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Sorption of lindane from water using a macroporous copolymer based on glycidyl methacrylate

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Organochlorine pesticide - lindane, according to the US EPA classification, is considered as potentially carcinogenic compound. Although the usage of this pesticide is banned in many countries, it is still used in some. As persistent organic compound, lindane and its residues can persist in the environment for a very long time, migrating over long distances, potentially causing environmental pollution. Lindane residues can reach the human body through the food chain, because this potentially toxic compound is prone to bioaccumulation, and this is serious toxicological problem especially at industrial and agricultural sites where lindane has been used directly, or has reached due to improper wastewater disposal. Despite bans on its use, lindane contamination remains a global problem, and its removal from the environment is of crucial importance. In this research, for the sorption of lindane from an aqueous solution, a macroporous copolymer based on glycidyl methacrylate was utilized, which proved to be a very effective sorbent, with lindane sorption of about 80 %. Analytical technique, Gas Chromatography with an Electron Capture Detector (GC-ECD), was used for determination of lindane concentration. In addition to sorption, desorption of lindane was also successfully performed using different solvents, which confirmed the possibility of recycling and reuse of the investigated polymer.

Introduction

Lindane is an organochlorine pesticide, which is prohibited in many countries because it is linked to numerous diseases, and it is also considered as a potential carcinogenic compound, which was established by the US EPA [1]. However, in some countries this pesticide is still in use and is therefore the subject of numerous researches related to environmental protection. Due to the growing awareness of the toxic effects of pesticides, a large number of methods have been developed that enable their removal from the environment. The sorption method can be observed to eliminate different substances, and different specific sorbents can be developed as needed. In this sense, polymer materials are the most popular sorbents due to their easy modification and versatility [2]. The subject and goal of this research was the investigation of the sorption and desorption of lindane from aqueous solutions by macroporous copolymer based on glycidyl methacrylate.

Results and Discussion

The results of the lindane removal from an aqueous solution using a macroporous copolymer are shown in Figure 1a. The efficiency of lindane removal in the first 5 minutes reaches a value of 85 %. After this fast phase, in the next 30 minutes, a second, slower phase is observed which leads to reaching the equilibrium state, and this phase can be seen

as a plateau (Figure 1a). In addition to sorption, desorption of lindane from the macroporous copolymer was also performed, and the results are shown in Figure 1b. Various desorption solvents were used for this purpose. The solvent with highest desorption efficiency was acetone (65.4 %), then 2-propanol (63.1 %), then acetonitrile (54.4 %), followed by a mixture of hexane/ethyl acetate (37, 8 %), then ethyl acetate (31.8 %) and methanol as the weakest desorption solvent (10.9 %). These results confirmed the multiple application of the synthesized polymer, with the sorption and desorption abilities, confirming that the same polymer can be used multiple times.

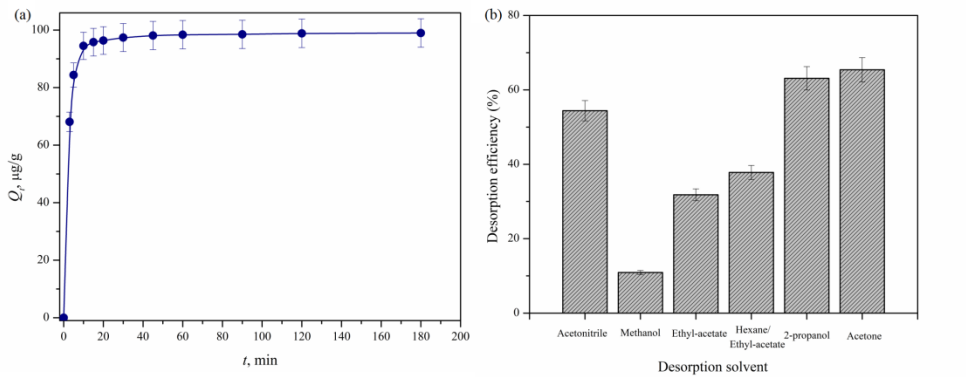

Figure 1. (a) Dependence of the removal efficiency of lindane by the macroporous copolymer on the contact time; (b) Lindane desorption with different desorption solvents.

Experimental Part

In this research, the cross-linked macroporous polymer poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate) (poly(GMA-*co*-EGDMA)) was used as a sorbent of lindane, with a particle size fraction of 0.15 to 0.30 mm, which were obtained by suspension copolymerization in the presence of an inert component [3]. An analytical standard of lindane with a purity of 98.2 % ± 0.1 % (CPAchem Ltd, Bulgaria) was used for testing lindane sorption. For lindane desorption, the following desorption agents/solvents were used: acetonitrile, methanol, ethyl acetate, a mixture of hexane and ethyl acetate in a ratio of 3:2 v/v, 2-propanol and acetone. Lindane was extracted according to US EPA method 505 [4] and analyzed using an Agilent 7890A gas chromatograph connected to electron capture detector (GC-ECD), and a capillary column Thermo Scientific™ TraceGOLD™ TG-5MT (30 m x 0.25 mm ID x 0.25 µm). The initial heating temperature was 50 °C for 3 min, and then heating was reached at a rate of 30 °C/min up to 210 °C and held at this temperature for 20 min. The mode of injection was splitless. Hydrogen was used as a carrier gas with a flow rate of 60 mL/min.

Experiments of lindane sorption using a macroporous copolymer were performed in a batch process at room temperature (25 ± 0.2 °C). In an erlenmeyer flask with a volume of 100 mL, 400 mg of sorbent was measured and poured with 50 mL of an aqueous solution of lindane with a concentration of 500 µg/L (initial pH of the solution 8; ionic strength 3 % w/v). The lindane solution that was brought into contact with the sorbent was shaken for 180 min on an orbital shaker at a speed of 300 rpm/min. At appropriate time intervals (3, 5, 10, 15, 20, 30, 45, 60, 90, 120 and 180 min), 1 mL of the solution was sampled with a micropipette, which was diluted with 4 mL of deionized water and prepared for

measurement by GC-ECD. All measurements were performed in duplicate and the results were expressed as the mean value. The efficiency of sorption (*E*, %) was calculated according to the following equation [5]:

$$E(\%) = \frac{(C_0 - C_e)}{C_0} \times 100\% \quad (1)$$

where C_0 (μg/L) and C_e(μg/L) are the initial and equilibrium concentration of lindane in the solution. After the sorption process (60 min), the dried samples of macroporous copolymer with bound lindane were dried and used in desorption experiments. Desorption was performed by mixing 50 mg of sorbent (with bound lindane) with 5 mL of desorption agent (acetonitrile, methanol, ethyl acetate, mixture of hexane and ethyl acetate in the ratio 3:2 v/v, 2-propanol and acetone) for 60 min, on an orbital shaker (300 rpm) at room temperature (25 ± 0.2 °C). The samples after the sorption process were filtered and analyzed by GC-ECD. All measurements were performed in duplicate and the results were expressed as the mean value. Desorption efficiency (*D*, %) was calculated according to the following equation [6]:

$$D(\%) = \frac{C_d V_d}{(C_0 - C_e) V_i} \times 100\% \quad (2)$$

where C_e (μg/L) is the equilibrium concentration of lindane in the solution after sorption, C_d (μg/L) is the concentration of lindane in the desorption solvent after desorption, V_i (L) and V_d (L) are the volume of the aqueous solution of lindane and the desorption solvent.

Sorpcija lindana iz vode pomoću makroporoznog kopolimera na bazi glicidil metakrilata

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Organohlorni pesticid - lindan, prema US EPA klasifikaciji, smatra se potencijalno kancerogenim jedinjenjem. Iako je upotreba ovog pesticida zabranjena u mnogim zemljama, u nekim se i dalje koristi. Kao perzistentno organsko jedinjenje, lindan i njegovi ostaci mogu da opstanu u životnoj sredini veoma dugo, migrirajući na velike udaljenosti, potencijalno izazivajući zagađenje životne sredine. Ostaci lindana mogu da dospeju u ljudski organizam kroz lanac ishrane, jer je ovo potencijalno toksično jedinjenje sklono bioakumulaciji, a to je ozbiljan toksikološki problem posebno u industrijskim i poljoprivrednim lokacijama gde se lindan direktno koristio ili je dospeo usled nepravilnog odlaganja otpadnih voda. Uprkos zabranama njegove upotrebe, kontaminacija lindanom ostaje globalni problem, a njegovo uklanjanje iz životne sredine je od ključnog značaja. U ovom istraživanju sorpcija lindana iz vodenog rastvora urađena je sa makroporoznim kopolimerom na bazi glicidil metakrilata, koji se pokazao kao veoma efikasan sorbent, sa

sorpcijom lindana od oko 80 %. Za određivanje koncentracije lindana korišćena je analitička tehnika, gasna hromatografija sa detektorom za hvatanje elektrona GC-ECD (Gas Chromatography with an Electron Capture Detector). Osim sorpcije, uspešno je urađena i desorpcija lindana korišćenjem različitih rastvarača, što je potvrdilo mogućnost reciklaže i ponovne upotrebe ispitivanog polimera.

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