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Removal of organochlorine pesticides from water using virgin and regenerated granular activated carbon

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Abstract: Public water systems use granular activated carbon in order to eliminate pesticides. After saturation, the used activated carbon is regenerated and reused in order to reduce the costs of water production and minimize waste. In this study, the adsorption of 10 different chlorinated pesticides from water using columns packed with commercial virgin and regenerated granular activated carbon was simulated in order to compare their adsorption capacities for different chlorinated pesticides. The breakthrough curves showed that chlorinated pesticides from the group of hexachlorocyclohexane (HCH) were poorly adsorbed, followed by cyclodiens as averagely adsorbed and the derivatives of halogenated aromatic hydrocarbons (DDT) as strongly adsorbed. However, the adsorption capacity of regenerated granular activated carbon was considerably lower for tested pesticides compared to the virgin granular carbon. In addition, rinsing of the pesticides after the saturation point is a far more efficient process on regenerated carbon.

Keywords: granular activated carbon; adsorption; organochlorine pesticides; gas chromatography.

INTRODUCTION

Pesticides are artificially synthesized, toxic bioaccumulative agents. The on-going and uncontrolled use of pesticides to fight pests and improve agricultural production constitutes a risk for water quality. Thus, pesticides have been detected by monitoring surface and underground waters. According to the European Union Directives and Regulations for drinking water hygiene,[1] the maximum allowed concentration of total pesticides is 0.5 μg dm^{-3}. Different types of pesticides can be found in water. The most frequently found pesticides are derivatives of urea, pyridazinone, phenoxy acetic acid, tryazin and the group of chlo-

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rinated pesticides. Chlorinated pesticides are divided according to their chemical structure into 3 basic groups: derivatives of DDT, hexachlorocyclohexanes (HCH) and aldrin. Derivatives of DDT are halogenated aromatic hydrocarbons, while hexachlorocyclohexanes (HCH) and derivatives of aldrin are halogenated alicyclic hydrocarbons. The main characteristic of halogenated hydrocarbons is their huge chemical stability and consequential persistence in water and soil. The second important characteristic of chlorinated pesticides is their very poor solubility in water, due to their lipophilic character.

Pesticides can be eliminated from water in different ways, most frequently by adsorption on granular activated carbon (GAC) and/or by ozonization.[2] When GAC is saturated, it is usually regenerated and reused. In the majority of cases, spent GAC is thermally regenerated either on-site or transported to a thermal regeneration facility. During regeneration, the contaminants are transformed into less toxic byproducts and the sorption capacity of the carbon is re-established; thus, increasing the useful life of the GAC is increased and the costs of water treatment are reduced.

Many studies concerning the adsorption capacities of selected types of pesticides on commercial activated carbons, as well as on other carbon materials, have been published recently.[3–5] Gerard and co-workers [3] examined the adsorption of diuron, MCPA, atrazine and chlorydazon on Chemviron's coal-based commercial granular activated carbon. They came to the conclusion that the strongest adsorption was achieved for diuron and the weakest for MPCA. A study of the impact of temperature and size of the molecule on adsorption on commercial activated carbon[4] showed that the adsorption at higher temperatures was enhanced and smaller molecules were better adsorbed. Martin-Gullon[5] compared the adsorption of atrazine on commercial activated carbon Norit GAC 1240 and carbon fibers Donacarbo and found that the efficiency was several times higher on the carbon fibers.

The aim of the present study was to compare the adsorption capacities and removal efficiency of virgin and regenerated granular activated carbon for different chlorinated pesticides. The test columns used in the experiments were filled with virgin commercial granular activated carbon as well as with regenerated activated carbon. Both GAC materials are used in the public water system that supplies Belgrade with drinking water.

EXPERIMENTAL

Materials

Commercial activated carbon Trayal K-81/B was used in all experiments, as virgin or regenerated. Both GAC materials are used in the public water supply system in Belgrade and were taken directly from the filters of the plant for the preparation of drinking water. The characteristics of the virgin and regenerated GAC are given in Table I.

All organic solvents were of chromatographic purity as supplied by JT Baker and Fluka. Water of high quality (0.054 μS cm^{-1}) was obtained by deionization through a Milli-Q system (Millipore water). The mixture of pesticides was supplied by Supelco. The main physical and chemical data of the analyzed pesticides are given in Table II.

TABLE I. Characteristics of the employed virgin and regenerated GAC Trayal K-81/B

Parameter	Carbon samples	
	Virgin Trayal K-81/B	Regenerated Trayal K-81/B
Total pore volume, $cm^3\ g^{-1}$	1.0	0.8
Specific surface BET, $m^2\ g^{-1}$	1237	950
Micropore volume, $cm^3\ g^{-1}$	0.50	0.39
Iodine number, mg g^{-1}	1239	998
Methylene Blue index, cm^3	22	17
Apparent density, kg m^{-3}	462	492
Granule size, mm	Granule size distribution, %	
> 1.6 mm	4.1	4.0
0.8 – 1.6 mm	91.5	90.8
< 0.8 mm	4.4	5.2

TABLE II. Main physical and chemical data of the tested pesticides

Group	Pesticide	Formula	M_r g mol^{-1}	Solubility in water (25 °C) mg dm^{-3}	log K_{ow}[a]	Maximum limit of concentration μg dm^{-3}
Hexachloro-cyclohexane	α-HCH	$C_6H_6Cl_6$	287.86	2.0	3.08	n.r.[b]
	β-HCH	$C_6H_6Cl_6$	287.86	1.5	3.78	n.r.
	γ-HCH	$C_6H_6Cl_6$	287.86	10	2.67	0.1
Chlorinated alicyclic hydrocarbon	α-endosulfan	$C_9H_6Cl_6O_3S$	403.82	0.32	3.83	n.r.
	β-endosulfan	$C_9H_6Cl_6O_3S$	403.82	0.33	3.62	n.r.
	Heptachlor epoxide	$C_{10}H_5Cl_7$	369.82	0.056	5.44	0.03
	Dieldrin	$C_{12}H_8Cl_6O$	377.87	0.19	3.69	0.03
Aromatic chlorinated hydrocarbon	4,4'-DDT	$C_{14}H_9Cl_5$	354.49	0.025	6.91	0.1
	4,4'-DDD	$C_{14}H_{10}Cl_4$	320.05	0.090	6.02	n.r.
	Methoxychlor	$C_6H_{15}Cl_3$	345.65	0.045	4.68	n.r.

[a]Partition coefficient; [b]not recommended

Methods

On column experiments were based on the use of test columns[6] filled with virgin or regenerated GAC, in order to determine their adsorption capacities for pesticides. A mixture of pesticides, listed in Table II, was spiked into Millipore water to obtain a concentration of 2 μg dm^{-3} of each pesticide and passed through the columns at room temperature using a flow rate of 0.15 $cm^3\ min^{-1}$. The experimental conditions on the test columns are given in Table III.

Preconcentration of the pesticides from the effluent water was achieved by solid phase[7,8] extractions on Chromabond cartridges C8 (500 mg, 6 cm^3). The cartridges were conditioned with 3 cm^3 of methanol and rinsed with 2 cm^3 of Millipore water. Using a vacuum manifold, the effluent water was drawn through the cartridge at a flow rate of 5 $cm^3\ min^{-1}$. Subsequently, the column was rinsed with 1 cm^3 of Millipore water and the pesticides were eluted

with 1.5 cm^3 of solvent mixture, hexane:diethyl ether. The solution was evaporated and then reconstructed to 1 cm^3.

TABLE III. Experimental conditions on the test columns

Carbon sample	m / g	Bed height mm	Bed volume cm^3	Influent flow cm^3 min^{-1}	Contact time, min
Virgin Trayal GAC K-81/B	0.400	7	0.95	0.15	6.5
Regenerated Trayal GAC K-81/B	0.400	6	0.90	0.15	6.5

An Agilent gas chromatograph 6890, equipped with an electron capture detector,[9,10] was used for quantification of the pesticides. The chromatographic separation of pesticides was realized on a capillary column (30 m×0.32 mm) coated with 5 % diphenylmethylsiloxane film, 0.25 μm thick. High quality nitrogen was used as the supporting (1.8 cm^3 min^{-1}) and the make up gas (30 cm^3 min^{-1}). The injector and detector temperatures were 250 and 320 °C, respectively. The sample splitless injection volume was 1 μl. The initial column temperature of 100 °C was maintained for 2 min, then programmed to 160 °C at a heating rate of 15 °C min^{-1} and held for 10 min at 160 °C. Subsequently, the temperature was raised to 220 °C at a heating rate of 5 °C min^{-1}, held for 2 min and the raised to the final temperature of 270 °C at a heating rate of 10 °C min^{-1}.

RESULTS AND DISCUSSION

The analyzed pesticides (Table II) were divided in three groups according to their chemical properties and structure. The concentrations of the effluent solutions (c_e) from the test columns for each group of pesticides are presented in Figs. 1–3, in which breakthrough curves are apparent.

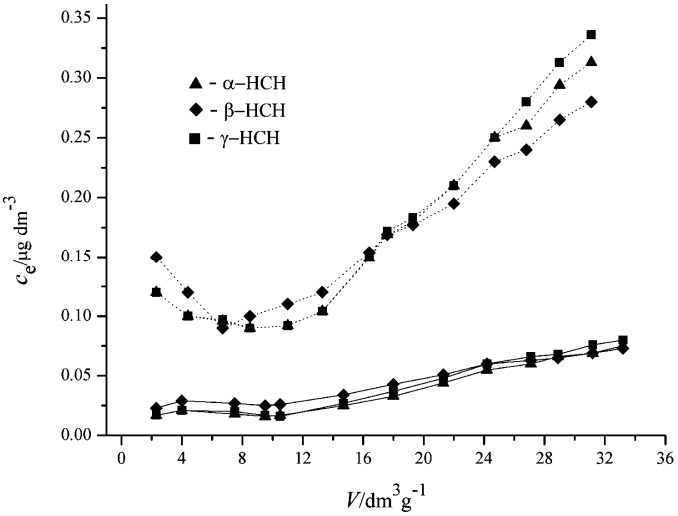

Fig. 1. Breakthrough curves for the chlorinated cyclohexane pesticide mixture in Millipore water (c_e – pesticide concentration in the effluent, V – effluent volume per unit mass of GAC) on virgin (—) and regenerated (- - -) GAC. Pesticide concentration in the influent was 2 μg dm^{-3}.

The starting concentration (2 μg dm^{-3}) of each pesticide was thoroughly reduced to approximately 0.02 μg dm^{-3} for all pesticides tested on the column with virgin GAC at saturation point, confirming that the adsorption on activated carbon is a very efficient technique for the removal of pesticides from water. However, it is not a destructive process. The pollutants pass from one medium (water) to another (carbon), thus producing a new pollution problem. When the columns are saturated, rinsing of pollutants commences, as is visible in Figs. 1–3. The adsorption efficiency depends on both the surface properties and porosity of the GAC as well as on the chemical assets and geometry of the pesticides. The most soluble pesticides (HCH) are very efficiently rinsed from the saturated column containing virgin GAC. However, derivatives of DDT, due to their highest partition coefficient (Table II), were firmly bound to the virgin GAC column with minor rinsing observed during the experiment, predominantly for the methoxychlor derivative. Chlorinated alicyclic hydrocarbons showed intermediate behavior compared to the HCH and DDT derivatives. Thus, pesticide solubility in water is in reverse correlation to the adsorption affinity of the activated carbon.

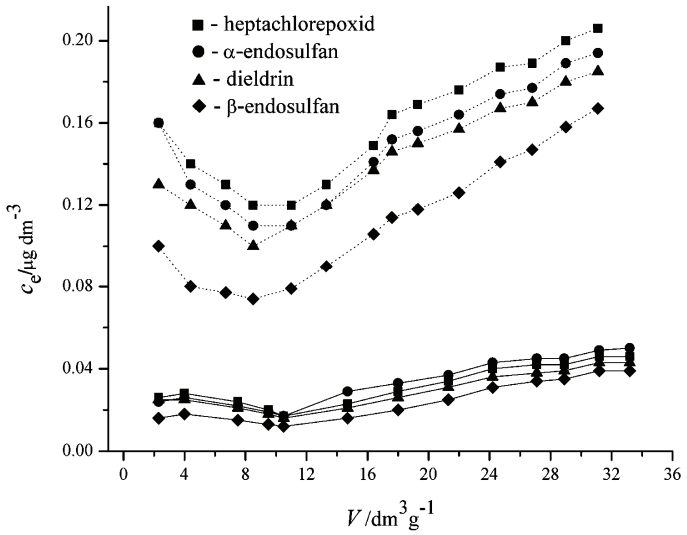

Fig. 2. Breakthrough curves for the chlorinated alicyclic hydrocarbon pesticide mixture in Millipore water (c_e – pesticide concentration in the effluent, V – effluent volume per unit mass of GAC) on virgin (—) and regenerated (- - -) GAC. Pesticide concentration in the influent was 2 μg dm^{-3}.

Based on the appearances of the breakthrough curves displayed in Figs. 1–3, it is evident that both virgin and regenerated activated carbon exhibit similar adsorption affinities towards the examined pesticide: highest for DDT derivatives and lowest for HCH. However, the concentration of the pesticides in the effluent from the regenerated GAC column was several times higher compared to the

effluent fro m the virgin GAC. The adsorption pr operties of regenerated GAC could be adv ersely affected b y incomplete carbon regeneration an d b y surface deterioration during heatin g. Table I clear ly shows the deterioration of surface properties of GAC after r egeneration. Th e specific surface ar ea, total pore volume[11] and micropore vo lume were reduced b y a pproximately 20 % . Co nsequently, the i odine number and Meth ylene Blue ind ex were reduced in the same proportion. T hese r esults are consistent with other studies on regeneration of GAC using a variety of regeneration methods.[12–14]

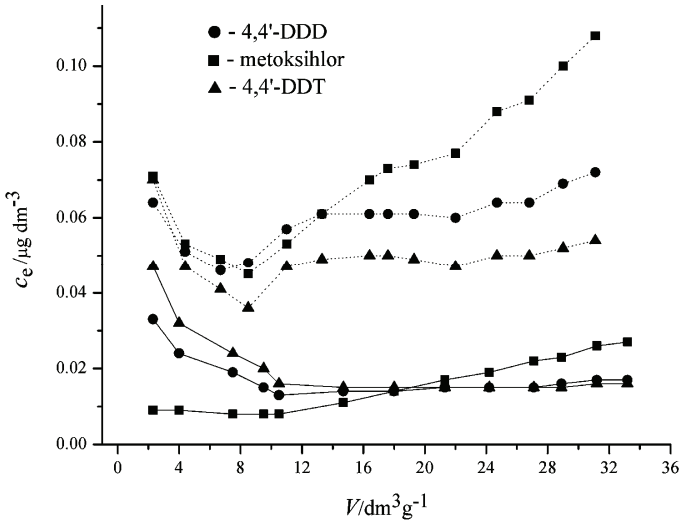

Fig. 3. Breakthrough curves for the aromatic chlorinated hydrocarbon pesticide mixture in Millipore water (c_e – pesticide concentration in the effluent, V – effluent volume per unit mass of GAC) on virgin (—) and regenerated (- - -) GAC. Pesticide concentration in the influent was 2 μg dm^{-3}.

The adsorption of the tested pesticid es on the regenerated GAC w as affected by regeneration. The differential factors of the pesti cides (w eighted against the firmly adsor bed 4,4 ’-DDT) on vir gin and regenerated activated carbon, aft er transmitting 30 dm^3 g^{-1} o f the standard organ ochlorine pesticide m ixture (2 μg dm^{-3}) are li sted in Table I V. The differ ential factors for each pesti cide adsorbed on virgin activated carbon were higher th an these on regenerated carbon. Accor-ding to Gerard, [3] com pounds with a differential fact or less than 0.40 are poor ly adsorbed, co mpounds with a differenti al factor in range from 0.40 to 0.8 0 are averagely adsorbed, while co mpounds with a differential factor higher than 0.8 0 are considered as strongly adsorbed on GAC. Thus, 4,4’-DDT and 4,4’-DDD are strongly adso rbed pesticides, methoxychlor and β-endosulfan are averagely ad-sorbed pestic ides and α-HCH, β-HCH, γ-HCH, α-endosulfan, hep tachlorepoxide and dieldrin are considered as poorl y adsorbed pesti cides on virg in GAC. After

regeneration of GAC, 4,4'-DDT remained the only strongly adsorbed pesticide, methoxychlor and 4,4'-DDD averagely but all the remaining pesticides were poorly adsorbed. The discrepancy between the differential factors before and after regeneration was 20 to 30 %.

TABLE IV. Pesticide differential factors compared to 4,4'-DDT. Effluent concentration ratio through regenerated (c_r) and virgin (c_v) GAC

Pesticide	Differential factor for virgin GAC	Differential factor for regenerated GAC	c_r/c_v
α-HCH 0.23		0.17	4.5
β-HCH 0.23		0.19	4.1
γ-HCH 0.21		0.16	4.4
α-endosulfan 0.33		0.28	4.0
β-endosulfan 0.41		0.32	4.3
Heptachlorepoxide 0.35		0.26	4.4
Dieldrin 0.37		0.29	4.3
4,4'-DDT 1		1	3.3
4,4'-DDD 0.94		0.75	4.2
Methoxychlor 0.62		0.50	4.2

The effluent concentration ratio after passing 30 d m^3 g^{-1} of standard pesticide mixture through the test columns with regenerated (c_r) and virgin GAC (c_v) are also given in Table IV. The influent flow was adequately adjusted so that the contact time of 6.5 min was sufficient for adsorption of the organic compounds on GAC according to the suggestions of the U.S. Environmental Protection Agency. The astonishing result was that the concentrations of pesticides in the effluent from the column with regenerated GAC were 3.3 (for DDT) up to 4.5 (for α-HCH) times higher, depending mostly on the rinsing efficiency.

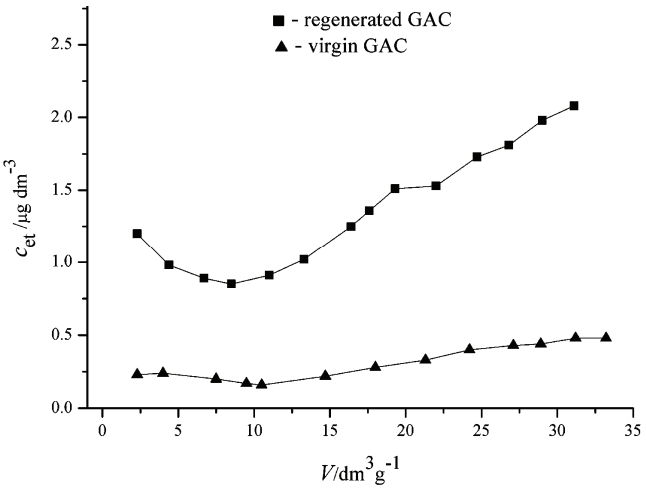

Fig. 4. Cumulative breakthrough curves for pesticides (c_{et} – total pesticide concentration in the effluent, V – effluent volume per unit mass of GAC) on virgin and regenerated GAC. Total pesticide concentration in the influent is 20 μg dm^{-3}.

The cumulative breakthrough curves for the total pesticides are shown in Fig. 4, which clearly indicates that the regeneration process adversely affected the adsorption affinity of GAC towards the tested pesticides by limiting the sorption sites and the quantity of pesticides that could be absorbed. In this respect, this study indicates the potential risk of reusing regenerated GAC.

CONCLUSIONS

From the results obtained on the test columns with virgin and regenerated granular activated carbon, it is possible to compare the adsorption affinity towards selected pesticides. Activated carbon adsorption is an efficient treatment for the majority of the studied pesticides. The concentration in the effluent was reduced to 1 % of initial concentration for all pesticides at the breakthrough point on the column with virgin carbon. Derivatives of DDT were the firmly adsorbed on activated carbon, derivatives of aldrine were moderately adsorbed, while the hexachlorocyclohexanes (HCH) were poorly bound and labile to rinsing after saturation.

The adsorption capacity of regenerated carbon was reduced during the conventional heating process due to blockage of the porous structure, the reduced number of active sights and, probably, incomplete removal of the adsorbed matter. Differential factors for all tested pesticides were 20 to 30 % lower and rinsing of all pesticides after saturation into the effluent was several times higher from regenerated GAC as compared to virgin GAC. The activated carbon used in the present experiments was regenerated a few times, whereby the adsorption properties decreased gradually with subsequent regeneration cycles. Therefore, this study indicates to a potential risk of reusing regenerated carbon.

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ИЗВОД

УКЛАЊАЊЕ ПЕСТИЦИДА ИЗ ВОДЕ НА ГРАНУЛИСАНОМ АКТИВНОМ УГЉУ

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Постројења за припрему воде у многим земљама користе гранулисани активни угаљ за уклањање остатака пестицида. Уобичајено је да се активни угаљ регенерише и поново користи да би се смањили трошкови производње воде за пиће и да би се смањила количина отпада. У овом раду смо испитивали адсорпцију органохлорних пестицида из воденог раствора 10 различитих пестицида на колонама испуњеним комерцијалним свежим и регенерисаним гранулисаним активним угљем. Утврђене су адсорпционе способности гранулисаног угља за различите пестициде. Криве пробоја на овим колонама показују да се органохлорни пестициди из групе хексахлороциклохексана најслабије адсорбују, затим хлоровани циклодиени, а најјаче пестициди из групе ДДТ. Утврђено је да је адсорпциони капа-

цитет регенерисаног активног угља знатно мањи од адсорпционог капацитета свежег активног угља, а испирање пестицида је много ефикасније после регенерације.

(Примљено 15. јуна, ревидирано 3. септембра 2009)

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