spectrum of this mixture is shown in Figure 1. Six groups of signals can be seen in the spectrum in the mass ranges 272-284, 302-320, 340-357, 376-390, 412-424, and 446-456. Of these, the second, third, and fourth, which represent the fragment groups with 5, 6, and 7 chlorines, are the most intensive. In the following, the ion group with 6 chlorines (m/z 340-357) will be discussed. The calculated portions of the fragments in this mass range are listed in Table 2.

FIGURE 1 - ECNI-MS spectrum of CP10:59,1 measured at an ion source temperature of 100 $^{\circ}$ C.

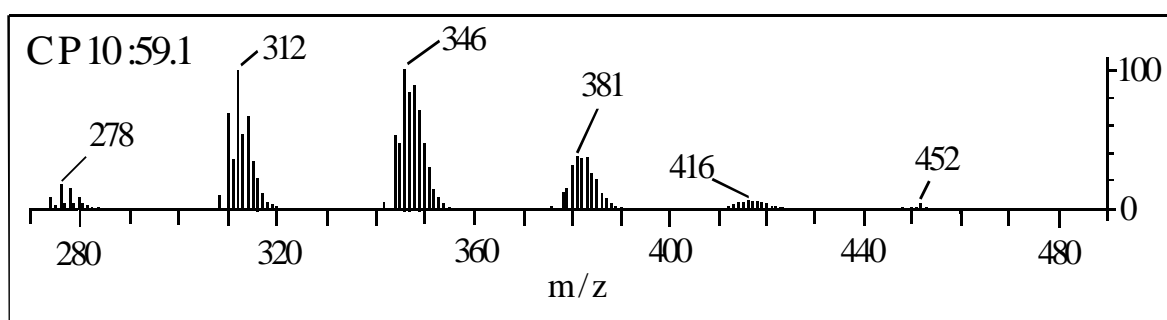


TABLE 2 - Measured peak intensities of the two clusters in the mass range m/z 340-357 from the mass spectrum of CP10:59.1 and calculated portions (%) of the different fragment ions

m/z	Measured peak intensity	Portions of fragment ions (%)			
		[C ₁₀ H ₁₃ Cl ₉ -3HCl] ⁻ (F1)	[C ₁₀ H ₁₄ Cl ₈ -2HCl] ⁻ (F2)	[C ₁₀ H ₁₅ Cl ₇ -HCl] ⁻ (F3)	[C ₁₀ H ₁₆ Cl ₆] ⁻ (F4)
340	180	180			
342	3,587	345	3242		
344	23,463	276	6222	16965	
346	42,487	118	4978	32562	4829
348	37,468	28	2122	26050	9268
350	19,026	3	510	11103	7420
352	5,892	<1	62	2670	3160
354	1,087		2	325	760
356	111			19	92
358	5				5
S	133,306	950	16,628	89,694	25,534
		[C ₁₀ H ₁₄ Cl ₈ -HCl ₂] ⁻ (F1)	[C ₁₀ H ₁₅ Cl ₇ -Cl] ⁻ (F2)		
343	549	549			
345	20,889	1053	19836		
347	38,915	843	38072		
349	30,817	359	30458		
351	13,068	86	12982		
353	3,123	1	3122		
355	380	<1	380		
357	23		23		
S	107,764	2,891	104,873		

TABLE 3 - Portion of fragment ion clusters (sum of all mass ranges per mixture/total ion current) of all short-chain CP mixtures analysed in dependence on chlorination degree and chain length at an ion source temperature of 100 °C.

	[M-4HCl] ⁻	[M-3HCl] ⁻	[M-H ₂ Cl ₃] ⁻	[M-2HCl] ⁻	[M-HCl ₂] ⁻	[M-HCl] ⁻	[M-Cl] ⁻	M ⁻
CP10.65	0.14	2.09	0.06	11	5.47	32.95	41.43	6.86
CP10.59	-	0.87	-	8.88	1.36	41.01	37.81	10.07
CP10.49	-	-	-	7.23	0.07	54.02	31.67	7.01
CP11.66	0.13	2.38	0.4	11.11	7.99	27.2	41.55	9.26
CP11.57	-	0.3	-	9.73	2.1	40.08	37.58	10.17
CP11.48	-	0.12	-	8.75	0.3	46.77	34.6	9.43
CP12.69	0.52	3.56	1.6	11.24	9.06	17.55	46.58	9.79
CP12.55	-	0.54	-	10.1	1.42	40.8	34.74	12.38
CP12.46	-	0.14	-	8.02	0.39	48.15	30.42	12.8
CP13.66	-	1.09	0.33	11.96	9.48	23.72	39.7	13.7
CP13.57	-	0.32	0.12	10.89	2.78	37.9	33.53	14.42
CP13.47	-	-	0.16	7.9	0.6	45.9	30.86	14.57

The ion at m/z 340 can be explained either as the first isotop peak of the cluster resulting from $C_{10}H_{13}Cl_9$ by triple HCl cleavage or from $C_{10}H_{12}Cl_{10}$ by fourfold HCl cleavage, the latter interpretation being based on the assumption that the first ion of the cluster at m/z 338 has too low an intensity to be detected. Nevertheless, because there is no real basis for the latter interpretation, the total of the intensity of 180 at m/z 340 has been assigned to $[C_{10}H_{13}Cl_9-3HCl]^-$ (Table 2). The three following isotop peaks of this cluster at m/z 342/344/346 are expected to have intensities of 345/276/118 according to the theoretical isotopic distribution of Cl atoms, with the intensity of the peak at m/z 342 being the sum of $[C_{10}H_{13}Cl_9-3HCl+2]^-$ and $[C_{10}H_{12}Cl_6]^-$ resulting from $[C_{10}H_{14}Cl_8-2HCl]^-$ or $[C_{10}H_{13}Cl_9-HCl_3]^-$.

To judge on the presence of portions of $[M-2Cl]^-$ is always a problem. This is an important point, because the same empirical formula is derived from the fragment ions $[C_xH_yCl_z-2Cl]^-$ and $[C_xH_{y+1}Cl_{z-1}-HCl]^-$. It is not possible to distinguish two such fragment ions by mass spectrometry, if the mass spectra are taken without complete gas chromatographic separation. Nevertheless, in our experiments with the 30 m column it was possible to obtain some significant scans, where, for example, only heptachlorodecanes were detected, but no hexachlorodecanes. In these spectra, the $[M-2Cl]^-$ ions had a relative intensity of less than ca. 6 %. The same result was obtained with single substances [14]. Only two exceptions were found. Two unsaturated single compounds (9,11,11,11,-tetra-chloroundeca-1,5-diene and 1,1,1,3,10,12,12,12,-octa-chlorododecene-6) gave significantly higher intensities of the $[M-2Cl]^-$ peak. But these compounds are presumably of less importance for technical polychloroalkane mixtures or also for environmental samples, since perchlorinated methyl groups have been assumed to be lacking in mixtures synthesized by technical procedure [1]. For this reason, the $[M-2Cl]^-$ ion was not taken into account. The same is valid for the following fragment pairs $[C_{10}H_{14}Cl_8-H_2Cl_4]^- = [C_{10}H_{15}Cl_7-3HCl]^-$, $[C_{10}H_{14}Cl_8-H_2Cl_3]^- = [C_{10}H_{13}Cl_9-HCl_4]^-$, $[C_{10}H_{14}Cl_8-2HCl]^- = [C_{10}H_{13}Cl_9-HCl_3]^-$, $[C_{10}H_{14}Cl_8-HCl_2]^- = [C_{10}H_{14}Cl_8-HCl_3]^-$ and $[C_{10}H_{14}Cl_8-HCl]^- = [C_{10}H_{13}Cl_9-2Cl]^-$, where the loss of the first fragment from each pair is more probable judging from the mass spectra of single compounds.

At m/z 342, two clusters are possible, $[C_{10}H_{14}Cl_8-2HCl]^-$ and $[C_{10}H_{13}Cl_9-HCl_3]^-$, but the latter is rather improbable, as mentioned above. Therefore, the intensity of $[C_{10}H_{14}Cl_8-2HCl]^-$ can be obtained by subtraction of the calculated intensity of $[C_{10}H_{13}Cl_9-3HCl]^-$ from the measured total intensity (i.e. 3587). In the same manner, the intensity of the peak at m/z 344 has been divided between the third peak of the cluster of $[C_{10}H_{13}Cl_9-3HCl]^-$, the second peak of the cluster of $[C_{10}H_{14}Cl_8-2HCl]^-$, and the first peak of the cluster of $[C_{10}H_{15}Cl_7-HCl]^-$, excluding a participation of $[C_{10}H_{14}Cl_8-2Cl]^-$, because of the low intensity of the corresponding peaks in spectra of single CP. The rest of the mass range has been attributed

accordingly to the groups of isomers given in Table 2. At m/z 346 and above, the measured total intensities slightly differed from the calculated ones, which difference has, however, been neglected, because it was in the range of the normal limit of error of subsequent measurements. That this calculation is sufficiently correct can be seen from MS measurements of CP10:59.1 after normal gas chromatographic separation with a 30 m column. In the spectra obtained in this way the peaks of the fragments neglected in the calculation are also either missing or negligible.

The other mass ranges of CP10:59.1 (m/z 272-284, 302-320, 376-390, 412-424, and 446-456) have been also analysed accordingly to obtain the relative peak intensities and their sum. In the case of injection of only this mixture, the sum of the peak intensities of all mass ranges of the mixture should correspond to the total ion current of the single peak in the short-column GC-MS chromatogram. With different mixtures injected together, as is the case with environmental samples, the portion of each of these mixtures is obtained by dividing the calculated sum of intensities of its clusters by the total ion current. The results of this calculation for all mixtures analysed in this work are given in Table 3.

When comparing the fragmentation patterns of the different mixtures several trends can be observed. With increasing chlorination degree the main peak cluster is shifted to $[M-Cl]^-$ fragmentation. For instance, with low chlorinated short chain CPs, the main fragment is the $[M-HCl]^-$ cluster with a proportion of about 46-54 % of the total ion intensity, while $[M-HCl]^-$ and $[M-Cl]^-$ fragment ions have the proportions of total ion intensity similar to the middle chlorinated CPs with ca 38-41 % and 33-39 %, respectively. With high chlorinated CPs, the relative intensity of $[M-Cl]^-$ fragment ions amounts to 39.7-46.6 % followed by $[M-HCl]^-$ and M^- fragment ions with 23.7-33 % and 6.8-13 %, respectively. The relative intensities of the M^- ion are not changed significantly with the chlorination degree. This ion has a relative intensity of 10-13 %. The relative intensities of the $[M-2HCl]^-$ cluster are below 12 % and only slightly increase with increasing chlorination degree. Other fragment ions are only subordinate, although the $[M-HCl_2]^-$ cluster has an intensity similar to that of $[M-HCl]^-$ in compounds containing more than 8 chlorine atoms.

The results described above are valid only for measurements at an ion source temperature of 100 °C. At 250 °C, significant changes in the mass spectra and fragmentation pathways are noticeable, especially with CPs of high chlorination degree (Figure 3), as has been described for other compounds [15] and also for some single chloroalkanes [16]. Under these conditions, the main peak cluster at all chlorination degrees is the $[M-Cl]^-$ fragment ion, which reaches a relative intensity of about 65 % with high chlorinated CPs. The relative intensity of the $[M-HCl]^-$ cluster is below 10 % and,

now, in the same range as that of the M^- and $[M-2HCl]^-$ clusters. On the other hand, the relative intensity of $[M-HCl_2]^-$ increases up to 10 %, being now the ion second in importance.

Because the location of the main fragment ion depends on the chlorination degree, while the ion source temperature can be held constant, it should be possible to estimate the chlorine content of CPs from their mass spectra. Unfortunately, this is valid only with restrictions even at lower ion source temperatures and the estimation is too inaccurate with mixtures of a chlorine content below 55 %. For example, the empirical formula $C_{10}H_{15.54}Cl_{6.46}$ is derived for CP10:49.6 from the ion intensities in the MS spectrum without consideration of response factors at an ion source temperature of 100 °C. From this, hexachlorodecanes should be expected to be the main components, because the ions starting with 310 are the most

intensive ones. But the chlorine number of this mixture obtained by gravimetric methods is 3.83. This difference is the result of the fact that the low chlorinated decanes, which amount to a great portion of the mixture, can be either not detected or detected only with very low sensitivity with ECNI-MS under the usual measurement conditions, because of their low response factors compared to that of the high chlorinated one (Table 4). The difference in chlorine number between the value derived from the MS spectrum and that obtained by gravimetry is less pronounced with higher chlorination degrees. For example, the gravimetrically measured chlorine number of CP10:65.6 (7.27) is rather near the calculated one (7.59) at 100 °C ion source temperature, and even at 250 °C, the calculated value (7.92) is still not very misleading. The error becomes more serious with CP13:66.6 for which the mass spectrum suggests a chlorine number of 9.36 at 250 °C and of 8.45 at 100 °C, while the actual value from gravimetric measurement is 9.81.

FIGURE 3 - Distribution of relative intensities of fragment ions of high chlorinated CPs in dependence on the ion source temperature (above: 250 °C; below: 100 °C).

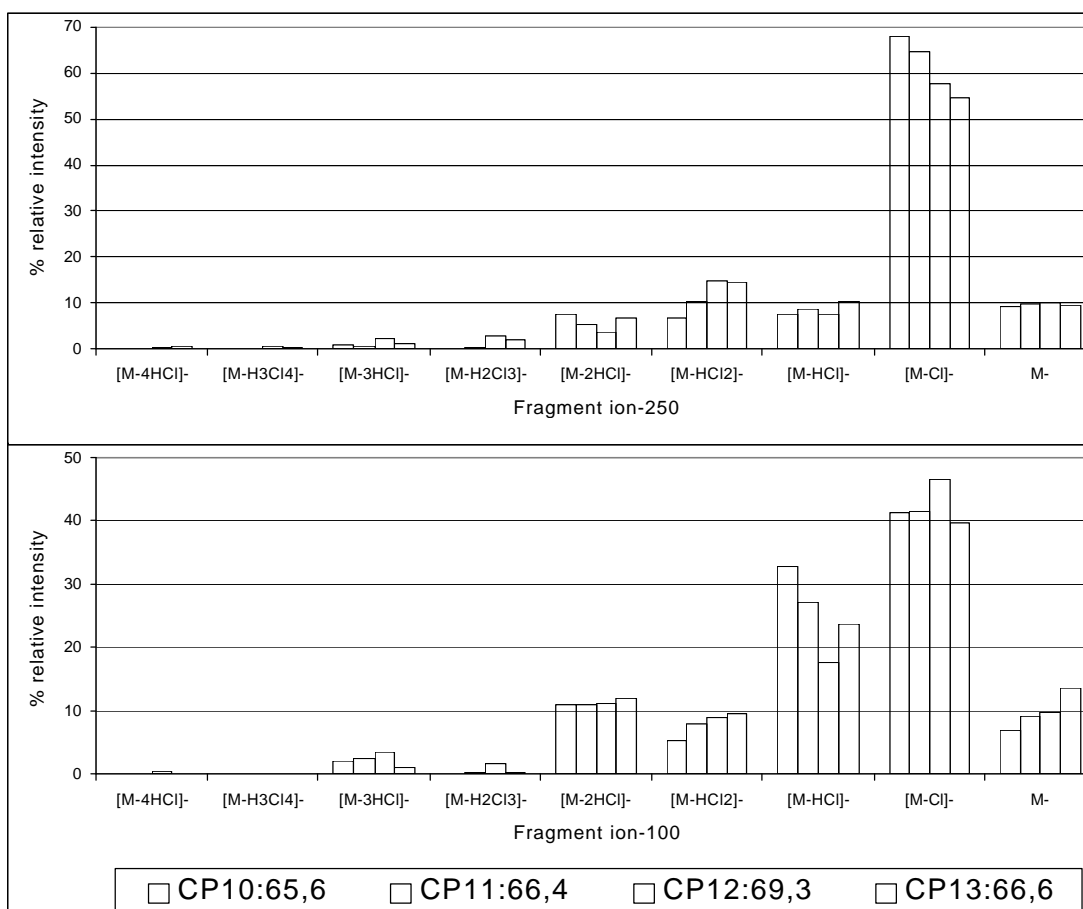
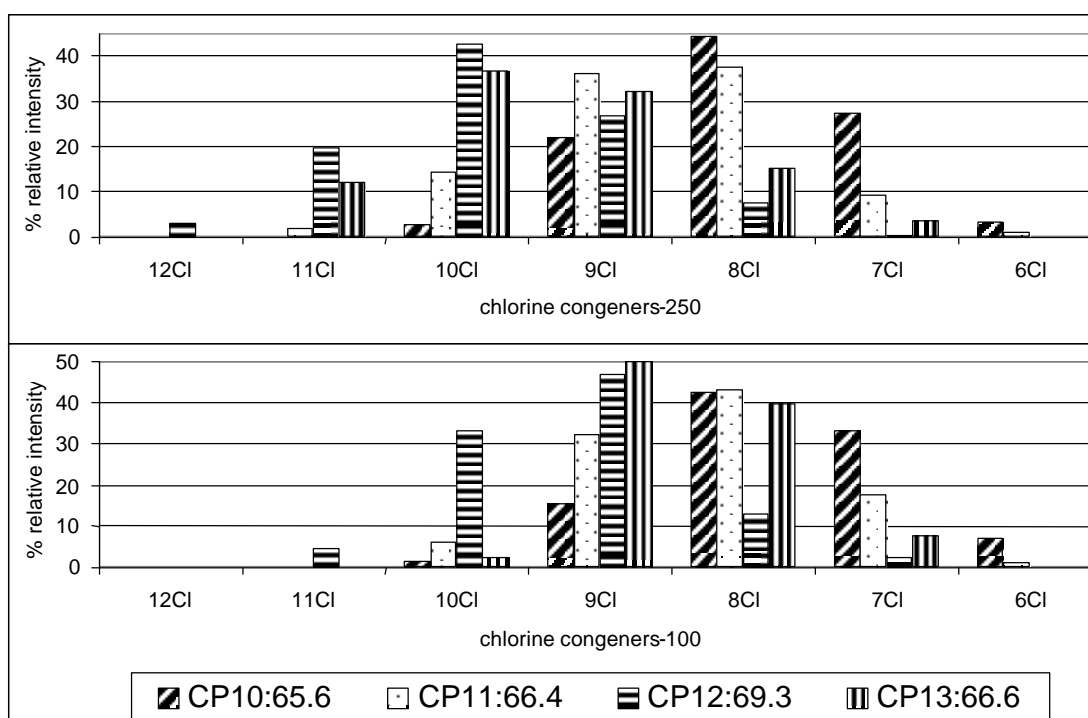


FIGURE 4 - Distribution of calculated chlorine congeners in high chlorinated CPs in dependence on the ion source temperature on the (above: 250 °C; below: 100 °C).



The dependence of the calculated chlorine number on the ion source temperature can be seen in Figure 4. For example, CP13:66.6 shows significant differences in the calculated chlorine content for congeners with more than 8 chlorine atoms. According to the mass spectrum measured at 100 °C, compounds with 9 chlorine atoms should be the main components with a relative concentration of about 50 %, while the proportion is only 33 % in the spectrum measured at 250 °C, and now compounds with 10 chlorine atoms are the main components with a relative concentration of 36 %. Compounds with 10 chlorine atoms have a proportion of only 3 % at the low temperature measurement. This phenomenon possibly arises from incomplete vaporization of high boiling components of poly-chloroalkane mixtures at low ion source temperatures. With increasing chlorination degree or chain length this effect should be more pronounced, as indicated by some experiments, which have been made with a CP13:81 and a CP16:61 (unpublished results). This means, that even temperatures of 280 °C in the injector and 250 °C in the ion source are not high enough for a complete vaporization of low boiling CPs.

Compared to the influence of the chlorination degree on the fragmentation, that of the chain length is less important. It can be seen from Table 3 that the fragmentation patterns are not significantly influenced by the change of the chain length. The greater effect of the ion source tem-

perature on the mass spectra of long chain chloroalkanes can be explained with the increase in boiling temperature with increasing molecule size.

TABLE 4 - Relative response factors (RRF) of different CP mixtures studied at 100 °C ion source temperature

CP10		CP11		CP12		CP13	
Cl %	RRF	Cl %	RRF	Cl %	RRF	Cl %	RRF
49.6	1.00	48.5	2.27	46.6	1.86	47.8	1.89
59.1	4.04	57.1	5.76	59.8	8.24	57.7	4.26
65.6	10.22	66.4	13.28	69.3	15.77	66.6	7.34

$[M+Cl]^-$ ions are often reported to have been detected, especially with compounds of low chlorine number, but we could not observe these ions in our experiments with short-column chromatography. Only with gas chromatographic separation, this fragment ion was detected, as has been reported for low chlorinated compounds. This fragmentation could also be seen in the spectra of single components. It has formerly been shown, that the formation of $[M+Cl]^-$ ions is significant only with lower chlorinated compounds [11]. The reason for the lacking of this fragment in spectra obtained with short-column chromatography is probably due to the very small amount of the different groups of chloroalkanes normally

injected in this mode. With normal gas chromatographical separation, the absolute amount injected was 50 times higher. To detect this fragment, inspite of the low concentrations injected, other mass spectrometric conditions would have been necessary.

Taken together, the following generalization is possible: In a homologous series, when mixtures of similar chlorination degrees are compared, the mass spectrometric fragmentation shows tolerably similar results. Differences occur especially between the spectra of compounds with different chlorination degrees, but also with spectra obtained at different ion source temperatures. Due to the comparatively low responses of low chlorinated portions of the CP mixtures, it is impossible to derive correct values for the chlorination degree from the mass spectra especially with low chlorinated CPs. While the calculated value will be too high with low chlorinated C10 mixtures in the whole temperature range, with C13 mixtures with decreasing chlorine content it will be either too low or too high, depending on the temperature.

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MICROWAVE ASSISTED DIGESTION PROCEDURES FOR THE DETERMINATION OF METALLIC ELEMENTS IN COAL, FLY ASHES AND SLAG BY ATOMIC ABSORPTION SPECTROMETRY

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ABSTRACT

The efficiency of two digestion procedures using microwave heating in combination with closed vessels was evaluated for the determination of 10 elements by atomic absorption spectrometric techniques (electrothermal (ET)- and flame (F)-AAS) in coal and its combustion residues. The extractants assayed were aqua regia (AR) and aqua regia plus hydrofluoric acid (AR + HF). For coal, AR allowed a reliable extraction of Cd, Co, Cu and Mn, while for Cr, Fe, Ni and V the AR + HF mixture was necessary. Regarding fly ashes and slag, the presence of HF was required to solubilize all the elements, except Cd that was efficiently extracted with the AR mixture. For Sb, in both matrices, none of the methods provided good results. The methods were validated using two certified reference materials, NIST SRM 1635 Coal and NIST SRM 1633a Coal Fly Ash.

KEYWORDS:

Microwave digestion, metals, coal, fly ash, slag, AAS.

INTRODUCTION

In recent years the regulation of pollutant discharges from coal fired power plants has become more stringent. For this, as much information as possible about the trace element contents of coal and coal derived residues is required in order to evaluate the impact of this kind of anthropogenic activity on the environment. The reliability of metal determination in these complex matrices mainly depends on the dissolution process used. In the last decade, microwave (MW) assisted digestions in closed vessels have been developed as a rapid and reproducible sample preparation method for a great variety of complex

matrices (1-4). Several combinations of mineral acids have been reported: HNO₃ (1, 5), aqua regia (AR) (6, 7), AR + HF (4, 8, 9), etc. If geological samples are considered, AR is sometimes required and in many cases the AR + HF mixture must be used.

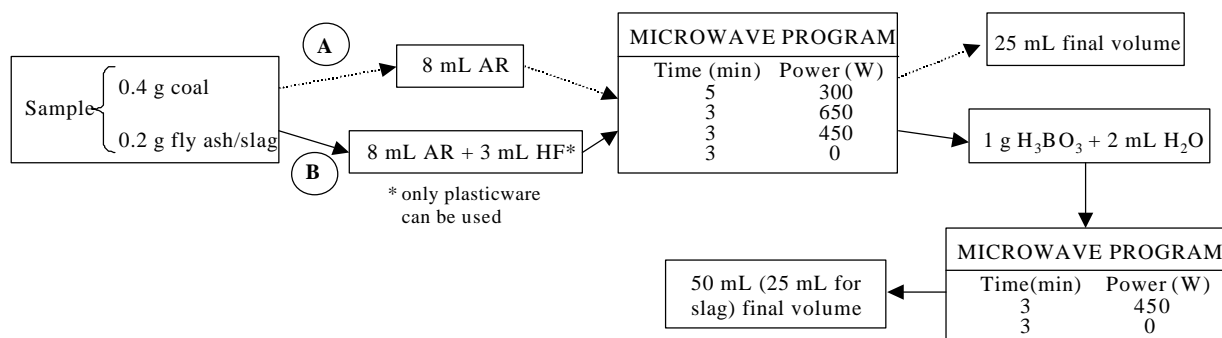
In this work, two sample digestion procedures based on microwave heating in combination with closed vessels using AR and AR + HF mixture, respectively, were evaluated in order to achieve a quantitative dissolution of Cd, Co, Cr, Cu, Fe, Mn, Ni, Sb, V and Zn. They were determined using both flame and electrothermal atomic absorption spectrometry.

MATERIALS AND METHODS

Apparatus and Reagents: For sample digestion, a laboratory microwave digestion system fitted with a Milestone (Sorisole, Italy) microwave oven model MLS 1200 was used. The determination of metals was performed on two Perkin Elmer atomic absorption spectrometers (Überlingen, Germany) Model 2380 and Model 4100. Nitric (70%), hydrochloric (35.5-38%) and hydrofluoric (40%) acids were Baker Instra-analyzed, for trace metal analysis, from Baker (Holland). Boric acid (99.5%) ACS reagent was from Aldrich (Germany). Standard metal solutions (1000 µg mL⁻¹) for atomic absorption spectrometry (AAS) were all from Panreac (Spain). Ultrapure water (18 MΩ cm specific resistivity) was obtained from a Millipore Milli-Q System (Millipore Corp.).

Procedure: The coarse samples were freeze-dried, ground and sieved (φ 200 µm), if needed. Two digestion procedures were carried out which are schematized in Figure 1. In all cases, PTFE vessels were used and 1 mL of ultrapure

FIGURE 1 - Microwave assisted extraction procedures using AR and AR + HF mixtures.



water was added in order to increase the digestion temperature. When HF was used, H₃BO₃ was required to eliminate the remaining acid. Acid extracts were analyzed by FAAS for the determination of Cu, Fe, Mn and Zn, and by ETAAS for Cd, Co, Cr, Cu (coals), Ni, Sb and V using the optimized operational conditions. Accuracy and precision were checked by using the following certified reference materials: Trace Elements in Coal SRM 1635 (subbituminous) and Trace Elements in Coal Fly Ash SRM 1633a, from the National Institute of Standard and Technology (NIST, USA). Analytical recovery studies were also carried out for slag.

RESULTS AND DISCUSSION

The amount of sample utilized was in relation with the metallic content. Thus, the sample mass selected for a fixed extractant volume (8 mL) was 0.4 g for coal. Regarding fly ashes and slag a medium to low sample amount was enough (0.2 g), because most of the metals present in coal are concentrated in these combustion residues. The results obtained using both acid mixtures for the above-mentioned certified reference materials are presented in Table 1.

When coal samples were digested with AR, an efficient recovery was obtained for Cd, Cu, Mn and an almost quantitative for Co. The remaining elements were not com-

pletely solubilized. For Sb and Zn the values obtained were lower than the corresponding limit of detection. In the case of coal fly ashes the recovery was acceptable only for Cd, which is the most soluble metal from the studied ones. For the other metals, very low recoveries were attained, probably due to the refractory nature of the sample matrix.

In order to achieve a more efficient solubilization of the studied elements HF was added to the AR mixture. The minimum volume of HF necessary to obtain a good recovery of most of the elements considered here, was 4 mL. For H₃BO₃, higher masses than 1 g could not be used due to the formation of floccules. Good recoveries were achieved for Cu, Fe and Mn for both samples. In the case of coal, slightly low Cr extraction was found; low recoveries were obtained for Ni and V and worse results for Co. Sb and Zn, because of their low contents in NIST SRM 1635 were not detected. In general, these results were very similar to those obtained using AR as extractant. Regarding fly ash, Co, Ni and Zn were almost completely extracted, while Cr and V were quantitatively recovered. Thus, the addition of HF is crucial to achieve an efficient solubilization of the metals studied, except for Cd and Sb, because this procedure caused an atomic signal enhancement during their analysis by ETAAS probably due to a boron-salt formation, being more drastic for Sb giving an anomalous high recovery.

TABLE 1
Percentage of recovery (expressed as value obtained/certified value) achieved for the elements studied with AR and AR + HF (n= 3).

Certified Reference Material	Digestion Procedure	Element									
		Cd	Co	Cr	Cu	Fe	Mn	Ni	Sb	V	Zn
NIST SRM 1635	AR	110	81	45	90	62	87	65	nd	66	nd
Coal	AR + HF	147	67	85	96	89	104	73	nd	76	nd
NIST SRM 1633a Coal Fly Ash	AR	80	20	18	20	22	30	20	60	26	30
	AR + HF	130	87	111	109	95	105	85	280	101	82

nd: not detected

In brief, the microwave digestion procedure including AR was selected for the determination of Cd, Co, Cu and Mn in coal samples because of its simplicity and rapidity, but for the analysis of Cr, Fe, Ni and V the AR + HF mixture was required due to the refractory nature of these elements. Regarding fly ashes, only Cd could be analysed in AR extracts as a result of the siliceous matrix of this kind of samples. Sb could not be determined using either acid mixture, requiring further assays. In the case of slag, a certified reference material of this type of sample was not available. Therefore, the analytical recoveries were studied. Slags have a matrix composition similar to fly ashes, so the same extraction procedures selected were applied. In all cases, quantitative analytical recoveries ranging from 92% to 113% were obtained.

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COMPARATIVE STUDY OF REMOVAL OF LEAD(II) BY ADSORPTION ON VARIOUS CARBONS

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SUMMARY

Kinetic studies on the removal of Pb(II) ions from aqueous solution were carried out by adsorption on various indigenously prepared activated carbons (IPACs) from agricultural wastes *viz.*, kapok fruit coats and groundnut shells. The effect of various process parameters has been investigated. The percentage of uptake of lead increased with decrease in initial concentration of lead (II) ions and particle size of IPACs but increased with the increase in agitation time, dose, and initial pH. Adsorption results at 35 °C were fitted with various first order kinetic equations/models. The intra-particle diffusion was found to be the rate-controlling step for these systems. Desorption studies with nitric acid were carried out and the feasibility of reusing these carbons was also tested. The results when compared with commercial activated carbon (CAC) reveal that these two IPACs could be considered as cost-effective adsorbents alternative to CAC for the removal of lead (II) ions.

KEYWORDS: Adsorption, groundnut shell carbon (GC), commercial (CAC) and indigenously prepared activated carbons (IPACs), ionic strength, Freundlich isotherm, kapok fruit coat carbon (KC), kinetics of adsorption, intra-particle diffusion model, lead ions, wastewater treatment.

INTRODUCTION

Major anthropogenic sources of heavy metals are metal processing, metal finishing, plating, paints and pigments, as well as battery manufacturing industries [1]. Heavy metals are perilous to human physiology and other biological systems, when they exceed the tolerance limit [2]. The implications of lead pollution in animal and human beings are their interference with the activities of intracellular enzymes [3], ill-effects causing e.g., anemia, kidney failure, impairment of central nervous system and damage to DNA and RNA. Among the heavy metals, lead seems to be one of the serious categories and its permissible discharge limit is 0.1 mg L⁻¹ for inland surface water and 1 mg L⁻¹ for public sewers [4].

Activated Carbon (AC) adsorption is the most widely used technique in industrial wastewater treatment, due to its high efficiency and easy operation [5, 6]. Despite of its extensive application, CAC is highly expensive and not economic. This has accelerated the search for new low cost alternative materials *viz.*, carbons were prepared from various agricultural wastes – olive stones, almond shells and peach stones [7], wood, coconut shells, bamboo dust [8, 9]. In accordance with the dual aim of cost as well as effectiveness of adsorbents, the above list is not complete. Hence, attempt is made in this regard to prepare low-cost ACs by indigenous methods from the abundantly available agricultural wastes *viz.*, kapok fruit coats (KC) and groundnut shells (GC). The results of studies on the kinetics of adsorption of indigenously prepared ACs (IPACs) on the removal of Pb(II) ions were compared with those of CACs.

MATERIALS AND METHODS

Commercial activated carbon (CAC) (E. Merck) and Pb(NO₃)₂ (AR sample, S.d. Fine-Chem. Ltd., India) were used in this study. Double distilled (DD) water was used for the preparation of all the reagents. The raw materials for the preparation of ACs, such as kapok fruit coats (*Ceiba pentandra*, Family: *Bombacaceae*) and groundnut shells (*Arachis hypogea*, Family: *Fabaceae*), were collected locally, cut into small pieces, carbonised at 300 °C with limited exposure of air in a muffle furnace (AUSCO, India) and then thermally activated at high temperature (700 °C) along with NaHCO₃ in CO₂ atmosphere to enhance porosity and prevent ash formation. Pyrolysed charred materials were sieved (Jayanth Scientific Industries, Mumbai) into different particle sizes (range: 75 - 150 micron), activated with 4 N nitric acid, washed and then dried.

Adsorption Studies

Adsorption experiments (Table 1) were carried out under batch mode at 35 °C as reported in literature [10, 11]. The equilibrium (final) concentration of Pb(II) ions

(C_e) was estimated spectrophotometrically using UV-Vis spectrophotometer (ELICO, SL 159, India), with the help of 4-(2-pyridylazo)resorcinol (PAR) reagent [12]. Percentage removal and the amount adsorbed (q) were computed by using the usual equations [8, 9].

Adsorbents with known amounts of adsorbed Pb (II) ions were tested for desorption by agitating with water and different concentrations of nitric acid solution for 60 min.

RESULTS AND DISCUSSION

Effect of Process Parameters

The uptake of lead(II) ions on various ACs was carried out by varying any one of the process parameters, such as initial metal ion concentration, agitation time, dose, initial pH and particle size at fixed experimental conditions (Table 1). The extent of removal (% R) of Pb (II) increased with the decrease in the initial concentration of Pb (II) ions (Table 2). This is probably due to the non-availability of required number of active sites for the uptake of increased Pb (II) concentration [6, 11]. Adsorption data at 35 °C were fitted with the linearised Freundlich isotherm [8, 9]. Linear curves, obtained by plotting $\log q_e$ versus $\log C_e$, indicate the validity of Freundlich isotherm [k_f , $1/n$ and r values are, respectively, for CAC: 0.91, 0.58 and 0.995;

for IPKC: 1.11, 0.48 and 0.981; and IPGC: 1.33, 0.29 and 0.967. The linear relationships observed, as supported by the correlation coefficient values (close to unity), predict the applicability of Freundlich isotherms. As the time of agitation increased, the percentage removal of Pb (II) increased, reached a maximum and then levels off for further increase in time (Table 2). This may be due to the penetration of Pb (II) ions into the micropores of ACs, which is supported by the intra-particle diffusion process [8-11]. The optimum agitation time for CAC, IPKC and IPGC are fixed as 40, 40 and 45 min, respectively.

The extent of removal of lead(II) increases with increase in the dose of carbon, as evidenced by the linear plots of $\log (\%R)$ versus $\log (\text{dose})$ (r -values for CAC = 0.971; IPKC = 0.991 and IPGC = 0.999) and the amount adsorbed exponentially varies in accordance with the fractional power term of the dose of AC, *ie.*, $q \propto (\text{dose})^{-n}$ with correlation coefficients close to unity, where, 'n' is a fraction [for CAC: 0.389 ($r = 0.932$), IPKC: 0.702 ($r = 0.998$) and IPGC: 0.134 ($r = 0.899$)]. This is due to the increase in the surface area of adsorbent and number of active sites for the adsorption of metal ions, due to increase in dose and as a result of conglomeration of adsorbent at higher doses [8-11]. Relative extent of adsorption of Pb(II) was found to be insignificant after a dose of 24 g L⁻¹ (CAC and IPGC) and 28 g L⁻¹ (IPKC), which were fixed as optimum doses.

TABLE 1 - Experimental conditions for the removal of Pb(II) on various carbons.

Parameters varied	Initial Pb(II) concentration (mg L ⁻¹)	Agitation time (min)	Dose (g L ⁻¹)	Initial pH	Particle size of IPACs (μ)
Initial concentration(C_i)	100-400	45	20	4.0	75
Agitation time	100 ^a	5-50	20	4.0	75
Dose	100	CAC = 40 ^a IPKC = 40 ^a IPGC = 45 ^a	4-28	4.0	75
Initial pH	100	CAC = 40 IPKC = 40 IPGC = 45	CAC = 24 ^a IPKC = 28 ^a IPGC = 24 ^a	2.0-6.0	75
Particle size	100	CAC = 40 IPKC = 40 IPGC = 45	CAC = 24 IPKC = 28 IPGC = 24	6.0 ^a	75 ^a - 150

'a'- indicates the optimum condition fixed for experiments;

CAC = commercially activated carbon; IPKC/IPGC = indigenously activated kapok carbon/groundnut shells carbon

TABLE 2 - Adsorption of Pb(II) ions on various carbons at 35 °C.

Variation	Range	% Removal (amount adsorbed, mg g ⁻¹)		
		CAC	IPKC	IPGC
Initial [Pb(II)] (mg g ⁻¹)	100-400	84.6 – 71.5 (4.3 – 14.3)	81.7 – 59.9 (4.1 – 12.0)	69.0 – 32.4 (3.4 – 6.5)
Agitation time (min.)	5 – 45	59.4 – 84.4 (2.9 - 4.2)	52.4 – 81.7 (2.6 – 4.1)	33.4 – 69.1 (1.7 – 3.5)
Dose of adsorbent (g L ⁻¹)	4 – 28	29.5 – 87.8 (7.4 – 3.1)	28.5 – 85.0 (7.1 – 3.0)	15.2 – 75.8 (3.8 – 2.7)
Initial pH of the metal solution	2 – 6	32.0 – 92.5 (1.3 – 3.9)	37.4 – 90.6 (1.3 – 3.2)	45.5 – 81.8 (1.9 – 3.4)
Particle size (micron)	75 – 150	-	89.6 – 81.3 (3.2 – 2.9)	81.8 – 71.8 (3.4 – 3.0)
Ionic strength* (by NaNO ₃)	0.01 – 0.5	90.3 – 84.2 (3.8 – 3.5)	89.0 – 84.6 (3.2 – 3.0)	80.4 – 74.6 (2.9 – 2.6)

* Without added NaNO₃ (% R, q) for CAC (92.5, 3.9), IPKC (89.6, 3.2) and IPGC (81.8, 3.4); for further explanations see Table 1.

TABLE 3 - Results of statistical analysis of kinetic equations and models for the adsorption of Pb(II) ions on CACs and IPACs at 35 °C.

Equation/model	CAC	IPKC	IPGC
i) Natarajan & Khalf equation:			
10 ³ k (min)	27.11	26.97	18.48
Correlation coefficient (r)	0.994	0.990	0.973
ii) Lagergren equation:			
10 ² k (min)	7.26	8.59	9.12
Correlation coefficient (r)	0.965	0.993	0.987
iii) Bhattacharya & Venkobachar equation:			
10 ² k (min)	7.25	8.59	9.11
Correlation coefficient (r)	0.966	0.993	0.987
iv) Intra-particle diffusion model:			
Intercept	0.31	1.94	0.99
10 k _p (mg g ⁻¹ min ^{-0.5})	2.26	3.52	3.89
Correlation coefficient (r)	0.993	0.992	0.981
v) log (%R) versus log (time)			
10 slope	1.69	2.17	3.27
Correlation coefficient (r)	0.984	0.997	0.990

The extent of removal of Pb^{2+} ion increases with the increase in the initial pH of solution and reached a maximum at pH about 6.0 (Table 2). Further increase in pH (>6.0) leads to precipitation of Pb (II) species as $Pb(OH)_2$ [12]. The extent of removal (in % R) of Pb (II) in the lower pH region (attained by adding 1 N solution of nitric acid) is relatively poor [*i.e.*, at pH 2.0: CAC (32.8), IPKC (37.4) and IPGC (45.5)] due to the electrostatic repulsion between the positive charge on the surface of AC (due to adsorption of H^+ ions) and Pb^{2+} ions in solution and competitive adsorption of H^+ [12].

It was observed that as the particle size decreases, the percentage of uptake of lead(II) ions by IPACs increases (Table 2). The particle size of IPACs and amount adsorbed (q) were found to be linearly correlated with negative r -values (IPKC = - 0.997 and IPGC = - 0.996) confirming this fact [8, 9].

Ionic strength is a significant factor, which affects the transport of metal ions from liquid to solid phase. The decrease in ionic strength (maintained by adding required amount of $NaNO_3$) increased the percentage removal of Pb(II) ions (Table 2). The added ions facilitate the formation of electrical double layer due to increase in ionic strength and, hence, decrease the removal of Pb (II) ions (Table 2).

Relative Adsorption Capacity

The adsorption capacities of IPACs were compared with those of CACs, for the uptake of Pb (II) ions at optimum (maximum removal) conditions, and the relative adsorption capacities of IPACs are:

$$IPGC (86.3\%) < IPKC (96.7\%) < CAC (100\%).$$

The adsorption capacity of IPACs was found to be comparable with that of CACs and hence, it could be considered as low cost alternative to CAC for the removal of Pb(II) ion from water/wastewater.

Kinetics of Adsorption

Kinetics of adsorption of lead(II) ions on various ACs have been tested by applying the following first order kinetic equations/models:

Natarajan Khalaf equation [11]:

$$\log(C_i / C_t) = (k/2.303) t \quad (1)$$

Lagergren equation [13]:

$$\log(q_e - q_t) = \log q_e - (k/2.303) t \quad (2)$$

Bhattacharya and Venkobachar equation [14]:

$$\log [1-U(T)] = - (k/2.303) t \quad (3)$$

where C_i and C_t are the concentration of Pb^{2+} ions (in ppm) at time zero and at time 't', respectively; q_e and

q_t are the amounts adsorbed per unit mass of adsorbent at optimum time and at time 't', respectively; $U(T) = [(C_i - C_t) / (C_i - C_e)]$ and C_e is the equilibrium concentration of Pb^{2+} ions at optimum agitation time, and 'k' is the first order rate constant for adsorption (min^{-1}).

Correlation of the values of $\log(C_i / C_t)$, $\log(q_e - q_t)$ and $\log [1-U(T)]$ with time were found to be linear with almost unit r -values (Table 3), indicating the applicability of these kinetic equations. The rate constants derived from Bhattacharya and Venkobachar equation and Lagergren equation are found to be almost identical for any given AC. And hence, the use of any one of these kinetic equations is enough for future studies on the removal of metal ions by any adsorbent.

Intra-particle Diffusion Model

The possibility of penetration of metal species into the internal pores which may be the rate limiting step could be tested by the intra-particle diffusion model [15].

$$q_t = k_p t^{1/2} + c \quad (4)$$

where q_t is the amount of Pb(II) adsorbed ($mg\ g^{-1}$) at time 't', k_p and 'c' are the intra-particle diffusion rate constants and intercept, respectively. Plots of q and $t^{1/2}$ are found to be linear as evidenced by correlation coefficients close to unity ($r = 0.981-0.993$), indicating that intra-particle diffusion is the rate-determining step. Values of $\log(\% R)$ and $\log(\text{time})$ were also found to be linear, further confirming this fact.

Desorption Studies

The extents of desorption with DD water were found to be negligible (1-2 %). But it was found to increase with the increase in nitric acid concentration (range of % R for 0.01 – 0.5 M HNO_3 for cycle 1, 2 and 3: CAC = 11.0-43.2, 8.6-32.1 and 6.6-20.8; IPKC = 12.0-45.4, 9.2-37.5 and 7.3-22.9; IPGC = 12.6-44.6, 10.5-35.5 and 7.3-21.6, respectively). The relative extents of desorption decreased with increase in number of cycles and stagnated after three cycles. However, the cumulative percentage desorbed increased with the increase in number of cycles.

Regenerated ACs were further tested for their reuse for the adsorption of Pb(II) ions. The desorbed ACs show nearly 60-65 % (*i.e.*, for CAC = 60.1%, IPKC = 57.7% and IPGC = 49.4%) efficiency for the uptake of Pb(II) ions (100 ppm) relative to their pure ACs. Even though their adsorption capacities were reduced, they could be reused for the treatment of metal ions in lower concentration, *e.g.*, 50 ppm; 80% - 92% (*i.e.*, for CAC = 91.2%, IPKC = 88.0% and IPGC = 80.7% removal). Therefore, IPACs and regenerated IPACs could be considered cost-effective adsorbents alternative to CACs.

CONCLUSIONS

The following conclusions have been arrived at from the results of the present investigation:

- The removal (% R) of Pb(II) increased with increase in dose of ACs, agitation time and initial pH of the solution but decreased with increase in initial Pb(II) ion concentration, particle size of IPACs and ionic strength.
- Adsorption data were fitted with Freundlich isotherm, various first order kinetic equations and intra-particle diffusion model.
- Adsorption capacities of IPACs were found to be almost comparable to that of CAC and, IPACs, could be considered as cost-effective alternative to CAC for lead(II) removal.
- Desorption studies reveal that nitric acid is more effective than DD water for leaching out the adsorbed Pb(II) ions. The regenerated ACs are reusable.

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5th INTERNATIONAL CONFERENCE of the Balkan Environmental Association ?n TRANSBOUNDARY POLLUTION 7-10 November 2002, Belgrade - Yugoslavia

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