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Removal of naproxen from water by ionic liquid-modified polymer sorbents

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ABSTRACT

The goal of this research was to investigate the recovery of naproxen from an aqueous solution using solid polymer sorbents (Sepabeads® SP850, Amberlite® XAD-4 and Diaion® HP-20) impregnated with 1-propyl-3-undecanoylpyridinium bromide. In the experimental section, the extraction kinetics of naproxen in the aqueous solution was investigated. The influence of different parameters such as the resin dose, pH of the aqueous phase and the naproxen initial concentration on the recovery was studied. Also theoretical models were used in order to fit the experimental data.

It was indicated, that the selected polymer sorbent impregnated with 1-propyl-3-undecanoylpyridinium bromide can be effectively employed in the naproxen removal from wastewater and the efficient recovery was a result of both the adsorption by the resin and the reactive extraction with 1-propyl-3-undecanoylpyridinium bromide inside the resin pores

1. Introduction

The development of civilization has contributed to the enormous technological progress in many areas of our lives as well as a global problem, which is the deterioration of the quality of drinking water and aquatic ecosystem. As the demand for new technical inventions has been increasing, the need for novel pharmaceuticals has been growing. One of the most popular drugs groups is well known as NSAIDs (non-steroidal antiinflammatory drugs) (Domínguez et al., 2011). They are among the most commonly used drugs in the pharmacotherapy of pain. NSAIDs are sometimes referred as nonnarcotic-analgesics, which do not cause euphoria and their use does not lead to addiction. All pharmaceuticals belonging to this group are acidic in nature with pK_a in the range of 3–5 (Gentili, 2007). Majority of them are carboxylic acid and enolic acid derivatives. These medicines are available without prescription in many different types. Because of easy availability of pharmaceuticals, is possible that pharmaceuticals get into the environment in very fast and uncontrolled manner causing water and soil pollutions. Aside from pharmaceuticals taking by the humans also large group are veterinary drugs (Petrovic and Baceló, 2006). Drug residues as well as other micropollutants, have become a significant contamination factor in surface water during recent years. Due to the presence of drug residues in the aqueous, scientists from around the world became interested in this subject. Particular attention was paid to the agents, whose existence has never been studied like identified by the term EDCs – endocrine disruptors (Kima et al., 2007). Also the increasing use of pharmaceutical products becomes a serious problem for our environment. The detection of these compounds is possible thanks to advances in analytical techniques. The most common pathways of entering into the environment for medicines are emissions during manufacturing, excretion by humans and animals, leachates from landfills and also improper waste disposal of drugs (Santos-Lúcia et al., 2010). Aforementioned reasons of presence of the medicines in environment have led to significant concentrations of various pharmaceutical compounds in the environment (Kosjek et al., 2007). Traditional water treatment plants are not designed to allow the purification of

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Table 1 – Main physicochemical properties of the polymer sorbents used to resins preparation (Soto et al., 2012).

Properties	Polymer sorbent		
	Amberlite XAD-4	Diaion® HP-20	Sepabeads® SP850
Matrix	Cross-linked polystyrenic polymer		
Particle size [mm]	0.25–0.84	0.25–0.60	0.3–0.80
Surface area [m^2/g]	750	600	1000
Porosity [mL/g]	0.98	1.3	1.2
Pore radius [Å]	40	260	38
Density [mL/g]	1.02	1.01	1.01

polar compounds present in trace amounts. The main reason that wastewater treatment cannot prevent to the entry of pharmaceuticals into surface water is high stability of some drug substances and their metabolites in the face of biological degradation. Removal of pharmaceuticals depends on the nature of the compound (Marchese et al., 2003). It was observed that acidic pharmaceuticals e.g. acetylsalicylic acid, ibuprofen, ketoprofen, diclofenac and naproxen, which presents in ionic form in an inert environment, almost do not undergo the processes of sorption by activated sludge and for the most part it remains in the liquid phase. While, basic and hydrophobic pharmaceuticals such as antibiotics—sorption on the particles on the activated sludge occurs with a high yield. One of the more studied methods of removing pharmaceuticals from water and wastewater are: biological methods, membrane bioreactors, adsorption on activated carbon, chlorination and ozonation and photolysis. Studies efficiency of removal various drugs showed that only 1/5 of the analyte can be removed up to an undetectable level in the classical two-stages sewage treatment plant (Jørgensen and Halling-Sørensen, 2000; Togunde et al., 2012). Removal of naproxen from wastewater by an adsorption on activated sludge undergoes in 50–80%, ozonation in 90%, ozonation/H_2O_2 in 98% and by using a photolysis in the range of 99–100%. Adsorption on activated carbon removes only 52% of naproxen (Onal et al., 2007; Bo et al., 2016).

Extraction with solvent impregnated resins is a feasible treatment method and is one of the most extensively studied methods for the removal of organic and inorganic pollutants from industrial wastewater (Kabay et al., 2010). The most interesting examples are removal of phenols from fermentation broth (Gao and Su, 1991; Burghoff et al., 2008; Burghoff et al., 2009), benzaldehyde and furfural from ethanol production (Babić et al., 2006; Weil et al., 2002), as well as, amino acids (Kostova et al., 2007), flavonoids (Kitazaki et al., 1996), methyl *tert*-butyl ether (Burghoff et al., 2010) from different aqueous solutions. Recovery of carboxylic acids from aqueous solutions has been carried out using resins impregnated with trioctylamine (Juang and Chang, 1995; Juang and Chou, 1996, Traving and Bart, 2002), tributyl phosphate (Ruiz et al., 2004) and with ionic liquid - Cyphos IL-104 (trihexyl(tetradecyl)phosphonium *bis*(2,4,4-trimethylpentyl)phosphinate) (Blahušiak et al., 2011). The presented works have indicated that the extraction of carboxylic acids (citric, butyric, valeric or tartaric) using the solvent impregnated resins occurs by a formation of acid-extractant complexes in the resin phase.

Ionic liquids have demonstrated specific extracting abilities towards different organic and inorganic species. A broad range of pyridinium based ionic liquids were proposed to removal of aromatic heterocyclic sulphur compounds from diesel (Hongshuai et al., 2008), as extractant of benzene from alkanes (Gómez et al., 2010) to recovery of organic acids (Yu et al., 2007) and in many fields of analytical chemistry (Liu et al., 2005). Extraction of organic acids by ionic liquids has been extensively studied by Marták and Schlosser (2006a, 2006b, 2007, 2008), Matsumoto et al. (2004) and McFarlane et al. (2005). The best results so far have been achieved with Cyphos IL-104 which has been proposed as the extractant of lactic (Marták and Schlosser, 2007), butyric (Marták and Schlosser, 2008) and mineral acids such as HCl, H_2SO_4, H_3PO_4, $HClO_4$ and HNO_3 (Kumari et al., 2016). However, a removal of naproxen from aqueous solutions using solvent impregnated resins and resins impregnated with ionic liquids has not been studied so far.

The goal of this research was to investigate the recovery of naproxen from an aqueous solution using solid polymer sorbents (Sepabeads® SP850, Amberlite® XAD-4 and Diaion® HP-20) impregnated with a novel ionic liquid – 1-propyl-3-undecanoylpyridinium bromide.

2. Experimental

2.1. Reagents and solutions

Sigma-Aldrich Chemical resins Amberlite XAD–4, Sepabeads® SP850 and Diaion® HP-20 (highly crosslinked polystyrenic polymers) were used in this study as a matrix of solvent impregnated resins and their main physicochemical properties are represented in Table 1.

Mg, 3-pyridinecarbonitryle, 1-bromodecane and 1-bromopropane used to the extractant synthesis were also supplied from Sigma Aldrich (Steinheim, Germany). All of components were of reagent grade. Feed aqueous solutions were prepared by dissolving naproxen (98%; Aldrich, Germany) in ultrapure water. The initial pH was regulated using HCl or NaOH aqueous solutions and was measured using a pH meter (T50, Metler Toledo).

A synthetic wastewater was used to confirm the applicability of the resins. This solution, made according a procedure described by Nguyen et al. (2012), contained glucose (400 mg/L), urea (35 mg/L), KH_2PO_4 (17.5 mg/L), $FeSO_4$ (10 mg/L), $MgSO_4$ (17.5 mg/L) and CH_3COONa (225 mg/L). Concentration of naproxen in the synthetic wastewater was 0.7 mg/L.

1-propyl-3-undecanoylpyridinium bromide (Fig. 1) was synthesised in a two-stage reaction (Wieszczycka et al., 2013). In the first stage 1-(3-pyridyl)undecan-1-one was synthesised by treating 3-pyridylcarbonitrile with decylmagnesium bromide. In the second stage, the synthesised ketone was stirred (23 °C) for one week with propyl bromide in acetnitryle as diluent to give the quaternary pyridinium salt with yield of 69%.

NMR (^{1}H, ^{13}C) spectra proved the structure of the synthesised compound: ^{1}H NMR ($CDCl_3$) δ in ppm: 8.85 (s, 1H, OH); 8.60 (d, 1H, $H_{py}^{[2]}$); 8.00 (d, 1H, $H_{py}^{[6]}$); 7.95 (d, 1H, $H_{py}^{[4]}$);

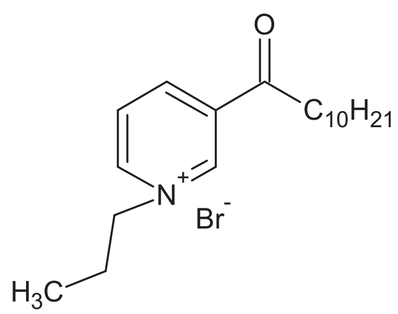

Fig. 1 – Structure of 1-propyl-3-undecanoylpyridinium bromide.