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Magnetic chitosan graphene oxide composite for solid phase extraction of phenylurea herbicides

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ABSTRACT

Magnetic chitosan graphene oxide composite was successfully prepared and used as an adsorbent for the simultaneous removal and extraction of three phenylurea herbicides monuron, linuron and isoproturon and determined using high performance liquid chromatography with UV detector. The composition and morphology of the composite was studied through Fourier transformed infrared spectroscopy, Scanning electron microscopy, Energy dispersive X-ray and X-ray diffraction analysis. Several factors such as pH of solution, adsorption time, temperature, kinetics and isotherms were studied. The maximum adsorption capacity was 35.71 mg/g for monuron, 33.33 mg/g for linuron and 29.41 mg/g for isoproturon at room temperature and pH 5. The adsorption process best fitted to pseudo second order kinetics and Langmuir adsorption isotherm. Thermodynamic study suggested exothermic and spontaneous adsorption process. The % recoveries for linuron, monuron and isoproturon were 94.09% ± 2.68, 92.37% ± 1.14 and 90.32% ± 1.23 respectively. The proposed method was successfully applied to spiked samples of rice and river Kabul water.

1. Introduction

Phenylurea herbicides (PUHs) are used as post- and pre-emergence weed control in cereal and cotton crops as well as in small fruits crops worldwide (Liu, Wang, Wu, & Wang, 2015). The herbicides residue remains in the surrounding and adversely affect the aquatic and human life (Kumar et al., 2017; Li et al., 2016). The European Union allows an acceptable limit of 100 ng L^{-1} for any one of the herbicide in drinking water and 500 ng L^{-1} for the sum of all compounds (Chou, Lin, & Fuh, 2009; D'Archivio, Fanelli, Mazzeo, & Ruggieri, 2007; Li, Dörfler, Munch, & Schroll, 2017). PUHs gained attention due to their toxicity and carcinogenic effects at low concentration to wildlife and human (Benitez, Acero, Real, & Garcia, 2009; Medved & Cifrek, 2012).

Different chemical treatments for the elimination of these contaminants have been published (Benitez, Real, Acero, & Garcia, 2006; Oturan & Aaron, 2014; Rubí-Juárez et al., 2016). However, due to the high cost and production of toxic by-products these methods are not acceptable (Naushad et al., 2018). Good separation and quantitative determination have been achieved with gas chromatography (GC). However, it required derivatization of phenylurea herbicides due to its thermal instability which is a time-consuming process (Chou et al., 2009; Gerecke, Tixier, Bartels, Schwarzenbach, & Müller, 2001). Membrane separation technology with high pressure was also used but it also suffers from the decline of flux due to several factors (Benitez et al., 2009). High performance liquid chromatography (HPLC) has the advantages of PUHs determination without derivatization before chromatographic separation. In the literature substantial data is available for PUHs determination in water samples (Li et al., 2016; Mughari, Vázquez, & Galera, 2007), different crops samples (Hiemstra & de Kok, 2007; Liu et al., 2015; Mou, Chen, & Zhi, 2008) and soil samples (Langeron, Sayen, Couderchet, & Guillon, 2014; Molins, Hogendoorn, Dijkman, Heusinkveld, & Baumann, 2000) using HPLC.

Sample pretreatment is a major step in chemical analysis as it concentrates the trace analyte in the sample containing complex metrices (Catalá-Icardo, Gómez-Benito, Simó-Alfonso, & Herrero-Martínez, 2017; Shah, Jan, Zeeshan, & Iqbal, 2016). Among the various sample preparation and extraction techniques, solid phase extraction (SPE) is the most common and popular one (Lasáková & Jandera, 2009). A relatively recent development in SPE is the magnetic solid phase extraction (MSPE). The adsorbent in MSPE possess magnetic properties due to the presence of magnetite (Fe_3O_4) and maghemite (Fe_2O_3) (Dos Reis, Vidal, & Canals, 2017). The use of adsorbent with magnetic nanoparticles is an excellent option for extraction of different types of chemical species due to synergistic effect of high adsorption capacity with easy handling of adsorbent using external magnet (Kumar et al., 2016). Other benefits are the use of small amount of adsorbent, reduce

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extraction time, reduce consumption of solvents and reusibility of the adsorbent (Alqadami et al., 2017; Khan & Lo, 2017). But the main disadvantages of magnetic nanoparticles are agglomeration of these particles which reduce the surface area as well as affect its paramagnetic properties (Shah et al., 2016). To overcome this complication different surface modifying agents like sodium dodecyl sulphate, decanoic acid (Guo, Wang, Tjiu, Pan, & Liu, 2012), silica (Yao et al., 2012), xanthate, ethylene diamine tetraacetic acid, thiourea, poly(acrylic acid), ethylenediamine, triethylenetetramine and different polymers like chitosan (Alqadami et al., 2017; Fan et al., 2012; Khan & Lo, 2017) are used. Chitosan is a multifunctional polymer having hydroxyl and very reactive amino groups (Kyzas, Travlou, Kyzas, Lazaridis, & Deliyanni, 2015). Due to nontoxic, biodegradable and biocompatible nature of chitosan it is used in food, pharmaceuticals and agriculture for the last two decades (Albadarin et al., 2017; Al-Naamani, Dobretsov, & Dutta, 2016; Shan et al., 2010). As chitosan dissolves below pH 5.5 which reduce its stability in acidic media, therefore chitosan is crosslinked with different reagents like epichlorohydrin and glutaraldehyde. However, during crosslinking of chitosan most of the amine and hydroxyl groups are consumed which reduce the adsorption capacity of chitosan. Hence the crosslinked chitosan is further modified to enhance its properties as adsorbent (Fan et al., 2012; Ge & Ma, 2015). For further modification an attractive new carbon material graphene oxide (GO) is used (de Toffoli, Maciel, Fumes, & Lanças, 2018; Depan, Girase, Shah, & Misra, 2011; Zhang, Rhee, & Park, 2017). Oxygen functional groups (epoxy, hydroxy and carbonyl groups) present in GO sheets change the interaction between the layers of GO and increase ist solubility in water and other organic solvents. similarly these funtional groups alter surface of graphene to improve interfacial interaction between GO and other polymers (Ahmadi, Elmongy, Madrakian, & Abdel-Rehim, 2017; Tong, Huang, & Wu, 2016).

Green Analytical Chemistry (GAC) emerged from green chemistry in 2000 and it concerns with the role of analytical chemists for promoting sustainable development in laborateries and industry. The main objectives of green analytical method (GAC) are to develop new analytical technologies or to adjust the old methods in such a way that use non toxic or less toxic chemicals. Among the 12 principals of green chemistry the most important for analytical methodology are: use of nontoxic solvents, reduction of energy consumption, prevention of waste generation, reduction of derivatization steps, and increased safty of the operator. For the assessment of an analytical method wether it may be considered green, guidelines and scoring approaches are required to compare the methods. The national environmental methods index (NEMI) model provide simple and popular approach to process assessment (Keith, Gron, & Young, 2007). The greeness of analytical method is also evaluated by some of the latest approaches including life cycle assessment (LCA) of the solvent used (Adu, Sugiyama, Fischer, & Hungerbühler, 2008; Capello, Fischer, & Hungerbühler, 2007). A simple and rapid metric has been proposed by sheldon for the assessment of environmental impact of a process known as environmental factor (E factor). The E factor is calculated as a total weight of all waste generated in a process (kg) per kg of a product. Closer to zero the value of E factor will indicate a more greener process. The E factor value is required for the calculation of another important and popular green metric called environmental quotient (EQ), the product of E factor and Q value. The Q value is known as Environmental Hazard Quotient, related to ecotoxicity of waste generated in a chemical process. In some cases more than one green metric is used for assessment of environmental impact of a chemical process (Constable, Curzons, & Cunningham, 2002; Ribeiro & Machado, 2013; Tobiszewski, Marć, Gałuszka, & Namieśnik, 2015). These are explained here one by one. Effective Mass Yeild (EMY) quantifies percentage of the final product in all the chemicals used in chemical synthesis. It is calculated by the formula

$$\text{EMY (\%)} = \frac{\text{mass of the final product}}{\text{mass of hazardous and toxic reagents}}$$

The Carbon Effeciency (CE) is given by the formula,

$$\text{CE (\%)} = \frac{\text{mass of carbon in the product}}{\text{total carbon present in the reactants .}}$$

Mass intensity (MI) explaines reaction effeciency, stoichiometry, amount of solvents and all the chemicals and reagents used in synthesis. The ideal value is 1 for MI.

$$\text{MI} = \frac{\text{total mass used in a process}}{\text{mass of final product}}$$

The most important green chemistry metric is Atom Economy (AE) that forms the basis for all of the other metrics.

$$\text{AE (\%)} = \frac{\text{molcular weight of product} \times 100}{\text{of molecular weight of all the reactants}}$$

Reaction mass effeciency (RME) is a comprehensive tool in terms of mass balance of a chemical process. Methematically it is expressed as

$$\text{RME (\%)} = \frac{\text{mass of the product} \times 100}{\text{total mass of all the stiocometric reagents}}$$

Both the AE and RME have an ideal value equal to 100%

Recently analytical methods are evaluated on the basis of introduction of penalty points. Accordingly, 100 score means an absolutely eco-friendly method, but subtracting penalty points of the method due to toxicity and volume of reagents used, energy consumpion, operator hazards and waste generation, methods are classified as: excellent green analysis (> 75 points), acceptable green analysis (> 50 points), inadequate green analysis (< 50 points) (Anastas & Eghbali, 2010; Armenta, Garrigues, & de la Guardia, 2015; Gałuszka, Migaszewski, & Namieśnik, 2013). The term “Green Analytical chemistry” has been proposed by J. Namieśnik where several aspects were dicussed to make the analytical methods more greener. (Namiesnik, 2001; Tobiszewski & Namieśnik, 2012).

Various adsorbents have been used for simultaneous determination of phenylurea herbicides in the recent past. Some of these adsorbents are polymeric sorbents (Carabias-Martínez, Rodríguez-Gonzalo, Herrero-Hernández, & Hernández-Méndez, 2004), nanoporous carbon (Liu et al., 2015) and graphene oxide frame work (Li et al., 2016). To the best of our knowledge no data available for the simultaneous extraction of phenyl urea herbicides using magnetic chitosan graphene composite. The aim of the present work is to synthesisze magnetic chitosan graphene composite as an adsorbent for the simultaneous extraction of phenyl urea herbicides. The composite adsorbent synthesized is environment friendly, safe, nontoxic, degradable, reusable and used as novel SPE adsorbent for the simultaneous determination of three phenyl urea herbicides, monuron 3-(4-Chlorophenyl)-1,1-dimethylurea, isoproturon 3-(4-isopropylphenyl) 1,1-dimethylurea and linuron 3-(3,4-dichlorophenyl) 1-methoxy 1- methylurea. The proposed extraction method was validated and applied for analysis to water and rice samples.

2. Materials and methods

2.1. Materials

All the chemicals used were analytical grade purity. Powder graphite (50 mesh) and chitosan with a degree of deacetylation have above 88% were purchased from Daejung Chemicals and Metals CO., LTD Korea. Sodium nitrate, sulfuric acid (98%), potassium permanganate, N-hydroxyl succinimide (NHS) and 1-ethyl-3-3(3-dimethyl- aminopropyl) carbodiimide hydrochloride (EDC) were obtained from Merck, Darmstadt Germany. (Papageorhiou, Lambropoulou, Morrison, Namiesnik, & Plotka-Wasylka, 2018) Glutaraldehyde, ammonia (35%), hydrogen peroxide (35%), hydrochloric acid (37%), ferric chloride ($FeCl_3.6H_2O$), and ferrous sulphate ($FeSO_4.7H_2O$) were purchased from BDH Laboratory Supplies, Poole, England. Methanol (99.9%) was supplied by BioM Laboratories, Chemical division, Malaysia and acetonitrile (99.9%) by Lab-Scan Analytical Sciences, Asia Co., Thailand. Standard monuron, linuron and isoproturon and glutaraldehyde were