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Alkyl chain length dependent Cr(VI) transport by polymer inclusion membrane using room temperature ionic liquids as carrier and PVDF-co-HFP as polymer matrix

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ABSTRACT

In this study, the relationship between transport performance of Cr(VI) through PVDF-co-HFP based ionic polymer inclusion membranes (IPIM), alkyl chain length of symmetric imidazolium bromide based room temperature ionic liquids (RTILs) and morphological changes of these IPIMs has been comprehensively described. Butyl, hexyl, octyl, and decyl substituted RTILs containing IPIMs were prepared in different compositions and their effectiveness on Cr(VI) transport was experimentally optimised. In optimum conditions, the initial mass transfer coefficient (J_o) value of Cr(VI) was found as 5.0×10^{-6} $mols^{-1}$ m^{-2}, and also, we found that the optimised process is significantly selective for chromium in existence the other heavy metal ions. Morphological and structural characterizations of IPIMs have been performed before and after Cr(VI) transport to illuminate the morphological and the structural changes. Also, the additional plasticizing effect of RTILs as an unusual morphological phenomenon have come forward. In today's industrialised world, the demand for environmentally friendly processes for removal or recycle of toxic substances by simpler and cheaper ways have been increasing day by day. As a result, our developed and optimised membrane-based process seems to be overcome some Cr(VI) dependent environmental and industrial difficulties.

1. Introduction

From industrial revolution up today, heavy metal based environmental pollution has been still considered as an enormous problem over the world. The specialists have deemed that the input or the output of industrial-based heavy metals or organic substances are the primary sources of the environmental pollution. Environmental Protection Agency (EPA) around the world and the local authorities have implemented strict regulations to provide environmental protection and sustainability. Also, they have continuously renovated these regulations under the light of novel scientific evidence. Industrial-based environmental pollution can be seen in the water, air, and soil. Each pollution types, existing in different environmental sources, affects a significant amount of the organisms who live in there [1–3]. Every day, an enormous amount of heavy metal containing industrial effluents has been released into the natural sources at the end of industrial activities especially in third world countries. The discharge limits of heavy metals at the end of the industrial activities should be held in the acceptable concentration limits according to the boundaries of World Health Organization (WHO) and EPA [4,5]. Therefore, new environmentally friendly, reversible and cheaper removal or recovery processes should be developed and optimised to eliminate or minimise the hazardous effects of the heavy metals on the environment and natural sources.

Cr(III) and Cr(VI) are the most common oxidation states of the chromium. Chromium compounds and its alloys with various metals have been widely utilised in different parts of industrial processes for various purposes. The high-level intake or exposure to the chromium can create bad results on survival conditions of humans, animals and plants depending on the chromium species [6,7]. Cr(III) in lower concentrations has less toxic than Cr(VI) on natural life. Cr(III) especially shows its toxic effects on the viscera of mammal organisms like liver and kidney [8–10]. Despite its less toxic nature, Cr(VI) creates serious health problems on the human and the animal metabolism in every condition due to its highly toxic nature and easily diffusivity from the cell wall. Today, we know that Cr(VI) is also the main reason for many types of cancer. Also, Cr(VI) dependent mutagenic deformations of DNA or RNA

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have been an attractive topic among biologists and genetic engineers in recent decades. Since all of the debated issues above, chromium species must be primarily removed from industrial waste waters or leach solutions prepared from chromium containing solid wastes or ores, before they discharged into the environmental sources [7,11,12]. If we think about higher industrial consumption of Cr(VI), it is called as the most common encountered environmental problem, especially in third world countries. Therefore, we should consider on developing new, cheaper and easily available processes and technologies for Cr(VI) removal will be more and more relevant for today's world.

Ionic liquids (ILs) were only known as molten salts like molten NaCl. By the time they were invented, they had no broad application areas for industrial and scientific purposes due to higher temperatures of them in the molten state [13,14]. This situation forced scientists to find a new compound family that should be ionic liquid form in available temperatures for many industrial and scientific purposes. The mentioned compound family was named as ionic liquids whose melting points are below 100 °C. If their melting point is below room temperature or near to that, they are designated as room temperature ionic liquids (RTILs). ILs are composed of the reaction with an anion and cation that can be organic or an inorganic. As cation side of ILs, the scientists have commonly utilised imidazolium, pyridinium, pyrrolidinium, ammonium type organic or inorganic based cations. Also, they used the inorganic or organic based anions like as Br^-, NTf_2^-, BF_4^-, phosphoric acid derivatives, etc. as an anion side of ILs. ILs can be acceptable as more flexible compounds regarding easily changeable physicochemical properties like model toys. Their remarkable chemical and physical properties can be easily modified with changing anion or cation groups depending on usage purposes (reaction medium, an organic solvent, catalyst, extractant, etc.). Especially organic amine, imidazole, pyridine, etc. derivatives ILs are commonly biodegradable. So, they are classified as environmental friendly chemical substances. For this reason, ILs have been replaced with toxic organic compounds (volatile organic solvents, extractants, catalyzer, etc.) in many industrial and scientific implementations. In recent years, their utilising in separation and purification processes as a solvent or extractant or carrier have been continuously raised [15–20]. So, ILs are known promising chemical substances in many discovered or undiscovered fields in science and technology.

Imidazolium-based ILs are classified as symmetric or asymmetric imidazolium salts. In many purposes, asymmetric imidazolium salts are used because of their easily synthesis and purification. Especially 1-butyl-3-methylimidazolium-based ILs with different substituents and alkyl or aryl groups are widely studied experimentally in various aspects [21–24]. However, there is no considerable number of a scientific study based on symmetrical imidazolium salts compared to the asymmetric ones in the scientific literature. The alkyl chain length and the total carbon number of carbon atom of the alkyl chain are directly responsible from water-solubility of the imidazolium salts and its physicochemical properties like viscosity, electrical conductivity, etc. For example, the viscosity and the physical state of the salts are affected by the H-H interactions between the imidazolium salts molecules. Therefore, imidazolium salts having ten or twelve carbon atom on the alkyl chain are found as solid. Otherwise, they are liquid. For asymmetric imidazolium salts (1-alkyl-3-methly imidazolium), solidification limit was determined as ten carbon atom by Toh, S. L. I. et al. [25,26].

Polymer inclusion membrane (PIM) has been known as a type of liquid membrane composed of a base polymer, plasticiser, extractant, and has been utilised in membrane-based separation or purification processes. Their usages among the other liquid membrane and membrane filtration processes have increased day by day when the scientists find new and efficient preparation techniques and application fields related to PIM. PIMs have been prepared by solution casting method with moulding the polymer solution in a petri dish or casting knife or membrane applicator on a glass surface. They are also called as a self-supporting membrane. Since their mentioned features, PIMs are more suitable for using ternary processes for separation and extraction purposes [27,28]. Polyvinyl chloride (PVC), cellulose derivatives, poly(vinylidene difluoride) (PVDF) derivatives polymers have been widely used in PIM processes [15,29]. The affinity between membrane material and extracted substance or hydrophilic-lipophilic nature of base polymer correlated to the extracted substance can be mentioned as the main factor in base polymer choice. At the same time, chemical and physical durability and resistance of base polymer are another important factors [30–33]. The fluorination is utilised as a surface modification technique to make the surface more hydrophobic. Fluorinated polymers, especially PVDF and its derivatives have excellent chemical and physical durability against harsh aqueous conditions due to their hydrophobic nature depending on the fluorine content [34–36].

In the present study, we aimed to illuminate Cr(VI) transport through PVDF-co-HFP based IPIMs by using RTILs involving different lengths of alkyl chains. For this purpose, butyl, hexyl, octyl, and decyl substituted RTILs were synthesised and characterised using spectral and physicochemical characterization techniques like NMR, viscosity measurement, electrical conductivity, density, refractometry, etc. Then, the RTILs were utilised in the preparation of IPIMs as an ion carriers. Cr(VI), transport performance of the IPIMs, were optimised towards changing IPIM compositions and properties like membrane thickness, plasticiser type and rate, RTILs type, and rate, etc. Also, chemical, physical and morphological characterizations were examined by SEM and AFM imaging and contact angle measurements before and after Cr(VI) transport on IPIMs to explain the changing membrane structures. In the optimum Cr(VI) transport conditions, the selectivity of the membranes towards Cr(VI) in the presence of the other metal ions was identified.

2. Experimental

2.1. Chemical materials

The reagents, 1H-imidazole, 1-bromo butane, 1-bromo hexane, 1-bromo octane and 1-bromo decane, employed in the synthesis of RTILs and were purchased from VWR (Seelze, Germany) and used directly in the RTIL synthesis without further purification. Dichloromethane, toluene, diethyl ether, hexane, N, N-dimethyl formamide, NH_4OH, Na_2CO_3, KOH, HCl, HNO_3, NaOH, and H_2SO_4 were purchased from Sigma-Aldrich (Sleaze, Germany) and used directly without any purification. Poly(vinylidene fluoride-co-hexa fluoropropylene), PVDF-co-HFP, average Mw ~400,000, average Mn ~130,000, was purchased from Sigma-Aldrich (Sleaze, Germany). 2-nitrophenyl octyl ether (2-NPOE), 2-nitrophenyl pentyl ether (2-NPPE), bis(2-ethylhexyl) adipate (B2EHA), tris(2-etilhexyl) phosphate (TEHP) were utilised as plasticizer in IPIMs. AAS grade standard metal solutions Cr(VI), Fe(III), Cu(II), Co(II), and Ni(II) (1000 ± 5 mg/L), which were used for the preparation of metal-containing feed phases, and purchased from Merck (Darmstadt, Germany).

2.2. Synthesis of symmetric imidazolium bromide-based RTILs

The synthesis procedure of Pernak et al. [25] was used in our study for the synthesising of symmetric imidazolium bromide salt-based RTIL. Also, this method was comprehensively explained