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Adsorption of DDT on Hydrophobic Nanospheres-New Analysis Method

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Abstract

Hydrophobic interaction chromatography (HIC) takes advantage of the hydrophobicity of organochlorine pesticides by promoting its separation on the basis of hydrophobic interactions between immobilized hydrophobic ligands and nonpolar organochlorine. Since removal of pesticides from environmental medium is very important, so the purpose of this study is to use poly(HEMA-MAPA) nanospheres as adsorbent for Dichlorodiphenyltrichloroethane (DDT) from its standard solutions depending on their hydrophobic interactions. p,p'DDT standards adsorption studies were performed in a batch system with continuous stirring of the adsorption medium. Adsorption conditions including contact time, initial DDT concentration, temperature, amount of polymer, ionic strength was also optimized. The best adsorption conditions were as follow: 30 min, 45 °C, 100 mg/l of DDT, and 400µl of poly(HEMA-MAPA) solution. Meanwhile, the adsorption capacity of poly (HEMA-MAPA) nanospheres was not significantly changed in the concentration range of 0.00-0.1M NaCl. It was concluded that poly(HEMA-MAPA) nanospheres can be effectively used as DDT adsorbent. For future studies, it seems possible for poly(HEMA-MAPA) nanospheres to be recommended for DDT's removal from environmental matrices.

Keywords: Organochlorine compounds, DDT, poly(HEMA-MAPA), HIC, Nanospheres, Adsorption.

Introduction

In recent years, the contamination of the environment by chemical contaminants such as pesticides has ascended due to the global increase of both, population and industrial development (Arellano et al., 1999). It is well known that pesticides are used to prevent and control harmful organisms being an acute tool to agricultural problems. Pesticides have also different usage areas such as wood preservation, disinfection or household uses (Pinto et al., 2010). In spite of the several advantages, extensive usage of pesticides in agriculture leads to accumulation of pesticide residues in soil, water, and food therefore this unconscious usage generates a serious risk to human health and the environment worldwide (Bektasoglu et al., 2014). Organochlorine insecticides are among the most important organotoxins and make a large group of pesticides. Generally, organochlorines (OCs) are hydrophobic substances, with low water solubility, frequently at the µg or ng per liter level. As a consequence, these organic compounds are highly concentrated by living organisms and concentrations can biomagnify along the food chain (Noble, 1993). Also OCs are known for their environmental persistence and global concerns (Doong, et al., 2002). Although their production, usage and disposal have been regulated or prohibited in most of the developed countries, OCPs are still used at present in many developing countries (Zhou et al., 2008).

Among organochlorine pesticides, DDT has been extensively used for the control of soil-dwelling insects and against diseases such as malaria and typhus all over the world. reports showed that DDT and its main metabolites were important persistent organic compounds (POPs) that are semivolatile, bioaccumulative, persistent and toxic (Vallack et al., 1998; Jones and de Voogt, 1999). DDT and its main metabolites are suspected to be carcinogens and mutagens (Zhou et al., 2013).
In many instances, derivatives of DDT, including DDE, DDD have been detected in surface waters, in sediments and as suspended solids more than 25 years after DDT was prohibited (Chan et al., 1994; Hung and Thiemann, 2002).
OCs present in the final extract in very small amounts and it needs to be individually separated and detected by selective separation techniques in order to be correctly identified and quantified. Environment pollution by pesticides during routine agricultural practices is a common and growing problem in major agricultural areas of the world. Several techniques for the removal of pesticides are known such as; various oxidation processes, membrane filtration, and adsorption onto different media are applied. Adsorption is one of the most effective and simplest approaches to remove toxic and recalcitrant contaminants from different matrices. Generally, polymeric adsorbents can effectively trap many of the ubiquitous organic pollutants (Pan et al., 2009). Because of their ability to produce a large specific surface area which magnify their binding capacity, nanostructural polymers have been investigated intensively due to their potential applications in many areas, such as biology, medicine and environment. Therefore, it may be useful to utilize nanosized particles contains hydrophobic ligands as adsorbents for non-polar organic contaminants depending on the hydrophobic interaction between both of the contaminant and polymer. Hydrophobic interactions are maximized when the electrostatic repulsion between the

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proteins and ligand reaches a minimum (Lienqueo et al., 2007). A lot of different type of hydrophobic molecules, which have side chains of nonpolar amino acids such as alanine, methionine, tryptophan, and phenylalanine on their surface can be used as a ligand in HIC (Pitiot et al., 2000).

Many studies were performed to remove pesticides from water samples using different nanostructural materials. Such particles included magnetic nanospheres coated with polystyrene (Fe_3O_4 @PS) (Jing et al. 2014), synthesized nanostructure (HEMA-MAT) polymer (Uçar, 2012), polysterene nanocomposites based on TiO_2 nanowires (Youssef et al., 2013), polymeric nanospheres based on cyclodextrins as building blocks (Baruch-Teblum et al., 2010), novel adsorption resins namely; DowexOptipore L493 and Lewatit VP OC 1064 MD PH (Tepus et al. 2009), XAD-7(nonionic aliphatic acrylic polymer) (Kyriakopoulos et al. 2005), and plain polystyrene-divinylbenzene resin (Shahin, 2004; Kyriakopoulos et al., 2005).

The aims of this study were to test the adsorption ability of poly[hydroxyethyl methacrylate-methacryloylamido phenylalanine] (poly[HEMA-MAPA]) toward OCs (DDT was used as model) depending on its hydrophobic interaction properties and to optimize some factors affecting the adsorption efficiency including polymer amount, contact time, initial concentration of DDT, temperature, and ionic strength.

Material and Method:

p,p’ DDT standard was supplied from Sigma (St. Louis, USA), 2-Hydroxyethyl methacrylate (HEMA) were obtained from Sigma (St. Louis, USA) and distilled under reduced pressure in the presence of hydroquinone inhibitor, and stored at 4 °C until analysis. Methanol used in HPLC analysis was HPLC grade and supplied from Merck A.G. (Darmstadt, Germany). Commercially ultra pure chemicals were used without further purification in the analysis. Ultra-pure water filtered by Millipore S.A.S 67120 whose quality management system is approved by the accredited registering body to the ISO 9001. Before use the laboratory glassware was rinsed with deionized water and dried in a dust free environment.

p,p’ DDT standards adsorption studies were performed in a batch system with continuous stirring of the adsorption medium. Variables such as amount of polymer, contact time between the poly[HEMA-MAPA] nanospheres and the DDT standard, initial DDT concentration, temperature and ionic strength were studied to optimize adsorption conditions. For DDT analysis dionex ultimate 3000 UHPLC (Thermo Scientific, United States of America) with Diode Array Detector and 3µm X 150mmHypersil ODS C18 Columns (Thermo) was used.

Poly [HEMAMAPA] nanospheres used in this study were provided from the laboratory of Dr. Tuzmen and synthesized in the another study of her group (Kalburcu et al., 2014). Briefly, poly [HEMA-MAPA] nanospheres were synthesized as the following procedure. Methacryloylamido phenylalanine (MAPA) was prepared as outlined in literature (Turkmen et al., 2008; Oncel et al., 2005; Say et al., 2003). L-Phenylalanine (5.0 g) and $NaNO_2$ (0.2 g) were dissolved in 30 ml of K_2CO_3 aqueous solution (5%, w/v). This solution was cooled to 0 °C. Methacryloyl chloride (4.0 ml) was slowly poured into this solution under nitrogen gas then this solution was magnetically stirred at room temperature for 2 h. At the end of this chemical reaction period, the pH of the solution was adjusted to 7.0 and subsequently the solution was extracted with ethyl acetate. The aqueous phase was evaporated using rotary evaporator. The residue (MAPA) was crystallized from ether and cyclohexane.

Poly(HEMA–MAPA) nanospheres were produced by surfactant free emulsion polymerization as outlined in (Kalburcu et al., 2014; Turkmen et al., 2008; Oncel et al., 2005; Say et al., 2003). The preparation method was as follows: the stabilizer, poly (vinyl alcohol) (PVAL) (0.5 g), was dissolved in 50 ml deionized water in the polymerization reactor to prepare the continuous phase. Then, the comonomer mixture [2-Hydroxyethyl methacrylate (HEMA) (0.6 ml) and methacryloylamidophenylalanine (MAPA) (0.3 ml)] was added to this dispersion, which was mixed in an ultrasonic bath for about 30 minutes. Before polymerization, initiator [potassium peroxydisulfate (KPS) (0.44 ml)] was added to the solution and nitrogen gas was blown through the medium for about 5 min in order to remove dissolved oxygen. Polymerization was carried out in a constant temperature (70 °C) with shaking under nitrogen medium for 24 hours. After the polymerization, the polymeric nanospheres were cleaned by washing with ethanol and water several times to remove the unreacted monomers. For this purpose, the nanospheres were precipitated at the rate of 20,000 g for 1 hour in a centrifuge (Zentrifugen, Universal 32 R, Germany), the collected precipitate was resuspended in ethanol and water several times. After that poly(HEMA–MAPA) nanospheres were further washed with deionized water and used for the extraction of DDT via adsorption. Figure 1 shows the hypothetic structure of poly(HEMA–MAPA) nanospheres. Characterization data of poly (HEMA-MAPA) nanospheres was given in the study of Kalburcu et al. (2014).

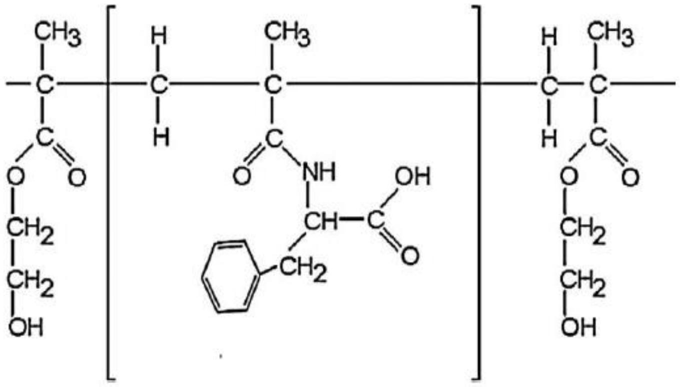
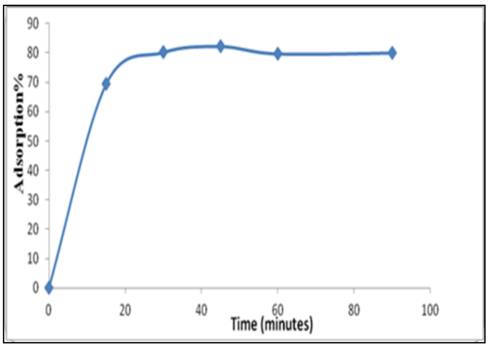


Fig. 1. The hypothetic structure of poly(HEMA–MAPA) nanospheres (Kalburcu et al., 2014; Oncel et al., 2005; Say et al., 2003)

Results and Discussion

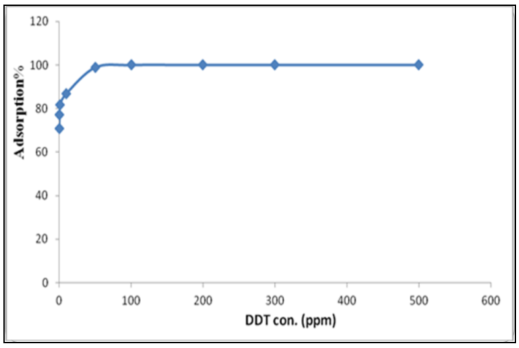
Adsorption ability of the nanospheres was tested in different periods of contact time between DDT solution and 400µl poly (HEMA-MAPA) nanospheres (Fig. 2a) on adsorption onto the poly (HEMA-MAPA) nanospheres. Adsorption studies were performed from 0 to 90 min. As DDT adsorption increased with time and reached a plateau of saturation at 30 min.

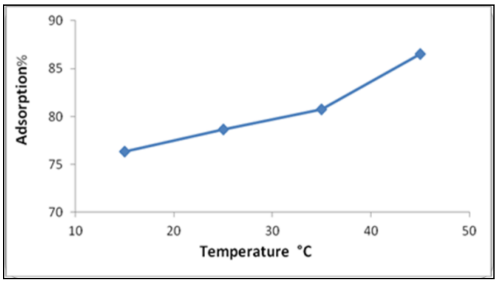
The concentration of DDT in the adsorption medium varied between 0.1 and 500 mg/l (Fig. 2b). An increasing of the adsorbed amount of DDT was observed according to the increasing in the initial concentration of DDT. Maximum adsorption efficiency of the prepared nanospheres was found to be 99% and adsorbed amounts per unit µl of poly (HEMA-MAPA) nanospheres reached a plateau at about 100 mg/l. These results agreed with some experiments from which it was concluded that sorption experiments in solutions with high concentrations of corresponding organic molecules show a high adsorption capacity until reaching the saturating state (Baruch-Teblum et al., 2010).



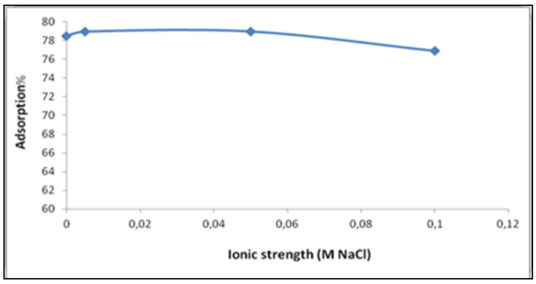
a

b





c



d

e

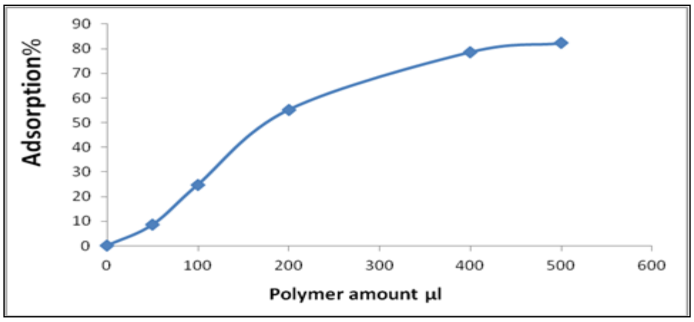


Fig. 2. Effects of contact time (a), initial DDT concentration (b), temperature (c), ionic strength (d) and polymer amount (e) on the DDT adsorption

The adsorption studies were performed over a range of temperatures from 15 to 45°C. As seen in Figure 2c, the adsorption capacity of the poly (HEMA-MAPA) nanospheres was found to have low affect with increasing the temperature between 15-35 °C. At temperature of 45 °C the adsorbed amount of DDT on poly (HEMA-MAPA) nanospheres increased about 10% than the amount that adsorbed at 15 °C. As DDT and poly (HEMA-MAPA) nanospheres are hydrophobic compounds and their interaction is an entropy-driven as in all hydrophobic interactions phenomena and as it is well known, if temperature is increased entropy will be increased also and as a result the interaction will increase (Queiroz et al., 2001). Moreover, according to equation (below) the capacity factor k' in hydrophobic interaction increases with increasing temperature (El Rassi, 1996):

$$\mathrm{Ln}k' = \ln\phi - \Delta G/RT$$

where R is the gas constant, ϕ is the phase ratio and T is the absolute temperature

To determine the effect of ionic strength on DDT adsorption, adsorption studies were carried out in the range of 0.001- 0.1 M NaCl (Fig. 2d) the adsorption capacity of poly (HEMA-MAPA) nanospheres was not significantly changed in the concentration range of 0.00-0.1M NaCl. This can be attributed to the high binding capacity (high hydrophbocity) and selectivity of the Phenylalanine group in poly [HEMA-MAPA] nanospheres which may need no promoter like a salt to enhance the connection ability between it and the phenyl groups of the non-polar DDT compound, as that the feature structure of the adsorbent is a very important factor in determining the adsorption ability of any material.

The concentration of poly (HEMA-MAPA) nanospheres in the adsorption medium varied between 0 µl to 500 µl. The results of the adsorption studies for poly (HEMA-MAPA) nanospheres are presented in Figure 2e. We observed that the amount of adsorbed DDT increased with the increasing amount of polymer. Maximum adsorption capacity of the prepared nanostructures was found to be 82% and adsorbed amounts per volume unit of poly (HEMA-MAT) nanospheres reached a plateau at about 400µl.

Conclusion

Present study aimed to test the adsorption ability of poly[hydroxyethyl methacrylate-methacryloylamido phenylalanine] (poly[HEMA-MAPA]) toward OCs (DDT was used as model) depending on its hydrophobic interaction properties. According to results the poly[HEMA and MAPA] nanosphere has high capacity for the adsorption of DDT from its standard solution via hydrophobic interaction phenomenon due to the large surface area of these nanospheres. Rising the temperature of the medium to about 45 °C the adsorbed amount of DDT on poly(HEMA-MAPA) nanospheres increased about 10% comparing to the amount that adsorbed at 15 °C. This result is attributed to the nature of HIC which is an entropy-driven phenomenon and as it is well known, if temperature is known an increase of entropy will be observed if the temperature increases. On the other hand, adsorption capacity of poly (HEMA-MAPA) nanospheres toward DDT standard was not significantly changed by changing the concentration of NaCl salt between 0.00 and 0.1M. By increasing the initial concentration of DDT in the adsorption medium an increasing of of poly(HEMA-MAPA) nanospheres adsorption capacity was observed. Solutions with high concentrations of corresponding organic molecules show a high adsorption capacity until reaching the saturating state. On the other hand, the adsorption was relatively fast, and the time required to reach equilibrium conditions was about 30 min. As a result, the low cost, less labor intensiveness, high separation efficiency of hydrophobic nanospheres containing phenyl functional groups as poly (HEMA-MAPA) make them most promising synthetic materials for the removal of DDT and such other organochlorine pesticides.