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REMOVAL OF ATRAZINE FROM WATER BY COAGULATION AND ADSORPTION

The application of coagulation and adsorption on activated carbon in the removal of atrazine from water solution was investigated. The efficiency of alum and ferric coagulants as well as different types of flocculants was evaluated. The influence of natural organic matter on process efficiency was also determined. Long-term adsorption experiments were conducted with the use of carbon bed. Atrazine concentration in model solutions ranged from 200 to 1000 mg/m³. The investigation showed that coagulation without and with the aid of polyelectrolytes was not suitable for removal of atrazine from water solutions, whereas adsorption process was characterised by high efficiency in pesticide separation.

1. INTRODUCTION

Pesticides, even at comparatively low concentrations, may produce disturbances in the biocenosis, thus making the water unfit for direct municipal supply. Because of their toxicity and long durability in water and soil, pesticides are classified as hazardous substances [1]. Reports on the detection of excess herbicide concentrations (from 0.3 to 0.9 mg/m³) by the surface- and groundwater monitoring systems all over the world (including Poland) have become increasingly frequent.

The need to remove pesticides from watercourses has become urgent also from the legal point of view. According to EU Directives [2] the admissible concentrations of pesticides and derivative products in drinking water must not exceed 0.1 mg/m³ for any individual compound or 0.5 mg/m³ for their total amount.

With a chemical structure and physicochemical properties which differ from one compound to another, pesticides are very difficult to remove from aquatic medium. That is why conventional treatment methods as well as some traditional unit processes are of little utility. Pesticides can be removed by oxidation (with chlorine,

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ozone, potassium permanganate, hydrogen peroxide or chlorinated lime), adsorption on activated carbon or on natural sorbents (peat, clay, humic substances, bentonites), polyelectrolyte-aided coagulation, infiltration and membrane processes. The efficiency of pesticide removal can be increased to some extent by combining, for example, ozonation and sorption on activated carbon or chlorination and coagulation, etc.

Sorption on activated carbon is best suited to hydrophobic substances, i.e., to the majority of chloroorganic pesticides. However, removal efficiency may vary from 5 to 85%, depending on the nature of the compound sorbed [3]. IGNATOWICZ-OWSIENIUK and co-workers [4], [5] investigated the removal efficiency of sorption of Chwastox extra on activated carbon. They found that the removal of this pesticide depended on the type of activated carbon and on the rate of liquid flow through the adsorption column. Thus, adsorption on CWZ-22-1 carbon at a filtration rate of 0.1 m/h yielded complete removal of Chwastox extra. When filtration rate was increased to 7 m/h, the removal efficiency amounted to 87.2%. When use was made of a powdered CWZ-22-type activated carbon, the removal of Chwastox extra ranged only between 20 and 64%.

The investigation reported by THACKER and co-workers [6] corroborates the utility of adsorption on GAC beds in removing chloroorganic pesticides from water. They reduced the concentration of DDT and Y-HCH in drinking water to 2 mg/m³, and there was a concomitant removal of TOC, which amounted to 99%.

Sorption on powdered or granular activated carbon seems to be a promising solution to the problem of pesticides in surface- and groundwater. However, there is competition between the water pollutants, which consequently limits the available sorption surface. Another limitation is the costly regeneration of carbon beds, which has to be done frequently. Because of these shortcomings it became necessary to find adsorbents with large specific surfaces and highly selective in the removal of specific substances.

Coagulation may be of utility in separating suspensions and colloidal solutions of some pesticides. It was found that alum coagulation yielded 95 to 98% removal of DDT, the least soluble pesticide [6]. Under the same conditions, the efficiency of separation for dieldrin, aldrin and lindane was very poor (55%, 35% and 10%, respectively). The coagulant doses (alum or ferric sulphate) were comparatively high (from 100 to 500 g/m³).

Sorption of phospho-organic pesticides on the surface of metal hydroxides is also very poor. The efficiency of parathion removal by alum coagulation varies from 10 to 20% only. Phosphamidon concentration remains unchanged regardless of the coagulant doses [7].

Coagulation with and without the aid of polyelectrolyte (Rokryzol WF1) was applied in order to remove two pesticides – enolofos and karbatox [8]. With an aluminium-based salt as coagulant, in the absence of Rokryzol, the maximum effi-

ciency of fenolofos and karbatox removal totalled 21% and 46.3%, respectively (at a coagulant dose of $120 \text{ g Al}^{+3}/\text{m}^3$). Rokryzol-aided (from 0.5 to $1.0 \text{ g}/\text{m}^3$) coagulation increased the removal of enolofos (by 3.0%), but decreased that of karbatox (by 23.9%). The application of an iron-based salt as a coagulating agent brought about much poorer treatment effects, with a maximum removal efficiency of 19.0% and 39.5% for the enolofos and karbatox, respectively. Addition of Rokryzol nearly doubled the removal of karbatox (37.7%) and noticeably reduced that of enolofos (15.8%) [8].

The aim of this paper was to verify the utility of conventional unit processes (coagulation and adsorption on activated carbon) in atrazine removal in view of possible integration with ultrafiltration to create an effective hybrid process of pesticide utilisation.

2. EXPERIMENTAL

2.1. EXPERIMENTAL SOLUTIONS

We made use of model solutions, using distilled water, which was treated with atrazine (AT) (Aldrich) at concentration ranging from 200 to $1000 \text{ mg}/\text{m}^3$. Atrazine (figure 1) is a chlorotriazine herbicide applied before and after germination against one-year grass, dicotyledonous and some monocotyledonous plants in corn, sugar beet and millet cultivation. The herbicide is also used in orchards, nurseries of young trees, etc., as well as in industrial areas in order to destroy useless plants. Atrazine has a molecular weight of $215.68 \text{ g}/\text{mol}$. Alkalinity of samples was adjusted up to $2.4 \text{ val}/\text{m}^3$.

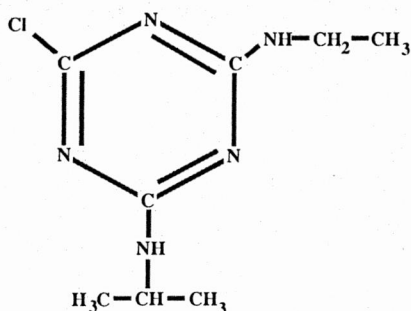


Fig. 1. Atrazine particle

Concentration of humic substances (HS) (Aldrich) in atrazine solutions varied from 10 to $50 \text{ g}/\text{m}^3$.

2.2. COAGULATION

Coagulation was performed by the jar test method with 3-minute rapid mixing and 30-minute slow mixing. Then the samples were allowed to sediment for 1 hour. The efficiency of two types of coagulants: $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 3 types of flocculants (LT22S, Z32, Z7653) was established during water treatment at natural pH. Coagulant doses ranged from 30 to 200 g/m^3 . Polyelectrolyte doses amounted to 0.1, 0.3, 0.5, 1.0, and 2.0 g/m^3 .

The effect of coagulant or flocculant type and natural organic matter concentration on atrazine removal was determined.

2.3. ADSORPTION

Sorption tests were carried out in a continuous flow mode with the use of adsorption column of a height equal to 0.5 m. The column was filled with GAC Filtrasorb®300. The characteristics of GAC used in the experiments are given in table 1. Atrazine solutions were passed through the adsorption bed at a flow rate of 3 m/h. During the experiment the atrazine concentration in a bed effluent was determined and the cumulative volume of solution forced through the bed was monitored.

Table 1

Properties of GAC Filtrasorb®300 (Chemviron Carbon)

Parameter	
Iodine number, minimum	950
Methylene number, minimum	230
Surface area, m^2/g (BET)	1000
Bulk density (back-washed and dried), g/dm^3	460
Particle density, g/dm^3	1.2
Mean particle diameter, mm	1.6
Uniformity coefficient	1.8
Pollutant load:	
phenol at 1 mg/dm^3 (%)	4.3
detergent (TPBS) at 1 mg/dm^3 (mg/g)	150
toluene at 1 $\mu\text{g}/\text{dm}^3$ (mg/g)	90
trichloroethylene at 50 $\mu\text{g}/\text{dm}^3$ (mg/g)	20

2.4. ANALYTICAL METHODS

Atrazine concentration was established spectrophotometrically (sample absorbance being measured at 222 nm wavelength), using Shimadzu QP2000 spectrophotometer.

3. RESULTS AND DISCUSSION

3.1. COAGULATION

In order to determine the usefulness of coagulation in herbicide separation from water solutions, laboratory tests were performed. In the experiments, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were added to the solutions containing atrazine and humic substances. Coagulant doses were equal to 30, 40, 50, 60, 70, 150 and 200 g/m^3 .

The influence of coagulant type and its dose on atrazine separation efficiency is shown in figure 2.

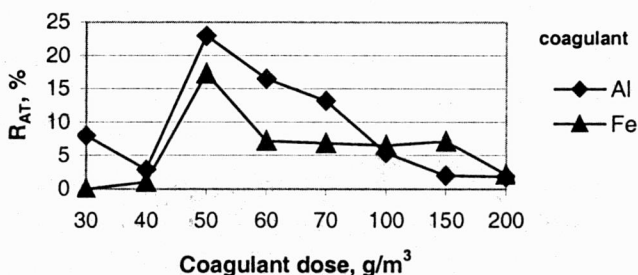


Fig. 2. Efficiency of atrazine removal versus coagulant type and coagulant dose (initial atrazine concentration, 1000 mg/m^3 ; HS concentration, 10 g/m^3)

Application of Al-coagulant results in a slightly higher removal of atrazine from treated solution than that obtained by the use of Fe-coagulant. When coagulant dose equal to 50 g/m^3 was applied, the concentration of atrazine was decreased by 23% and 17% for Al and Fe coagulants, respectively. At the same time, the increase of coagulant dose resulted in a decrease of herbicide separation. This phenomenon was the result of coagulant overdosing. As a consequence a colloidal, non-sedimental phase appears in treated water.

Taking into account that effectiveness of coagulation process is strongly influenced by the presence of organic matter colloides, the influence of humic substance concentration on atrazine removal was determined. The results are presented in figures 3 and 4.

As shown by the experimental data, the coagulation process is ineffective for both types of coagulants, when water containing only herbicide is treated. Flocs of $\text{Al}(\text{OH})_3$ or $\text{Fe}(\text{OH})_3$ have no sorption properties towards particles of atrazine. When treated water contains herbicide as well as organic macromolecules, a decrease of atrazine concentration after coagulation was observed. There was no strong influence of the increase of humic substance concentration (in the range of 10–50 g/m^3) on atrazine elimination.

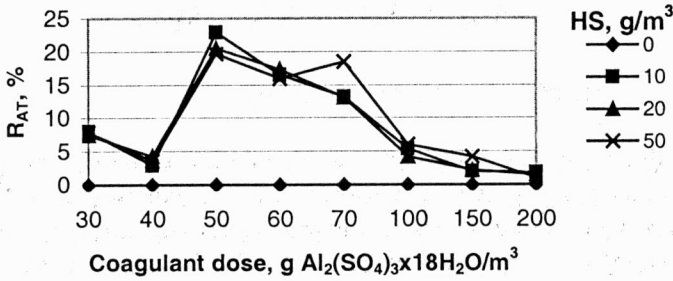


Fig. 3. Efficiency of atrazine removal versus Al-coagulant dose and humic substance concentration (initial atrazine concentration of 1000 mg/m³)

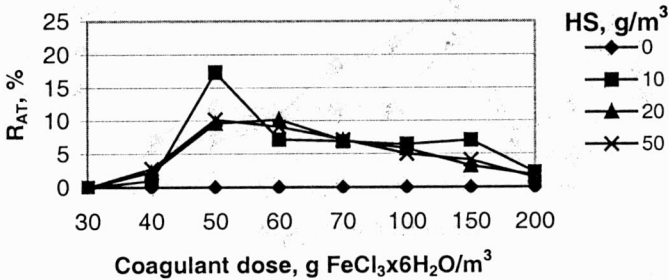


Fig. 4. Efficiency of atrazine removal versus Fe-coagulant dose and humic substance concentration (initial atrazine concentration of 1000 mg/m³)

The objective of the consecutive step of our study was to examine the influence of atrazine concentration in the bulk solution on its amount in water after coagulation. Figure 5 includes the results obtained for Al-coagulant.

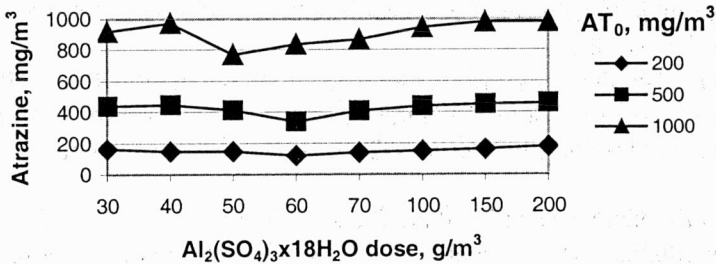


Fig. 5. Atrazine concentration in treated water versus its initial concentration (AT_0) and Al-coagulant dose (initial HS concentration of 10 g/m³)

The efficiency of atrazine separation reached 40% (at initial concentration of 200 mg/m³) but still the amount of herbicide is too high and exceeds levels accepted for potable water.

Due to the low, unsatisfactory efficiency of Al- or Fe-coagulants in atrazine separation from water solutions, the next series of experiments was intended for determination of usefulness of polyelectrolytes in herbicide flocculation. Experimental results obtained for 3 types of cationic polyelectrolytes are presented in figure 6.

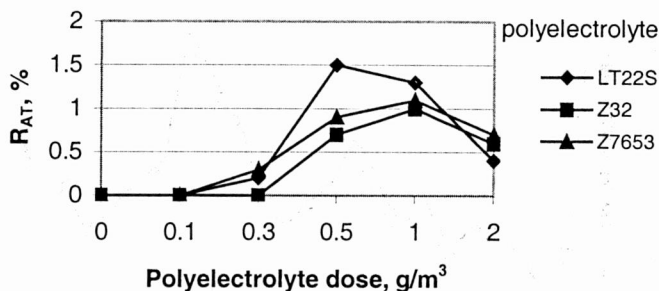


Fig. 6. Efficiency of atrazine removal versus cationic polyelectrolyte type and polyelectrolyte dose (initial atrazine concentration of 1000 mg/m³, HS concentration of 10 g/m³)

The results obtained in the experiment show that the flocculants tested are not effective in herbicide separation from water solutions. The decrease of zeta potential from -40 mV before coagulation to -19 mV after coagulation was not sufficient to destabilise organic colloids. Destabilisation of the colloids of humic substances can result in co-precipitation of adsorbed herbicide and organic macromolecules.

3.2. ADSORPTION ON ACTIVATED CARBON

The adsorption process was carried out with the use of activated carbon column in a continuous flow mode. The atrazine solutions were forced through the bed at a flow rate of 3 m/h. The pesticide concentrations in water solutions amounted to 200, 400, and 1000 mg/m³.

The variability of atrazine concentration in the effluent from carbon bed in relation to operation time is given in figures 7 a-c.

During three-months' experiments the adsorption process was very effective and stable. The cumulative volume of atrazine solution, which passed through the adsorption bed, amounted to about 800 volumes of the bed. The atrazine concentration in the effluent from the bed varied from 20 to 120 mg/m³ (at the initial atrazine concentration of 1000 and 500 mg/m³) and from 5 to 40 mg/m³ (at the initial atrazine concentration of 200 mg/m³).

Activated carbons are characterised by high sorption capacities and can be applied in pesticide removal from waters. According to the literature data [3]–[5], the adsorption efficiency can vary in a wide range (from 20 to 100%), depending on the carbon type, its granulation, flow rate through the bed, contact time of the treated water with

the sorbent, etc. However, due to direct competition of the various contaminants present in water, the available sorption surface is limited. The second disadvantage of the adsorption process is related to the necessity of frequent regeneration of carbon beds, which as a consequence makes the total cost of the process increase.

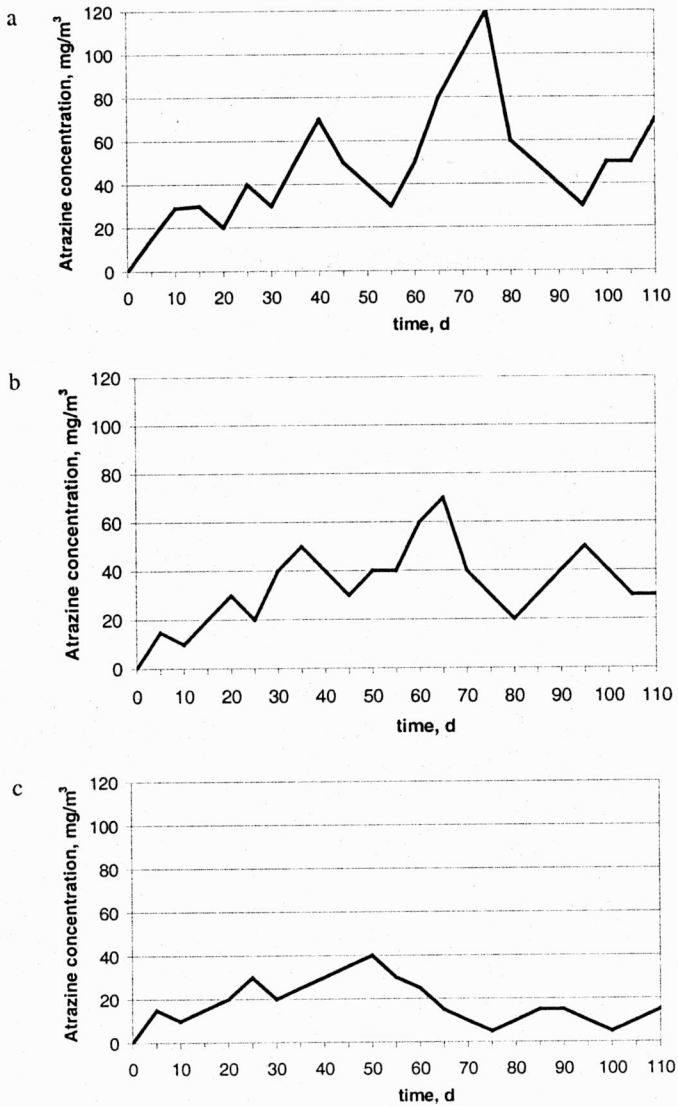


Fig. 7. Atrazine concentration in the bed effluent versus initial pesticide concentration and operation time: a) initial atrazine concentration – 1000 mg/m³, b) initial atrazine concentration – 500 mg/m³, c) initial atrazine concentration – 200 mg/m³

Based on the results obtained, it has been found that activated carbon Filtrasorb® 300 is characterised by high efficiency in atrazine removal irrespective of the pesticide initial concentration. However, taking into account the high cost of the adsorption process itself, it seems that adsorption should be integrated with other unit processes. The most reasonable system would be the hybrid process as follows: ultrafiltration with complexation and adsorption on activated carbon. Based on the investigations conducted [9] it can be anticipated that in such a hybrid process the atrazine concentration could be decreased to the level permitted for drinking water. The base atrazine load would be diminished by ultrafiltration, whereas in the adsorption process the residual amount of atrazine would be removed.

4. CONCLUSIONS

Coagulation of atrazine with the use of alum or ferric coagulants has been found ineffective in removal of this pesticide from water. The occurrence of humic substances in treated water increased atrazine separation up to 23%. Coagulation, as an independent process, cannot be applied in herbicide removal from waters.

Adsorption on activated carbon Filtrasorb® 300 has been characterised by high efficiency in atrazine removal irrespective of the initial pesticide concentration.

On the basis of the investigations conducted it can be anticipated that in a hybrid process integrating ultrafiltration with complexation and adsorption on activated carbon, the atrazine concentration could be decreased to the level permitted for drinking water.

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USUWANIE ATRAZYNY Z WODY W PROCESIE KOAGULACJI I ADSORPCJI NA WĘGLU AKTYWNYM

Zbadano możliwość wykorzystania procesu koagulacji i adsorpcji na węglu aktywnym do usuwania atrazyny z wodnych roztworów. Określono zarówno efektywność koagulantu glinowego i żelazowego, jak i skuteczność różnego typu flokulantów. Oceniono wpływ naturalnych substancji organicznych na efekt usuwania pestycydu w procesie koagulacji. Długoterminowe testy adsorpcyjne prowadzono z wykorzystaniem kolumny wypełnionej węglem aktywnym. Stężenie atrazyny w roztworach wodnych wynosiło 200–1000 g/m³. Badania wykazały, że koagulacja (nawet wspomagana polielektrolitami) nie nadaje się do usuwania atrazyny, podczas gdy adsorpcja na węglu aktywnym charakteryzuje się bardzo dużą skutecznością.