Carbohydrate Polymers 298 (2022) 120138



Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol



Review



Imidazolium based ionic liquids modified polysaccharides for adsorption and solid-phase extraction applications: A review

Ismaila Olalekan Saheed [a,b], Samsudeen Olanrewaju Azeez [b], Faiz Bukhari Mohd Suah [a,*]

[a] Green Analytical Chemistry Laboratory, School of Chemical Sciences, Universiti Sains Malaysia, 11800 Minden, Pulau Pinang, Malaysia
[b] Department of Chemistry and Industrial Chemistry, Kwara State University, Malete, P.M.B 1530, Ilorin, Nigeria

ARTICLE INFO

Keywords:
Adsorbent
Cellulose
Chitosan
Polysaccharides
Ionic liquids
Solid-phase extraction

ABSTRACT

Attempt to broaden the application of ionic liquids (ILs) towards synthesis and modification of polysaccharides as adsorbent have gained more attention in the last two decades. This development has been aimed mainly on the use of environmentally friendly chemicals for improving the physical, chemical and adsorptive features of polysaccharides-based adsorbents for various applications. In the build-up to improve the polysaccharides-based adsorbents' characteristics through modification, ILs have been utilised by researcher either as a solvent medium or as a component of the modified natural polymer-based adsorbent. Findings revealed that the imidazolium-based ILs have been the prominent ILs type utilised for polysaccharides modification owing to its ease of preparation and its solvation capability for most commonly applied natural polymer. This review uniquely summarised the trend in the use of imidazolium based ILs to improve the adsorptive features of various polysaccharides adsorbents for adsorption and solid-phase extraction applications.

1. Introduction

Polymers are giant molecules that comprise of repeating units of a monomer or dissimilar monomers in a linear or interconnected structural arrangement. Their physical characteristics including thermal and mechanical properties depend on their length, specific gravity and composition. Polymers are natural or synthetic materials, and could either be biodegradable or non-biodegradable. The biopolymer based adsorbent materials such as lignin, chitosan, cellulose, hemicelluloses, alginate, etc., offers a significant role in adsorption application due to their biocompatibility, biodegradability, recyclability, reabsorbability (Ahmad et al., 2017). In lieu of this, the interest driving in the path of producing natural polymer composites has gained attention in the last few decades owing to their sustainability and degradability matters (Nurazzi et al., 2021). The challenge on the use of polymer based adsorbents for various applications such as adsorption purpose and solid-phase extraction (Raoov, Mohamad, Bin Abas, et al., 2014; Yan, Gao, et al., 2014) of contaminants include, low adsorption capacities (Tang et al., 2013), relatively weak interactions and difficulties of separation and regeneration (Vakili et al., 2019). Efforts have been made to overcome these adsorbents' limitations through various polymer modifications such as fabrication of organic-inorganic hybrid polymers (Samiey et al., 2014), molecularly imprinted polymer (Ma & Row, 2018; Yan, Yang, et al., 2014), polymer composites (Wang et al., 2019; Wang et al., 2009) and functionalised polymers (Gao et al., 2013; Tang et al., 2021).

Various biosynthesis routes have produced polymers such as proteins, polysaccharides nucleic acids, polyesters, polyisoprene, polyethers (lignin), and some other complex polyaromatics compounds (Gomez-maldonado et al., 2019). Utilisation of natural polymers minimizes the complex industrial synthetic routes, and the purification could be accomplished with the aid of a more environmental friendly solvents system (Gomez-maldonado et al., 2019). Polysaccharides are well-known naturally abundant polymers (such as cellulose and chitin) that are cheap and easy to extract, and have been modified and utilised for adsorption (Bhatnagar & Sillanpää, 2009; Saheed et al., 2021a) and solid-phase extraction applications. Chitin is deacetylated to chitosan (Yong et al., 2018), which also retains the properties (such biocompatibility, biodegradability) that are favourable for environmental and biomedical applications (Mittal et al., 2018). Alginate is another polysaccharide with good water absorption ability due to its richness in carboxyl groups. Alginate and chitosan can be modified to hydrogels, beads and composites (Gomez-maldonado et al., 2019). Cellulose on the other hand often exists as networks or fibres having intermolecular hydrogen bonding interactions between the hydroxyl groups (Patil et al.,

* Corresponding author.
E-mail address: fsuah@usm.my (F.B.M. Suah).

https://doi.org/10.1016/j.carbpol.2022.120138
Received 12 June 2022; Received in revised form 11 September 2022; Accepted 18 September 2022
Available online 21 September 2022
0144-8617/© 2022 Elsevier Ltd. All rights reserved.

2018; Zhang et al., 2018). When brought to the nanoscale, cellulose has shown exceptional properties such as low solubility in aqueous medium, surface charge potential, for water remediation. Therefore, the development of nanocellulose materials offers an alternative into the fabrication efficient adsorbents with improved binding affinities (Gomez-maldonado et al., 2019). The mechanism of interactions of polysaccharides-based adsorbents also depends on the nature of the solute to be removed (Haque et al., 2020; Zhang et al., 2018). For instance, removal of cationic solutes onto polysaccharides-based adsorbents is characterized by the pores and surfaces, complexation and mechanisms of ion exchange. More so, their interactions with anions or larger molecules could involve hydrogen bonding and electrostatic interactions via the hydroxyl groups or amino groups (Özge & Asgar, 2021). Crystallinity has been reported to influence adsorption efficiency of fibres towards organic molecules, as the organic molecules tends to adhere onto the amorphous regions on the fibres, although at low concentrations, there is possibility of their adsorption onto the crystalline region (Gomez-maldonado et al., 2019).

Ionic liquids (ILs) are widely known green solvents with good solvent properties. Their preference arises primarily from their unique and interesting properties such as negligible vapour pressure, non-molecular solvents, high thermal stability, adjustable viscosity and miscibility with organic solvents and water (Nayebi et al., 2019; Saheed et al., 2022; Vidal et al., 2012). These distinct characteristics of ILs is connected to their molten salts features that support their existence as liquid below 100 °C (Liu et al., 2015; Nayebi et al., 2019), with structural combinations that consist of organic cation and inorganic or organic anion (Vidal et al., 2012; Wu et al., 2015). A quite large number of possible combinations make available many ILs in various viscosity, polarity and hydrophobicity (Vidal et al., 2012). Furthermore, the utilisation of ILs for the preparation of hybrid materials has broadened its application (Tang et al., 2021). Since ILs are considered as green solvents, it has been utilised to synthesize various polymer based adsorbents, with the advantage of minimizing the use of common volatile organic solvents, thereby reducing harm to the environment (Tang et al., 2021). The aprotic ILs comprises of large cations such as imidazolium, pyridinium, phosphonium, and the limited anions are the most often used. Typical ILs anions include inorganic anions such as bromine Br^-, chloride Cl^-, sulfate SO_4^{2-}, hygroscopic anions like hexafluoro-phosphate PF_6^- and tetrafluoroborate BF_4^-, the organic anion such as bis(trifluoromethane sulfonyl)amide or trifluoromethanesulfonate, and halogen-free ions such as dicyandiamide, tosylate and n-alkyl sulfates (Singh & Savoy, 2020; Zhao et al., 2007). The protic ILs are synthesized through proton transfer involving the reaction of a Brönsted acid with a Brönsted base, and could be utilised to develop a hydrogen-bonded network (Correia et al., 2020).

ILs is advantageous for modification of adsorbent, most importantly the polysaccharide-based adsorbents. The opportunities offered by ILs in this regard include (i) green solvent advantage for dissolution of polysaccharides and homogeneous reaction (ii) possibility of solvent recovery and reusability (Lemus et al., 2012) (iii) opening avenues for the design of grafting copolymers including the possibility of being grafted onto polysaccharides to improve the properties of the adsorbent (Dong & Zhao, 2018; Pourjavadi & Doulabi, 2014; Raoov, Mohamad, & Abas, 2014; Xu et al., 2015) (iv) the opportunity to control the degree of substitution and physicochemical characteristics of products (v) the possibility of combining ILs with specific polymers including polysaccharides to develop materials with different morphologies (such as films, membranes, sponges, fibres and printed), as well as developing stimuli-responsive materials (Correia et al., 2020; Prasad et al., 2018). ILs modifications of adsorbents were reported (Akpomie & Conradie, 2020) to be efficient for decontamination of pollutants as well as for water treatments. This is because, ILs treatment of materials possess the ability to produce adsorbents with efficient regeneration potentials, good stability and high selectivity (Akpomie & Conradie, 2020). For pollutants matrix system, the ILs could enhance the surface characteristics and selectivity of modified materials for targeting a particular contaminant, as its hinder the adherence of undesirable adsorbates to the surface of the adsorbent (Akpomie & Conradie, 2020).

Considering the use ILs for polymer modification to fabricate various adsorbents as reported in the literature, the ILs can simply serve as solvent medium (Alexandra et al., 2020; Rufato et al., 2019; Saheed et al., 2021b) or as component of the synthesized polymeric adsorbent (Gao et al., 2013; Kou et al., 2020; Monir et al., 2020; Yan, Gao, et al., 2014; Zheng et al., 2022). Polymeric-based adsorbents prepared through ILs modifications have been utilised for adsorption (Dong et al., 2020; Dong & Zhao, 2018; Isosaari et al., 2019; Zheng et al., 2022) and solid-phase extraction (Han et al., 2013; Ma & Row, 2018) applications. Various ILs have been applied to modify polymers for adsorption of various dyes (Gao et al., 2013), heavy metals (Ferreira et al., 2017; Wieszczycka et al., 2020; Zheng et al., 2022), pharmaceuticals, and also in the solid phase extraction (Li et al., 2020; Vidal et al., 2012) of organic compounds such as carbaryl (Chen et al., 2020), triazine herbicides (Han et al., 2013) and chlorophenols (Ma & Row, 2018). A multifunctional polymer adsorbent involving a grafted imidazolium IL had been prepared through radiation induced grafting method and electrospinning strategy for simultaneous removal of dyes, heavy metals and bacteria. The adsorption mechanism for the dyes (Congo red) was an electrostatic interaction while the Cd(II) adsorption was facilitated by the complexation through nitrogen atoms on the imidazolium ring of the grafted IL and Cd(II) (Zheng et al., 2022). There are several review article in literature on polysaccharides-based adsorbents (Crini, 2005; Mittal et al., 2016; Qi et al., 2021; Sheibani et al., 2021; Wang & You, 2021) but these articles have not critically highlight the trend in the use of ILs for the modification of polysaccharides-based adsorbents for adsorption and solid-phase extraction applications. Therefore, this review highlights the commonly used ILs in recent time for polysaccharides-based adsorbent's modifications, and their influence and performance towards adsorption and solid-phase extraction applications.

1.1. Adsorption

Adsorption is one of the best techniques for decontamination of water and air systems, due to its low cost, ease of operation, minimal waste disposal, and environment friendliness. It has additional advantage of suitability of being applied to a decentralized water supply system (Alzaydien & Manasreh, 2009; Mhemeed, 2018; Raghav & Kumar, 2018). Basically, adsorption involves a mass transfer process in which a substance is transferred from the liquid phase onto the solid surface, and subsequently adhered by either physical and/or chemical interactions (Awang et al., 2019). The physical or chemical interactions of material molecules in the active sites of a surface during adsorption occurs via the weak Van der Waals forces or through the formation of chemical bonds with the effective sites on the adsorbents' surface (Mhemeed, 2018). Adsorption can also involve the removal of dissolved solids from a solution onto a solid surface or recovery of liquids onto the solid surface. The adsorption of contaminants (either organic or inorganic species) has been reported to be influenced by solution pH, initial concentration, contact time, temperature and adsorbent dosage (Saheed et al., 2021c). The decontamination of wastewater via chemical and physical treatment can be achieved by several methods including precipitation, ion exchange, membrane processes, liquid-liquid extraction, coagulation, and adsorption. Adsorption is preferred over other methods for the retention of inorganic and organic substances in a simple, highly efficient and cost effective manner (Sharififard et al., 2018; Yadaei et al., 2018). The equilibrium correlation of adsorbent is commonly established to predict the behavior of adsorbent under various experimental conditions in order to ascertain the suitability of the adsorbent. The equilibrium correlations are developed through the use of equilibrium isotherms such Langmuir, Freundlich, Temkin and Dubinin-Radushkevich isotherms. The isotherms describe the way of interactions at the adsorbent surface, including inference on whether the

interaction is single-layer or multilayer adsorption. In a similar way, thermodynamics studies are significant for predicting the spontaneity of the adsorption process, providing information on the suitable temperature ranges for sorption, as well as the nature of adsorbent and adsorbate at equilibrium. The linear and nonlinear forms are often utilised to determine the appropriateness of isotherms, and the thermodynamic and kinetic models often performed to predict the reaction nature of the adsorption process (Batool et al., 2018).

Solid materials often exhibit a heterogeneous distribution of surface energy. The gaseous or liquid molecules could be attached to the surface while sufficiently close to interact. The solid is called the adsorbent; the gaseous molecule prior to being attached to the surface of solid is the adsorptive, and as well referred to adsorbate when attached to the solid surface (Webb, 2003). Physisorption process occurs as a result of relatively weak adsorbent-adsorbate interactions due to nonspecific, relatively weak Van der Waal's forces and adsorption energy usually below 80 kJ/mol, with the typical energies often being considerably less. The physically adsorbed species could diffuse along the surface of the adsorbent without having a location of attachment on the surface. More so, the physisorption process occurs on all surface inasmuch as the temperature and pressure are favourable and the process is easily reversed (Webb, 2003). A complex adsorption process can occur on a surface with heats of adsorption up to 600 kJ/mol for chemical bond formation between adsorbate and adsorbent, the process is therefore termed chemisorption. Chemisorption is highly selective and occurs only between some certain adsorptive and adsorbent species and is difficult to reverse. Physisorption result into the formation of multilayers adsorption of molecules while chemisorption only proceeds as long as the adsorbate can bind directly with the surface for a monolayer process (Mhemeed, 2018; Webb, 2003). Meanwhile, both physisorption and chemisorption may occur together on a given surface at the same time such that a layer of physically adsorbed molecules exist on top of an underlying chemisorbed layer. Sometimes, a surface can display physisorption at a particular temperature and chemisorption at higher temperature (Webb, 2003). The application of polymer materials including the polysaccharides-based adsorbent for adsorption process targeting the removal of contaminant from aqueous system is increasing daily. For instance, large volume of aqueous system are available for reduction of its heavy metal contents being a component of some industrial waste onto these adsorbents (Arora, 2019; Kenawy et al., 2019; Riedel & Brigham, 2019; Wang & Zhuang, 2017). Some special types of conducting polysaccharides-based materials have been utilised for the reduction of heavy metals from aqueous medium via adsorption process. For instance, two methods of treatment technologies are often used to remove Cr^{6+} from wastewater system: the first type involves the reduction of Cr^{6+} to Cr^{3+} followed subsequently by chemical precipitation process, and the second type on the other hand involves the direct removal of Cr^{6+}. In recent time, simultaneous adsorption and detoxification of Cr^{6+} is considered to be more economical and effective (Zhang et al., 2015). The use polyaniline/rice husk ash nanocomposite has also been applied for the removal of Hg(II) from aqueous medium. Composite materials fabricated with polyaniline and polypyrrole incorporated with sawdust, and the Fe_2O_3 based composite with conducting materials can also be utilised for the remediation of heavy metal contaminated water. The lone-pair electrons on the nitrogen atom serve as binding site for metal complex formation resulting into the binding of metal ions present in the wastewater with the composite. Therefore, heavy metal ions adsorption process onto composite materials may be described (Arora, 2019; Sajid et al., 2018).

1.2. Solid-phase extraction (SPE)

SPE is one of the most widely applied pre-concentration methods with variety of various materials employed as sorbents. SPE offers advantage of overcoming some possible shortcomings with liquid–liquid extraction such as inadequate phase separations, lower quantitative recoveries, and disposal of large amount of organic solvents (Vidal et al., 2012). SPE is often used for the extraction of semi-volatile/or non-volatile analytes of liquid samples, though solid samples could also be pre-extracted into solvents. Solid-phase sorbents suitable for extraction application, concentration and purification are available in wide variety of materials and sizes. Meanwhile, selected sorbents for SPE are defined with analytical parameters including selectivity, affinity and efficiency/capacity. Sample pretreatment step is crucial for the whole analytical process as it offers the opportunity to eliminate interference of matrix and as well concentrate the analytes, most especially for analytes in trace/ultra-trace amount (Liu et al., 2021).

Therefore, various methods have been applied for the modification classical solid-phase polysaccharide-based adsorbent to increase its selectivity, affinity as well sorption capacity. Development of modified SPE adsorbents featuring the immobilization of material surfaces, functionalization of SPE adsorbents has been widely studied. The ILs has been majorly applied in SPE to covalently bind the imidazole group to the silica surface. Whereas, ILs (the imidazole or pyridine groups) have also been used in polymerization process, and also various kind of alkyl branched chains at various positions on the imidazolium ring including some functional groups have as well been fabricated (Vidal et al., 2012). Thermal stability of the ILs is a prerequisite for determining the suitability and long term stability of the extraction media, during which ILs could tolerate the operating temperature effectively. The thermal stability of ILs is dependent on the cation and anion, and the anion of the IL is more prone to influencing the stability IL than its cation. For instance, the thermal stabilities of imidazolium-based ILs decrease in accordance with the descending order $[PF_6^-] > [NTf_2^-] > [CF_3SO_3^-] > [BF_4^-] > [Cl^-]$, $[Br^-]$, $[I^-]$. The imidazolium-based cations have been reported to be more thermally stable than the tetraalkylammonium ones (Zhang et al., 2013). A molecularly imprinted material (MIP) has also been developed as SPE adsorbent by Wang et al. to selectively adsorb tylosin (TYL) in animal muscle samples (Wang et al., 2021). The MIP fabricated in aqueous by using 1,4-butanediyl-3,3-bis-1-vinyl imidazolium chloride and 2-acrylamide-2-methylpropanesulfonic acid as bifunctional monomers had excellent selectivity towards TYL in water, with the maximum binding capacity up to 123.45 mg/g. In combination with high-performance liquid chromatography, the prepared MIP can be utilised as SPE adsorbent for the detection TYL in the range of 0.008–0.6 mgL^{-1} ($R^2 = 0.9995$) with the limit of detection and limit of quantification of 0.003 mgL^{-1} and 0.008 mgL^{-1} with good precision. Under the optimal condition, the validated MIP-SPE-HPLC method has been successful for the separation and determination of trace TYL in animal samples with recoveries ranged from 94.0 to 106.3 %. The MIP-SPE cartridge can reused for up to 20 cycles (Wang et al., 2021).

1.3. Polysaccharides-based adsorbents

Polysaccharides are class of carbohydrate polymers obtained from natural sources with a spiking application as adsorbent for wastewater treatment. Polysaccharides (e.g. chitin, starch, chitosan, cellulose, cyclodextrin and their derivatives) are of peculiar attention as adsorbent due to their interesting and attractive features relating to their structure, physico-chemical characteristics, chemical stability, high reactivity and excellent selectivity towards aromatic compounds and metals. This is associated with the presence of chemical reactive groups (hydroxyl, acetamido or amino functions) in their polymeric chains (Qi et al., 2021). The attention polysaccharides as adsorbent materials are due to unique adsorbent properties including relatively high abundant, renewability, biodegradability, biocompatibility, adsorptive performance, ease of modification, versatility to be used under different forms (e.g. beads, gels, sponges, films, membranes, capsules, or fiber) and good capacity to associate through physical and chemical interactions with a wide variety of molecules. Meanwhile, adsorption onto polysaccharide derivatives is a promising cost effective procedure in water decontamination for the separation and extraction of compounds, and a beneficial

tool for protecting the environment (Crini, 2005). Conversely, polysaccharides possess some inherent disadvantages such as low surface area and porosity, hydrophilic nature, difficulty in regeneration, reutilization, weak mechanical strengths in their polysaccharide matrix, dependent of performance on the type of material used, which make them unsuitable for direct use as adsorbents (Qi et al., 2021).

Polysaccharides are broad class of carbohydrate polymers in which the successive polymeric chain are linked by glycosidic bonds. Polysaccharides are divided into animal-based polysaccharides, plant-based polysaccharides and microbial-based polysaccharides according to their sources (Sheibani et al., 2021). Animal-based polysaccharides possess large number of functional groups such as —NH_2, —OH, —COOH and —SO_3H groups, that serve as adsorptive sites for removing adsorbate substances from water. The various animal polysaccharides available for the fabrication of adsorbents include chitin, chitosan and glycosaminoglycans (e.g. heparin, keratan sulfate and hyaluronic acid). Unlike chitin and chitosan which has been extensively utilised for preparing a low cost adsorbent, glycosaminoglycans are more expensive, and therefore the glycosaminoglycan-based adsorbents are not suitable as low cost adsorbents (Qi et al., 2021).

Plant-based polysaccharides are divided into two categories based on their functions in plants. One category serves as supporting tissues (e.g. cellulose) while the other promote nutrient supply via enzymatic reaction (e.g. starch) (Qi et al., 2021). Some common representatives of plant-based polysaccharides often utilised for the fabrication of adsorbent include cellulose (Li et al., 2016), starch, alginate (Tang et al., 2020), pectin, gum Arabic, cyclodextrin (Raoov, Mohamad, Bin Abas, et al., 2014) and carrageenan (Musarurwa & Tavengwa, 2020). The basic structure of cellulose is linear β-1,4-linked D-glucopyranose units with a high density of hydroxyl groups. The dissolution of natural cellulose in water and other frequently applied solvents is difficult due to crystalline regions in cellulose that is linked to intramolecular and intermolecular hydrogen bonds. However, some solvent systems such as ionic liquids (Zhang et al., 2017), alkali/urea system, have been utilised to dissolve cellulose. Cellulose can be processed into various forms such as nanocrystals, nanosheets, fibres, chain, films and sponges (Zhang et al., 2017) that make it a promising material for fabrication of adsorbent (He et al., 2015). Starch composed of a mixture of anhydroglucose units, namely amylose (a linear biopolymer) and amylopectin (a branched biopolymer). Starch swelling is slightly in water at room temperatures and could exist as granules due to the hydrogen bonds between amylose and amylopectin units. However, increasing the temperature of water tend to expand starch particles leading to the formation of amorphous suspensions due to disruption of crystalline arrangement formed by hydrogen bonds between amylopectin and amylose units. The numerous hydroxyl groups in starch have also made it useful for designing functional adsorbents for various applications (Crini, 2005; Qi et al., 2021).

Furthermore, alginate is also a renewable plant-based polysaccharide comprises of guluronic acid and mannuronic acid linked by β-1,4-glycosidic bonds. Alginate can be sourced from seaweed. The properties of alginate are adjustable by varying the guluronic acid/mannuronic acid ratio. Alginate has been utilised as adsorbents for inorganic (Tang et al., 2020) and organic contaminants in wastewater due to its good stability and non-toxic characteristics. Cyclodextrins on the other hand are natural macrocyclic oligosaccharides composed of repeating D-glucose units synthesized through enzymatic conversion of starch. The cyclodextrins have truncated cone structure with hydrophilic outer surface and hydrophobic inner cavity arrangement (Qi et al., 2021). This structural arrangement enables cyclodextrins to reversibly bind to compounds producing host-guest inclusion complexes. The frequently studied cyclodextrins are α-cyclodextrin, β-cyclodextrin and γ-cyclodextrin, and have accordingly been investigated as biopolymers adsorbent for removal of contaminants (Crini, 2006; Kyzas & Bikiaris, 2015; Zhao et al., 2017) from water due to their unique adsorption property and selectivity towards target contaminants (Qi et al., 2021).

Microbial-based polysaccharides are polymeric substances produced by microorganisms under the metabolic process. Examples of such polysaccharides include pullulan, xanthan gum, gellan gum (Mittal et al., 2016), curdlan, dextran and salecan (Li et al., 2017). They typically possess acyl substituents (ester-linked acetate or ketal-linked pyruvate) which could influence the structural conformation and performance of polysaccharides. In recent time, microbial-based polysaccharides have also gained attention in wastewater treatment due to their high production rates, simplicity of purification and production conditions and bio-friendly characteristics (Qi et al., 2021).

Polysaccharides have also been grouped based on their respective ionic character (see Fig. 1) as either cationic (example - chitosan), anionic (example - carrageenan, alginate and gum) or neutral (example - cellulose, starch and dextran) molecules (Wang & You, 2021). Therefore, preparation and modification processes of selected polysaccharides including chitin, chitosan, cellulose, alginate and cyclodextrins are given attention in this article due to their uniqueness and wide application. The influence of imidazolium-based ILs on their modification was also discussed.

2. Fabrication of polysaccharides-based adsorbents using ILs

The progress in the generation of eco-friendly biocomposite materials is a challenge due to their potential characteristics that could be associated with their interactions between other polysaccharides and other synthetic polymers (Patil et al., 2018). ILs have enticed researcher with substantial attention as environmentally friendly green solvents that serves as alternative to the conventional organic solvents. The attention towards the use of ILs has been associated with their attractive properties, such as negligible flammability, high ionic conductivity, good thermal stability and simplicity of recyclability (Patil et al., 2018; Wang et al., 2019). It was reported that ILs could influence the performance of ILs modified polysaccharides-based adsorbents by increasing the porosity and stability of the polysaccharides-based adsorbents (Raoov, Mohamad, & Abas, 2014). Some ILs such as the imidazolium ILs has been applied for dissolution of polysaccharides (Swatloski et al., 2002) and synthetic polymers for the purpose of polysaccharides' modification (Stefanescu et al., 2020; Wang et al., 2013). The use of these various ILs for modification of polysaccharides into adsorbent has also been reported to have influence on the characteristics of the adsorbents such as surface morphology, surface area and porosity (Saheed et al., 2021b; Wang et al., 2013). For instance, a novel process for the dissolution of chitin and chitosan has been developed in 1-butyl-3-methyl-imidazolium chloride (BmimCl) solvent, and the application of chitin and chitosan as an alternative for amino-functionalized synthetic polymers for CO_2 capture was exploited based on the process strategy (Xie et al., 2006). The BmimCl was able to dissolve chitosan, though the crystalline domains of the chitosan was not completely disrupted, and does not affect its utilisation (Xie et al., 2006).

Considering the dynamics and factors that are significant to dissolution of polysaccharides in ILs, properties such as ILs structures, degree of polymerization of polysaccharides, dissolution time, temperature, water content, and the use of co-solvent are significant. Therefore, the most studied ILs are imidazolium-based ILs, and is due to their finest properties among other ILs including lowest melting points, large spectrum of room temperature ILs, high conductivity, dispersive interactions in facilitating solute dissolution and a wide widow of electrical stability that makes them suitable for a various applications including solvents for the dissolution of polysaccharides (Meenatchi et al., 2017; Zhang et al., 2005). For instance, during dissolution process, the strong intermolecular and intramolecular hydrogen bonding of cellulose are broken through the formation of hydrogen bonding between ILs anions (Swatloski et al., 2002) such that the strong inter- and intramolecular —OH of cellulose foster its solubility (Meenatchi et al., 2017; Zhang et al., 2005). 1-Allyl-3-methyl-imidazolium chloride (AmimCl) 1-allyl-3-methyl-imidazolium bromide (AmimBr) has

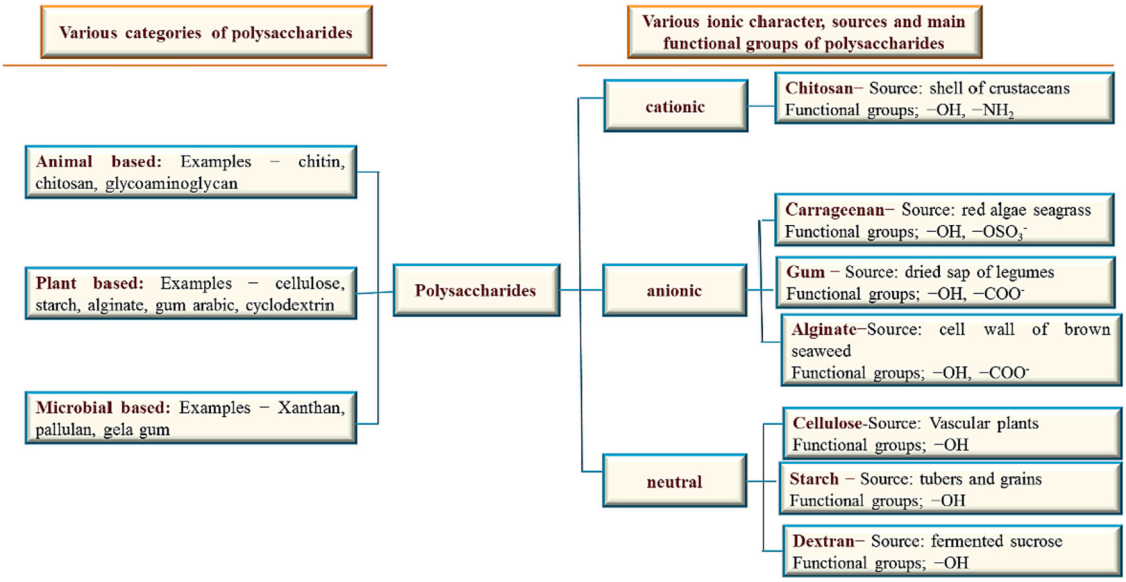


Fig. 1. Sources, ionic characters and functional groups of typical polysaccharides.

typically been utilised for polysaccharides dissolution with more frequency for AmimCl. This preference could possibly due to better affinity of AmimCl towards polysaccharides than AmimBr. Whereas, the solubility of polysaccharides in these 1-allyl-3-methyl-imidazolium ILs depends on their molecular mass, in which lower molecular mass polysaccharides dissolve easily (Shamsuri, Abdan, et al., 2021). Dissolution of cellulose in AmimCl is common when compared with chitin and chitosan due to a greater tendency to dissolve which is associated with the Van der Waals energy contribution between the glucose and imidazolium cations (Shamsuri, Abdan, et al., 2021). It is also perceived that BmimCl is often applied for dissolution of cellulose in comparison with other polysaccharides and could be linked to the chloride ion effectiveness in breaking down the hydrogen bonding network of cellulose (Shamsuri, Abdan, et al., 2021).

Furthermore, just as the methylimidazolium based cations, with allyl, ethyl, or butyl-side chains are effective for the dissolution of cellulose, the side chain with even number of carbon atoms displays better cellulose dissolution when compare with the odd number of carbon. Incorporation of hydroxyl groups in combination with C4 side chain attained a maximum dissolution. This could be associated with the additional polarity gained from hetero-atomic substituents of the imidazolium ring (Prasad et al., 2010). The hydrogen and oxygen atoms in the cellulose form electron donor–electron acceptor complexes with the charged species of imidazolium IL, and this occurs primarily between the C-6 and C-3 hydroxyl groups on the neighbouring cellulose chains. Therefore, this interaction could lead to the separation of hydroxyl groups of the various cellulose chains, thereby facilitating the dissolution of cellulose in imidazolium ILs. The ease of dissolution of cellulose is achieved due to the ability of ILs to break the extensive network of hydrogen bonds of the cellulose, and could further be enhanced by high chloride concentration in imidazolium IL ring (Prasad et al., 2010).

The influence of imidazolium based ILs on adsorption properties of the commonly applied natural polymer adsorbents' modification for adsorption (Saheed et al., 2021b; Tran et al., 2013; Wang et al., 2013) and solid-phase extraction (Yan, Yang, et al., 2014) application have been investigated, and therefore reviewed in this article.

2.1. Imidazolium-based ILs

ILs composed of bulky organic cations with the charge balanced with inorganic or organic anions (Ptak et al., 2020). Their unsymmetrical and bulky structural constituents' ions contribute into distinguishing them from the conventional salts such as sodium chloride. However, the relatively stronger ionic attractions among closely packed symmetrical ions in conventional salts are responsible for the higher melting point in comparison to ILs (Kaur et al., 2022). The charge of the anion of ILs could either be a diffuse or protected negative charge (Singh & Savoy, 2020). Though, various possible combinations of cations and counter anions are obtainable for ILs, however, the imidazolium-based ILs have been widely investigated. This is associated with their nitrogen-rich heteroatoms compound couple with a low melting point, high chemical stability and high ionisation performance features. The stable positively charged aromatic ring serves as a versatile cation framework and therefore a contribution to wide utilisation of imidazolium cation structure for an interesting molecular strategy (Noorhisham et al., 2021). Accordingly, among the various ILs cations, imidazolium-based ILs have been utilised in various separation applications including gas separation by relying on the advantage of their high CO_2 solubility, diffusivity, and permeability. Their permeation selectivity is quite higher in ammonium-based and phosphonium-based ILs (Correia et al., 2020). The acidic hydrogen in the cation has influence on solubility by hydrogen bonds. Metathesis process featuring (i) the exchange of halide salts or anion (ii) and acid-base neutralization reaction are the conventional routes for the preparation of IL. A single step imidazolium-based IL synthesis progresses via quaternization of imidazole to respective cationic (see Fig. 1), however hindrance to the desired anion directly via quaternization reaction resulted into multi-steps ILs synthesis (Fallah et al., 2021). Metathesis reaction process is usually utilised for the preparation of imidazole-based and the procedure could be divided into two as (i) silver salts-based reaction, or (ii) free acids or alkali metals/ammonium salts reaction. ILs synthesized through a reaction between imidazolium halide and Ag-salts in methanol are stable in water and air due to the lower solubility of Ag halides, that facilitates the separation of ILs, and consequently generating a water-miscible high-quality ILs with a good yield (Fallah et al., 2021).

Recycling of spent IL after use for polysaccharide reprocessing cycle could be hindered through various pathways including inherent thermal degradation of the IL, volatilisation of the intact IL ions, and reaction between the polysaccharides solute and IL (Clough et al., 2016). It has been demonstrated that, at C2 position with the reducing (aldehyde) end of polysaccharides-dissolving imidazolium IL, a reaction occurs through a transient N-heterocyclic carbene (NHC) intermediate, which is aided by the basicity of the IL anion to give a hydroxyalkylated adduct species (Clough et al., 2016). Exposing the mixtures of Emim and Bmim [OAc]

with polysaccharides to temperatures (100–120 °C) for an extended time (up to 24 h) could lead to sequence of decomposition reactions terminating in an equilibrium concentration of the 'C1 adduct' compound, which eventually represents a useful proxy for assessing possible polysaccharides degradation when dissolved in IL. The undesired side reaction arising from the sequence of degradation steps between the imidazolium IL and cellulose disturbs the recycling of the solvent and could also damage the carbohydrate fibres (Clough et al., 2016). It was reported that introducing a small amount of a benign and inexpensive co-solvent like glycerol reduces the rate of adduct accumulation, and therefore enhance the long-term thermal stability and recyclability of IL.

Furthermore, ILs are unlikely to act as contaminants in air, but could be a potential contaminant in water and soil through spilling, ineffective wastewater treatment and leaching of landfill sites. Therefore, their tendency of occurrence in the environment and bioaccumulation in aquatic or terrestrial organisms play an important role in their environmental impact and fate (Cvjetko Bubalo et al., 2014). The bioavailability of ILs is highly influenced by their sorption onto soil as studies revealed that imidazolium ILs could be adsorbed onto various types of soils and marine sediments. The hydrophobic long chain ILs adsorb more strongly than the short alkyl chains type and hydroxylated derivatives that minimally retained by geological adsorption into non-interlayer clay systems. This result into unhindered transport through soils and sediments and might contaminate the surface or groundwater. However, the more mobile hydrophilic ILs would likely enter the aquatic ecosystems (Cvjetko Bubalo et al., 2014).

The toxicity impact of imidazolium-based ILs on mammalian cell cultures that is useful to monitor changes in basic cellular functions has been assessed featuring the structural effects of the ILs such as alkyl chain length and types of anion (Cho et al., 2021). Elongation of the alkyl chain length increases the hydrophobicity of ILs, which is strongly associated with increased toxicity. Meanwhile, the influence of anions on the toxicity is still unclear (Cho et al., 2021). The toxic effects of IL in bacteria were also linked to the alkyl chain length of the cationic part and its head groups. It was perceived that cationic group of the IL have higher impact due to their high lipophilicity including affinity for phospholipid membrane of microorganisms through electrostatic attraction. Numerous computational results also revealed that the long alkyl chain of the cations could be inserted into the cell membrane lipid layer and interact with the negative charge of the phosphocholine or phosphoserine of the membrane layer (Cho et al., 2021).

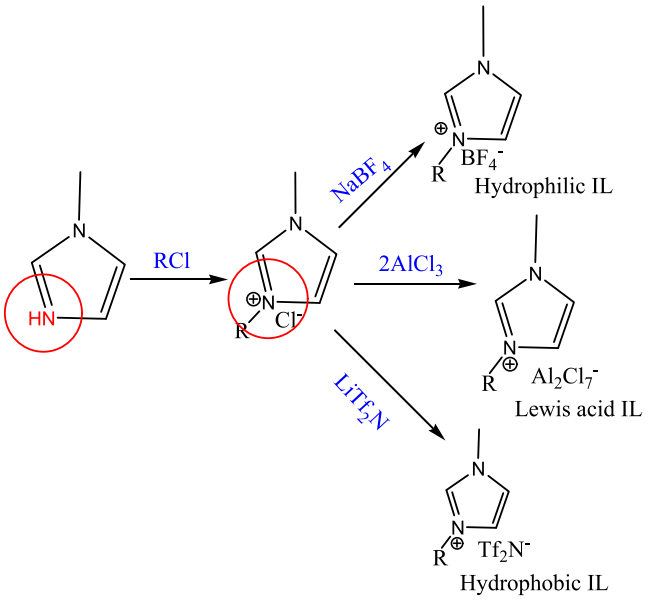


Fig. 2. Preparation pathways for imidazolium-based ILs.

Alkylimidazolium-based ILs can be synthesized by protonation, alkylation, or neutralization reactions (Fig. 2). The protonation process involves the use of hydrohalic acid for the protonation of N-alkylimidazole, and the reaction is usually carried out in a polar solvent, such as ethanol under continuous stirring at a temperature slightly above 25 °C (Shamsuri, Jamil, et al., 2021). In addition, the alkylation of N-alkylimidazole through a reaction with alkyl halide is conducted under a reflux condition with continuous stirring at an elevated temperature. Meanwhile, neutralization of alkylimidazolium hydroxide with hydrohalic acid to produce alkylimidazolium-ILs is usually carried out in a polar solvent such as ethanol under continuous stirring at room temperature. Therefore, it is perceived that alkylimidazolium-based ILs with halide counter anions are commonly employed in the modification of biodegradable polysaccharides composites compared to other counter anions (Fig. 3). This is probably because the use of the halide counter anion IL is cost-effective and can be applied to many polysaccharides-based matrices such as cellulose/polylactic acid blend, cellulose/polycaprolactone blend and chitin/polylactic acid blend (Shamsuri, Jamil, et al., 2021).

2.2. *Imidazolium ILs as solvent for preparation of polysaccharides adsorbents*

Recently, quite a number of porous adsorbents fabricated from polysaccharides for adsorption of contaminants from water have been prepared through a green technology approach featuring ILs as solvent medium (Alexandra et al., 2020; Tran et al., 2013). The adsorption capacity of some imidazolium-based ILs solvent-modified polymer adsorbents is presented in Table 1. Strong hydrogen bonding interactions and bio-recalcitrance could make natural lignocellulose materials to display poor solubility and processing ability, and therefore to a large extent limit their performance and practical utilisation. In recent time, the novel eco-friendly ILs are found useful and as an alternative for effective dissolution of cellulose, lignin and lignocellulose. This has provided a versatile and fascinating avenue for processing these renewable biomass resources (Xia et al., 2020). Dissolution of cellulose in ILs and subsequently regenerate with water or alcohol leads to the fabrication of cellulose hydrogels or alcogels. Subjection of hydrogels or alcogels to freeze-drying or supercritical CO_2 drying method leads to the fabrication of cellulose aerogels (Xia et al., 2020). Biopolymer such as chitosan could also be fabricated into aerogel. Aerogels possess a lightweight solid property with a 3D network skeleton. The interconnected porous structure in aerogel has many striking advantages including large specific surface area, high porosity, and low thermal conductivity. The porosity of the regenerated cellulose aerogels could be conveniently controlled through the selection of appropriate processing conditions for dissolution, regeneration and drying (Xia et al., 2020). Dissolution of chitosan in a series of 1-butyl-3-methylimidazolium-based ILs has been investigated by Chen et al. The solubility of chitosan in the various 1-butyl-3-methylimidazolium-based ILs increase almost linearly with increasing hydrogen bond acceptability of the ILs. The anions and the cation of 1-butyl-3-methylimidazolium-based ILs play significant roles in the dissolution of chitosan, and could be through the disruption of native hydrogen bonds in chitosan. In addition, good thermal stability was observed for the regenerated chitosan (Chen et al., 2011).

The reaction of chitosan with phthalic anhydride (PA) in either 1-butyl-3-methylimidazolium chloride (BmimCl) or 1-butyl-3-methylimidazolium acetate (BmimAc) IL in the presence pyridine, 1,4-diazobicyclo[2.2.2]octane (DABCO), or catalysed by N-bromosuccinimide (NBS) has been investigated and was reported to proceed homogeneously (Stefanescu et al., 2020). The products were soluble in dimethyl sulfoxide. The —OH and —NH_2 functional groups of chitosan were involved in the reactions, and the FTIR confirm that the products contain amide, imide, and esters functional groups. The cyclization of the phthalated chitosan is promoted by heating the isolated adducts to 200 °C leading to the formation of imide functional groups via elimination of water

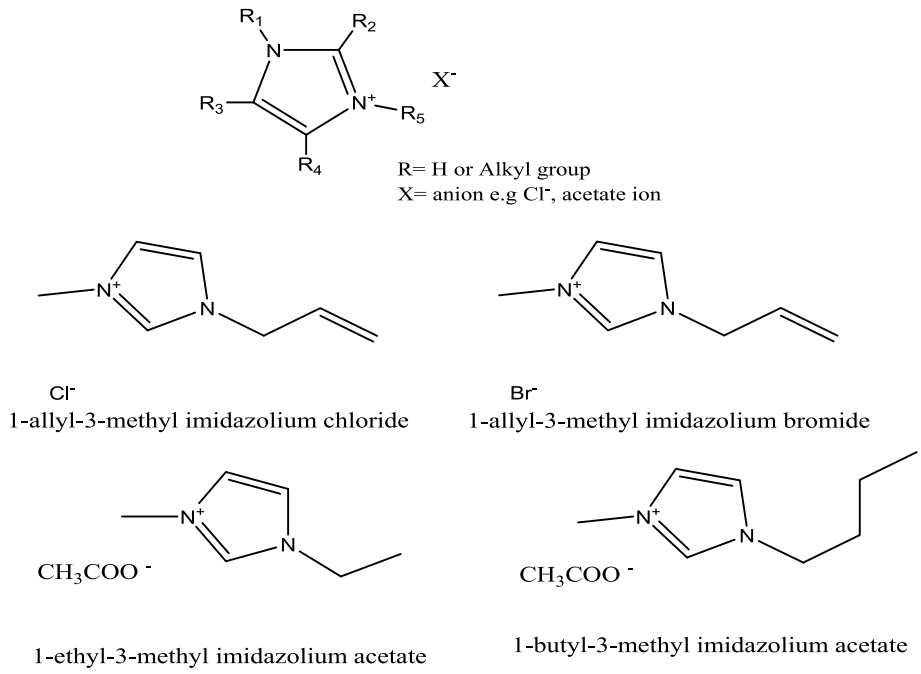


Fig. 3. Some commonly applied imidazolium based ionic liquids.

Table 1
Adsorption capacity reported in the literature for some imidazolium-based IL solvent-modified adsorbents.

Adsorbent	ILs solvent	Surface area (m^2/g)	Adsorbate	q_e (mg/g)	References
Collagen/cellulose hydrogel bead	BmimCl	43.2	Cu(II)	67.3	(Wang et al., 2013)
Cellulose/chitosan macrospheres	BmimAc; EmimAc	59.0	Cu(II)	26.7	(Alexandra et al., 2020)
		4.3		15.8	
Cellulose/chitosan	BmimCl		Microcystin	96	(Tran et al., 2013)
Cu(II)-immobilized iminodiacetic acid cellulose aerogel	BmimCl	355	Hemoglobin	367.0 (5.65 μmol/L)	(Oshima et al., 2014)
Cotton cellulose-*graft*-polycaprolactone	BmimCl		Ni(II)	50	(Xu et al., 2015)
Cellulose/chitosan hydrogel beads	EmimAc	2.28	Congo red	40	(Li et al., 2016)
Cellulose dinitrobenzoate	BmimCl		Creatinine	3.88	(Dai et al., 2015)
Alginate/chitosan (CHT/ALG)	[Hmim]HSO_4		Pb (II)	529.4	(Rufato et al., 2019)

(Stefanescu et al., 2020). The thermal stability of the modified chitosan obtained in the presence of alkaline majorly depended on the nature of the counter ion of the ILs used as solvent. The reaction conducted in BmimAc gave phthalated chitosan with a lower thermal stability than those conducted in BMIMCl which signifies an interference of the ILs in the reaction mechanisms. Meanwhile, the thermal behavior of the phthalated chitosan obtained from NBS catalysed reaction may be correlated with increasing degrees of substitution as the catalyst concentrations was increased; a higher degrees of substitution lead to a higher loss of weight at higher temperatures (Stefanescu et al., 2020). Chitosan/cellulose blend were successfully prepared using BmimAc solvent and then modified into films by manually spreading the solution on a flat surface follow by precipitation in methanol/water mixture. The shrinkage of the films was avoided by removing the absorbed through freeze drying under vacuum. The characterization revealed shifting of the bands that correspond to —NH and C═O groups of chitosan on FTIR, the absence of the diffraction peaks at $2\Theta = 10.7°$ and 14.9° on the XRD spectra, the increased activation energy for thermal decomposition for all the polymeric composite, and the apparent homogeneous structure without a phase separation of the two polymers observed via the SEM serves as an evidence for miscibility between cellulose and chitosan in the solid state (Stefanescu et al., 2012). In addition, a mass ratio 1:1 of cellulose and chitosan prepared in 1-ethyl-3-methylimidazolium acetate (EmimAc) has been reported (Li et al., 2016) to show optimum condition for shapes and the mechanical strength of the cellulose/chitosan hydrogel beads. The average size of the cellulose/chitosan hydrogel beads was 3 mm. The mean adsorption pore size of cellulose/chitosan hydrogel beads was 15.283 nm, while specific surface area was observed to be 2.28377 m^2/g (Li et al., 2016). Therefore, modification of natural polymers as adsorbent in some common imidazolium ILs solvents is discussed accordingly.

Imidazolium based ILs is a widely applied ILs' solvent for modification of adsorbents (Saheed et al., 2021b). The dissolution of polysaccharides such as chitosan and chitin in imidazolium based ILs such as 1-ethyl-3-methylimidazolium chloride (EmimCl) and 1-butyl-imidazolium acetate (BmimAc) have been utilised for the fabrication of materials into films, microspheres, sponges and aerogels (Silva et al., 2017). A significant role of ILs for enhance reaction efficiency have been mentioned with respect to chemical reactions, hydrolysis, acetylation, deacetylation and graft copolymerization of chitin/chitosan, supporting homogeneous media (Silva et al., 2017). The materials fabricated through these have been applied in wound healing, tissue regeneration and drug delivery systems (Silva et al., 2017). The dissolution of chitosan and cellulose blend and their re-precipitation mechanisms have also been investigated. As reported by Alexandra et al., targeting the optimization of the composition of the casting solutions make adequate the preparation of porous polymer spheres via "dropping *cum* phase separation" technique (Alexandra et al., 2020). Whereas, increasing the chitosan content in the sample, increases the time needed for the polymer dissolution but decreases the quantity of water required to destabilise the casting solution. The blend spheres fabricated in 1-butyl-3-methylimidazolium acetate (BmimAc) solutions present higher surface

areas and improved adsorption capacity for Cu^{2+} uptake, as the chitosan fraction in the polymer blend increases. However, no such observation was reported in the blend sphere samples prepared in 1-ethyl-3-methylimidazolium acetate (EmimAc) based solutions (Alexandra et al., 2020). EmimAc was utilised to dissolve cellulose coated onto chitosan hydrogel beads via a one-pot one-step process method for application as drug carriers (Song et al., 2020). The water molecules in the chitosan beads diffused outward upon contacting with cellulose–IL mixture and function as an anti-solvent to allow the coating of the beads' surface with the regenerated cellulose. The verapamil hydrochloride (VRP) used as the model drug was impregnated into the beads and the VRP-impregnated beads were subsequently dipped into simulated gastric fluid (pH 1.2). The VRP was discharged in almost ideal linear form. This fabricated cellulose-coated chitosan beads showed potentials for application as carriers for drug release control (Song et al., 2020).

Rufato et al. prepared an alginate/chitosan (ALG/CHT) and alginate/*N*,*N*-dimethyl chitosan (ALG/DMC) polyelectrolyte (PEC)-based composite adsorbents in 1-hydrogen-3-methylimidazolium hydrogen sulfate ILs [Hmim]HSO_4 (see Fig. 4) having good adsorption capacities for Pb (II) uptake in aqueous medium (Rufato et al., 2019). The [Hmim][HSO_4^-] used was recovered with the aid of rotary evaporator, characterized by ^{1}H-nmr and reused for the preparation of novel polysaccharide-based adsorbents. SEM image of CHT/ALG and DMC/ALG PECs revealed a porous non-homogeneous and compact structure. Obtaining PEC depends on temperature, pH and ionic strength of each resulting polyelectrolyte solution and molecular weights of the assembled polysaccharide-based material. Durable and compact structures' PEC are obtainable from a miscible polyelectrolyte blends in [Hmim][HSO_4^-] (Rufato et al., 2019). The adsorption studies was best described by pseudo-second-order kinetics and Redlich-Peterson isotherm, provide the best fits for the experimental data, respectively. q_{max} of 529.4 mg/g and 560.2 mg/g were obtained for CHT/ALG and DMC/ALG adsorbents respectively, and the adsorption process was chemisorption. The removal of Pb(II) was possible due to the occurrence of electrostatic interactions between the Pb(II) and the adsorbents (Rufato et al., 2019).

Patil et al. synthesized biodegradable and biocomposite materials from cellulose (microcrystalline cellulose (MCC)), guar gum (GG) and poly(vinyl alcohol) (PVA) in 1-butyl-3-methylimidazolium chloride (BmimCl). The effect of composition of GG and PVA contacted with MCC was evaluated by comparing the physical, chemical and mechanical properties of the prepared biocomposite films with the regenerated cellulosic films. The hardness and tensile strength of the biocomposite films is greater than that of the regenerated cellulosic film. The BmimCl used as a solvent in the synthesis of MCC/GG/PVA biocomposite material was removed from the biocomposite by washing with ethanol and recovering with the use of a rotary evaporator (Patil et al., 2018). The FTIR revealed a strong interaction between MCC, GG and PVA. The XRD revealed that cellulose/GG/PVA films exhibited lower crystallinity compared with raw cellulose, and the % crystallinity of MCC, GG and PVA was disrupted in the biocomposite. The mechanical characteristics of the prepared biocomposite films are higher than the regenerated cellulosic films (Patil et al., 2018).

A biocompatible cellulose/chitosan composite has also been prepared from BmimCl solvent and greater than 88 % of the ILs was recovered via distillation for reuse signifying that the method is recyclable. XRD, FTIR, NIR, ^{13}C CP-MAS-NMR and SEM were used to monitor the dissolution and to characterize the composites. The composite was reported to possess combined advantages including a superior mechanical strength and excellent adsorption capability for microcystin. The mechanical strength of the composites increased with an increase in cellulose loading. The kinetic of the adsorption process confirms that chitosan retains its unique properties in the composite. Also, the adsorbed microcystin was quantitatively desorbed, and the composite could be reused with similar adsorption efficiency for microcystin uptake (Tran et al., 2013).

A novel biodegradable collagen/cellulose hydrogel beads (CCHBs) was prepared by Wang et al. via reconstitution in 1-butyl-3-methylimidazolium chloride (BmimCl) solution (Wang et al., 2013) for the removal of Cu(II) ions. The adsorption features of CCHBs compared with cellulose hydrogel beads (CHBs) revealed a three-dimensional macroporous structure having amino groups as the main active binding sites for Cu^{2+} ions. The adsorption capacity of CCHBs is influenced by composition mass ratio of collagen/cellulose, which increases until the mass ratio of collagen/cellulose exceeds 2/1. BET surface area obtained for the prepared beads decreases with an increase in collagen/cellulose mass ratio, and was associated with the blocking of pores by collagen particles formed during reconstitution. The maximum adsorption for Cu (II) ions removal was obtained at pH 6. Meanwhile, Langmuir maximum adsorption capacity of CCHB3 (collagen/cellulose mass ratio of 3/1) is 1.06 mmol/g (Wang et al., 2013). Dai et al. also prepared cellulose dinitrobenzoate adsorbent in 1-butyl-3-methylimidazolium chloride ILs for the adsorption of creatinine in dialysate. The NMR analysis confirmed the grafting of 3,5-dinitrobenzoyl groups onto the cellulose backbone. The quantity of creatinine adsorbed onto cellulose dinitrobenzoate was 3.88 mg/g at 23 °C, pH 7.0, and creatinine concentration of 225 mg/L. The adsorption process conforms to Freundlich isotherm and pseudo-second-order kinetics. In comparison with traditional oral adsorbents, the cellulose dinitrobenzoate adsorbent was said to be biocompatible with a potential for adsorption of creatinine (Dai et al., 2015).

1-Allyl-3-methylimidazolium chloride (AmimCl) and 1-ethyl-3-methylimidazolium acetate (EmimAc) ILs have also been reported as suitable solvents for cellulose (Zhang et al., 2017). In comparison with BmimCl, the AmimCl and EmimAc possess lower melting point and less viscosity character, with a better dissolving capability. With the use of AmimCl or EmimAc as solvent, a solution holding up to 30 wt% cellulose with a high degree of polymerization was achieved within 30 min. Coagulation of cellulose/IL solutions in water leads to regeneration of high tensile strength cellulose fibres or transparent cellulose films. As reported by Zhang et al., cellulose/IL solution mixed with acetic anhydride give homogeneous acetylation without using a catalyst. Thus, cellulose acetates with a controllable degree of substitution were rapidly and simply synthesized (Zhang et al., 2017). A chitosan/porous carbon composite (C-PC) material modified in 1-allyl-3-methyl imidazolium bromide (AmimBr) has also been prepared for the adsorption of acid blue 25 from aqueous solution (Saheed et al., 2021b) and it adsorption capacity was compared with chitosan/activated carbon composite prepared in acetic acid. It was reported that the SEM images of C-PC show somewhat rough surfaces and cavities dominated with irregular shaped stone-like structure that differ from its precursors' micrograph. The

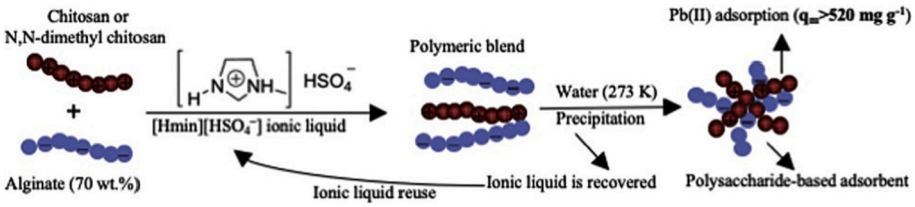


Fig. 4. Representation scheme of alginate/chitosan polyelectrolyte (PEC)-based adsorbents in [Hmim]HSO_4 (Rufato et al., 2019) (with permission Elsevier B.V.).

surface of C-PC was dominated by mesopores, and its hydroxyl and amino functional groups serves as primary adsorption sites for the uptake of acid blue 25 dye. Acidic medium was better for the adsorption of acid blue 25 onto C-PC (pH 2) and C-AC (pH 4) with qmax of 3333.33 mg/g and 909.90 mg/g respectively (Saheed et al., 2021b). Li et al. also prepared cellulose/chitosan hydrogel bead by extruding and regenerating the composite from 1-ethyl-3-methylimidazolium acetate ILs in ethanol (M. Li et al., 2016). BET analysis showed that the beads were porous with pores size range from 10 to 20 nm. The maximum adsorption capacity of 40 mg/g was obtained for the adsorption Congo red (CR) onto the bead from aqueous solutions. The adsorption was influenced by initial concentration of CR, dosage of beads and pH of the CR solution. The equilibrium adsorption was attained at 115 min, with the removal rate of 89.6 % for concentration of 30 mg/L and dosage of 2.0 g/L. The adsorption process followed Langmuir isotherm model and pseudo-second-order kinetic model (Li et al., 2016). The three-dimensional region of the chitosan crystalline structures has limited adsorption capability, and the metal ions could be adsorbed onto the amorphous region (Liu et al., 2012). The hydrogel form could improve the adsorption capacity by lowering the crystallinity of the chitosan (Liu et al., 2012), though poor mechanical strength and acidic resistance of hydrogel form limit its applications (Liu et al., 2012). A one-step process of preparation for magnetite cellulose–chitosan hydrogels microspheres has been made in ILs, and the prepared magnetic hybrid hydrogels had affinity for various metal ions (Cu(II), Fe(II), and Pb(II)), and could be recycled and reused (Liu et al., 2012).

Porous cellulose spheres (PCS) have been prepared by Ma et al. in BmimCl solution by precipitating cellulose spheres from a cellulose ILs solution, subsequently followed by freezing, solvent exchange and drying (Ma et al., 2016). Meanwhile, oven drying was utilised to prepare the solid cellulose spheres (SCS). The characterization conducted revealed that BmimCl disrupt the crystallinity and hydrogen bonding network in cellulose, while the ice particles created porous structure. A low crystallinity and large surface area observed in PCS was said to have facilitated its successful modification with trisodium trimetaphosphate (STMP), which introduce the phosphate ester groups into the porous structure. The STMP-modified PCS (SPCS) were used to remove heavy metal ions from aqueous solution and the mechanism of the sorption is presented in Fig. 5. Pb^{2+} ions diffused easily into the phosphate ester functionalized-cellullose walls through the pores. The sorption kinetics and isotherm model fitted into pseudo-second order and Langmuir model respectively, and maximum adsorption capacity of 150.6 mg/g was obtained for SPCS (X. Ma et al., 2016).

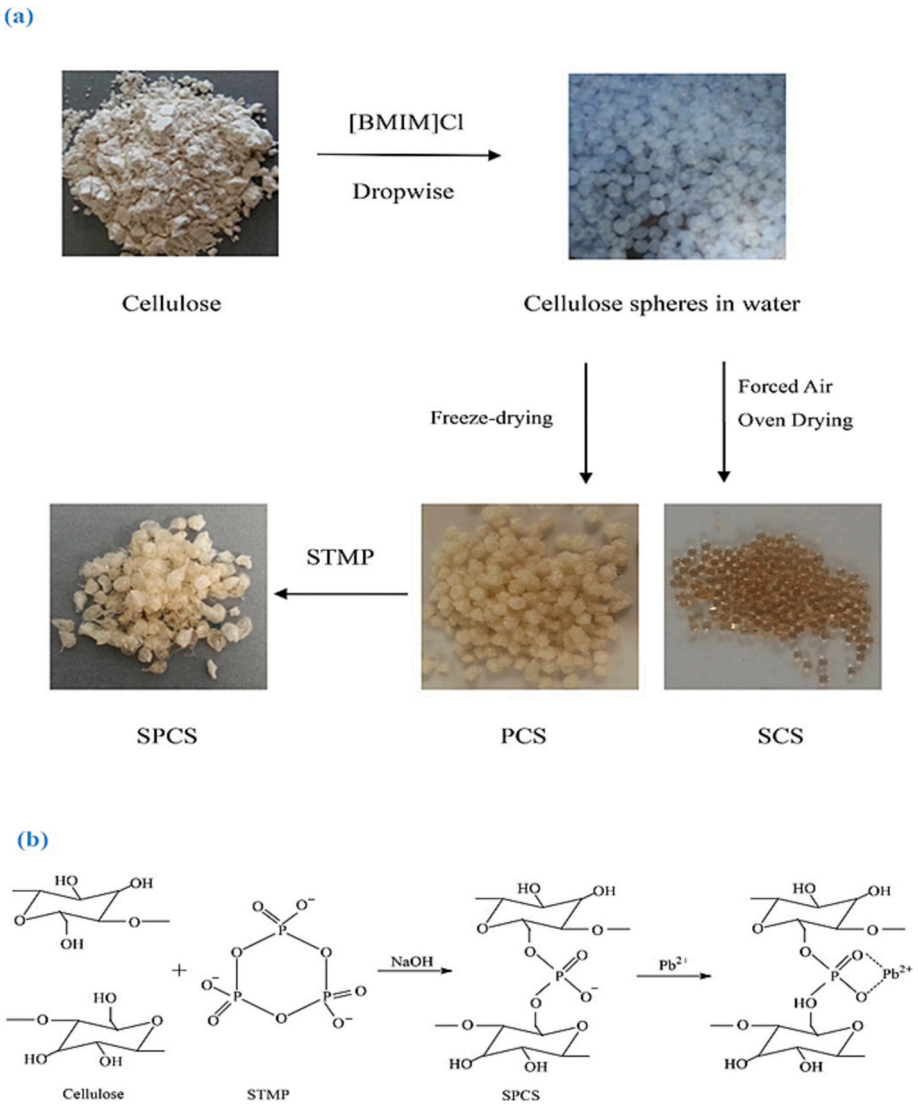


Fig. 5. (a) Preparation route and photograph images of SCS, PCS and SPCS; (b) Mechanism for modification of PCS and sorption of Pb^{2+} ions (Ma et al., 2016) (with permission Elsevier B.V.).

2.3. ILs modified polysaccharides adsorbents

ILs retains its main properties when being immobilized on organic polymer for the purpose of material applications (Fig. 6). Therefore, ILs-modified sorbent materials have been successfully utilised in separation science field owing to their certain characteristics such as level of hydrophobicity, dispersibility in organic/inorganic solvents, H–bonding, π–π interactions, dipole–dipole interactions, electrostatic interactions between analytes, and the functional groups of ILs (Yan, Gao, et al., 2014). Various ILs had been widely utilised to functionalise and improve the adsorptive characters of various polysaccharides for adsorption and solid-phase extraction applications (Isosaari et al., 2019; Zhang et al., 2018; Zhu et al., 2019). The modification processes including grafting and blending of ILs (such imidazolium based) onto polymers has been utilised to enhance the adsorptive feature of polymer-based adsorbents including the polysaccharides-based (Jiang et al., 2015; Tang et al., 2021; Zhu et al., 2019). In addition, the introduction of some ILs such as 1-allyl-3-methylimidazolium chloride to fabricate copolymer hydrogels have been reported to improve the hydrophilic property of copolymer hydrogels and as well increased the ionic conductivity of macromolecule (Jiang et al., 2015). The transport characters of ILs modified composites have also been investigated (Therattil & Kumar, 2020), and the quantity of the ILs offered specific role in diffusion parameters' determination such as solvent uptake, as well as diffusion and permeation parameters. Increasing the amount of IL leads to an increase in the diffusion of solvents as a result of the fine dispersion of CNTs in the NR nanocomposites. The plasticizing effect of the IL also lead to increase in the free volume in the nanocomposite, with the findings supported by SEM, TEM and positron annihilation lifetime spectroscopy (PALS) analysis (Therattil & Kumar, 2020). Magnetic chitosan and graphene oxide-ionic liquid (MCGO-IL) has been synthesized by impregnating magnetic chitosan and graphene oxide with IL. The MCGO-IL displayed extraordinary removal efficiency and rapid rate of adsorption of Cr(VI) in water due to the high surface area and abundant functional groups gained by the fabricated MCGO-IL adsorbent. Mechanical stability and strength of the adsorbents were considered suitable for metal ion adsorption (Li et al., 2014).

2.3.1. Imidazolium ILs-modified polysaccharides for adsorption application

Modification using imidazolium-based ILs offers attractive features for polymer-based adsorbents including the polysaccharide-based adsorbents for adsorption application. A novel ionic liquid modified copolymer hydrogel was successfully synthesized by a simple water solution copolymerization using acrylamide, dimethyldiallylammonium chloride and ionic liquid 1-allyl-3-methylimidazolium chloride; AmimCl as copolymerization monomers (Table 2). The modification of AmimCl significantly enhanced Cr (VI) adsorption and the energy of adsorption indicate a physisorption process (Jiang et al., 2015). IL (1-butyl-3-methylimidazolium chloride) loaded onto the surface of a polymeric β-cyclodextrin/toluene-2,4-diisocyanate adsorbent (βCD-TDI) grafted with modified magnetic nanoparticles (MNPs) was synthesized by Yusoff et al. for effective removal of selected parabens. The characterization results obtained for SEM and TEM revealed that the distribution of the mesoporous pore size on the material with a small surface area (BET analysis: 42.95 m^2/g) (Yusoff et al., 2018). The sorption experiment revealed an enhance sorption capacity for the removal of propyl, butyl, and benzyl parabens and the process is pH dependent with optimum at pH 6, and equilibrium time of 80 min (Yusoff et al., 2018). The host–guest inclusion complex interactions and the π–π interaction between βCD and benzyl paraben were identified via ^1H NMR and UV–vis spectroscopic analysis (Yusoff et al., 2018).

An ionic liquid-ferrofluid based adsorption/preconcentration of Cd over magnetic CMK–chitosan composite modified using 1-hexyl-3-methylimidazolium tetrafluoroborate IL has been investigated (Yadaei et al., 2018). A significant factor studied with respect to Cd adsorption using response surface methodology (Box – Behnken design) showed that solution pH, contact time, adsorbent dose and ionic strength were significant factors on cadmium adsorption. The maximum adsorption capacity of magnetic CMK and magnetic CMK – chitosan composite were 180 mg/g 251.9 mg/g respectively. The results obtained for the cadmium adsorption/preconcentration from the real samples revealed the efficiency of the process for Cd monitoring in complex matrices (Yadaei et al., 2018).

It has been reported (Xu et al., 2015) that IL functionalized cellulose cotton has been prepared for efficient adsorption of Cu(II) and Ni(II) ions. The adsorbent was prepared using 1-N-butyl-3-methylimidazolium chloride IL via a ring opening polymerization mechanism to develop

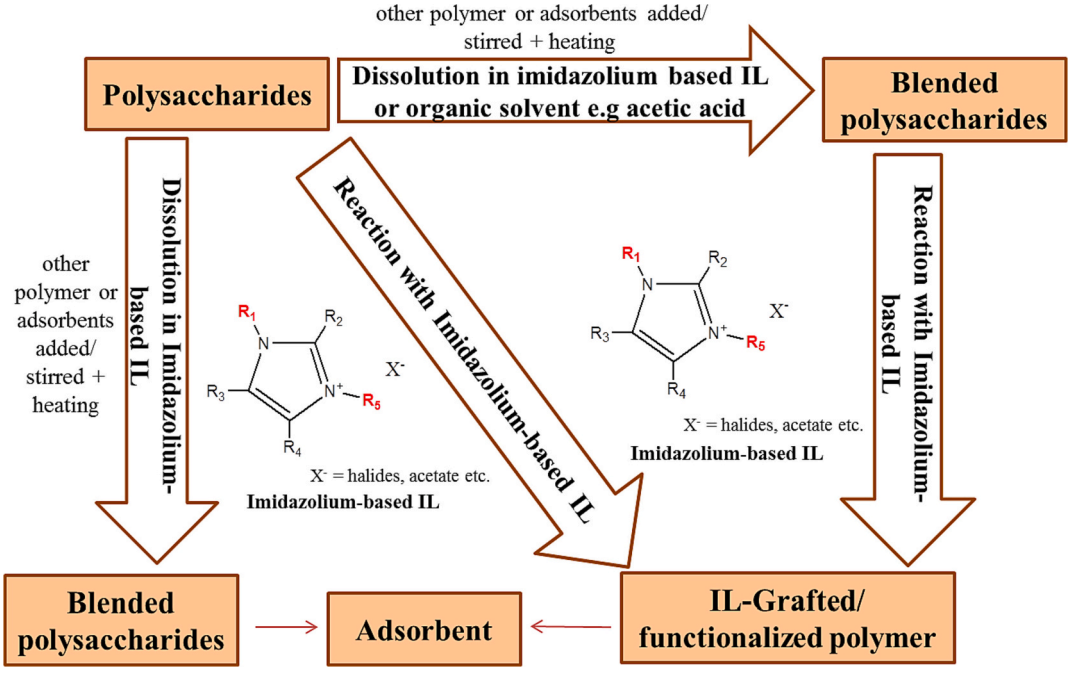


Fig. 6. Schematic preparation steps for imidazolium ILs polysaccharides-based adsorbents.

Table 2
Adsorption capacity reported in the literature for some imidazolium-based IL-modified adsorbents.

Adsorbent	ILs incorporated	Surface area (m^2/g)	Adsorbate	q_e (mg/g)	Reusability	References
Cellulose/chitosan macrospheres	BmimAc; EmimAc	59.0 4.3	Cu(II)	26.7 15.8		(Alexandra et al., 2020)
Magnetic chitosan and graphene oxide-ILs composite	Polyallyl-3-methylimidazolium		Cr(VI)	145.35	6th cycle	(Li et al., 2014)
IL-MNP-βCD-TDI	BmimCl	42.95	Propyl parabens	18.48	5th cycle	(Yusoff et al., 2018)
ILs functionalized cellulose	1-Aminopropyl-3-methyl imidazolium nitrate		Cr(VI)	181.8	6th cycle	(Dong & Zhao, 2018)
ILFC-NO_3	1-Aminopropyl-3-methyl imidazolium nitrate		Re(VII)	581	4th cycle	(Dong et al., 2020)
Nanohybrid adsorbent	1-Octyl-3-vinylimidazole bromide		Morphine, codeine	7.2, 8.4	6th cycle	(Tang et al., 2021)
A novel chitosan adsorbent (CS-MEIC)	MEIC		Re(VII)	185	5th cycle	(Lou et al., 2018)

copolymers of polycaprolactone grafted cellulose cotton (CPL), with various compositions for the grafting. The modified adsorbent material was amorphous compared to cellulose. An increase in surface roughness was observed from the SEM images attributed to the chains grafted onto the cotton material as reported with desirable features for enhanced metal removal. The effectiveness of CPL was observed as a result of high uptake for Cu(II) Ni(II) ions. The results of adsorption revealed that the selectivity sequence of the metal ions on graft copolymers was Cu(II) > Ni(II), and the maximum removal capacities Cu(II) (98.7 %) is higher than that of Ni(II) (35.6 %) ions (Xu et al., 2015).

Sorption interfacial interaction mechanisms of *p*-arsanilic acid (*p*-ASA) onto IL modified cellulose materials were systematically investigated by Peng et al. through the sorption models, spectroscopy determination, and the use of density functional theory calculations (Peng et al., 2021). The adsorption experiments revealed that the modified cellulose materials exhibited relatively high adsorption capacity (216.9 mg/g) with a rapid rate of adsorption (3.21×10^{-3} g mg^{-1} min^{-1}) towards *p*-ASA with good reusability. Adsorption model applied revealed a multilayer adsorption process dominated by the adherence of the adsorbates molecules onto the active site. The influence of environmental factors on *p*-ASA removal and spectroscopy determination revealed that outer-sphere complexes are formed through hydrogen bonding and π-π interaction between *p*-ASA and the adsorbent. The density functional theory calculation and independent gradient model analysis utilised for understanding the interfacial interaction mechanism showed that hydrogen bonding played significant and leading role in the adsorption process and the imidazole group was the preferential adsorption site (Peng et al., 2021). The x-ray photoelectron spectroscopy (XPS) results of the IL modified cellulose (MP-3) containing poly (vinylimidazole) to cellulose in mass ratio 2:1, *p*-ASA and *p*-ASA adsorbed onto MP-3 (see Fig. 7) confirms adsorbate-adsorbent interactions. 3d peak appeared at 55 eV after adsorption, whereas Cl 2p still observed in the spectrum with a slight change from 2.65 % to 2.25 % in the Cl content, indicating that the ion-exchange between *p*-ASA and Cl^- is negligible. Meanwhile, the C 1s spectrum revealed a decrease in the C—OH and C—O—C contents, while the C—N and C—C contents increased, suggesting π-π interactions between *p*-ASA and MP-3 (Peng et al., 2021).

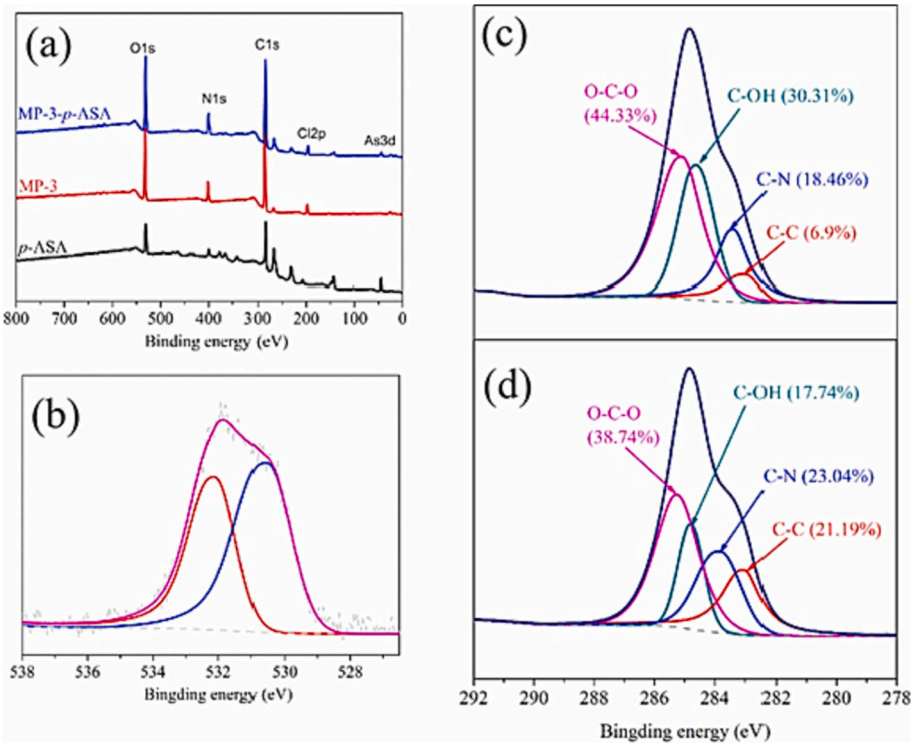


Fig. 7. XPS of *p*-ASA, MP-3 before and after adsorption of *p*-ASA (a), high resolution O 1s spectrum of *p*-ASA (b), and high resolution C 1s before (c) and after (d) *p*-ASA adsorption on MP-3 (Peng et al., 2021) (with permission Elsevier B.V.).

A chitosan-based adsorbents (CS-MEIC) modified with imidazolium-based ILs (1-(2,3-epoxypropyloxy)-3-methylimidazolium chloride (MEIC), and its ethylimidazolium (ETIC) and butylimidazolium (BUIC) derivatives) was prepared by Lou et al. (see Fig. 8) for efficient adsorption of Re(VII). CS-MEIC shows higher adsorption capacity for Re (VII) when CS-MEIC prepared by adding 0.3 g of chitosan with *N*-methyl imidazole/epichlorohydrin ratio 1:2 was used. Langmuir monolayer models best described the adsorption process with maximum adsorption capacity of 185 mg/g, also pseudo-second-order kinetic model describe the process well. Re(VII) adhered to CS-MEIC through anion exchange which was confirmed by FTIR, ion chromatography and X-ray photoelectron spectroscopy analysis. There was a good selectivity for Re(VII) compared to coexisting metal ions Mn^{2+}, Fe^{3+}, Cu^{2+}, and Zn^{2+}. CS-MEIC was utilised up to five adsorption-elution cycles suggesting that the adsorbent possess good durability and efficiency (Lou et al., 2018). The SEM images of chitosan and CS-MEIC revealed observable differences in their morphology, with the CS-MEIC showing a crumpled texture with more pronounce aggregated and corrugated morphologies in comparison with chitosan. Therefore the changes in morphology would suggest successful grafting of imidazolium-based IL onto chitosan.

A non-toxic biocompatible starch, having abundant O—H groups was incorporated with 1-butyl-3-methyl-imidazolium tetrafluoroborate IL ($BmimBF_4$) to augment the tuning of macromolecules into fibres, including enhancement of its hydrophilicity using polyvinyl alcohol (PVA) that could interact with starch through hydrogen bonding (Khurana & Balasubramanian, 2016). The sorption competency of ion imprinted starch/PVA/IL nanofibers, and molecular simulation to ascertain inter-polymer miscibility parameters and compatibility, using Materials Studio software, for effectual radioactive thorium ion exclusion. Experimental statistics obtained suggested high sorption efficacy (87 %) at pH 7, adsorbent dose 0.5 g, with best agreement with Langmuir isotherm model, among 2 parameter and 3 parameter models, and a close resemblance to pseudo second order kinetics. A monolayer sorption mode with chemisorption as rate restraining step was suggested. It was reported that the interaction between Starch-PVA estimated Chi parameter and mixing energy (kcal/mol) was 1.63 and 1.90, respectively, revealing better compatibility for Starch-$BmimBF_4$ blend (Khurana & Balasubramanian, 2016).

2.3.2. *Imidazolium ILs-modified polysaccharides for solid-phase extraction*

Solid-phase extraction (SPE) is among the most widely used methods for analyte pre-concentration. Common adsorbents such as silica, aminopropyl, and Al_2O_3–N, are limited due to lack of specific recognition for analytes in complex samples and this has attracted more attention towards the development of specific adsorbent for SPE (Yan, Yang, et al., 2014). ILs being molten salts with organic cation and inorganic/or organic anion has been utilised for the modification polymer to enhance its affinity and selectivity for SPE application (Table 3). The mechanism of separation of IL-based materials often entails multiple interactions like electrostatic, H-bonding, π–π interaction and ion exchange (Yan, Yang, et al., 2014). In addition, advantageous material with combined features involving magnetic polymers and ILs together have as well been prepared for SPE application (Yan, Gao, et al., 2014; Yan, Yang, et al., 2014).

Cyclodextrins (CDs) are cyclic oligosaccharides with a torus-shape containing six to eight glucose units (Raoov, Mohamad, Bin Abas, et al., 2014). Cyclodextrin-IL polymer (βCD-BIMOTs-TDI) has been prepared as macroporous adsorbent materials for SPE applications featuring extraction of contaminants (Raoov, Mohamad, Bin Abas, et al., 2014). Six phenols were extracted onto βCD-BIMOTs-TDI SPE cartridge, eluted with 2 mL of methanol/1 % acetic acid. A high sensitivity with detection limits of 0.23–0.35 mg/L and good recoveries 87–116 % were obtained under optimum condition 15 mL sample volume (sample at pH 6) and 2 mL of methanol/1 % acetic acid eluent solvent (Raoov, Mohamad, Bin Abas, et al., 2014). The βCD-BIMOTs-TDI adsorbent offers advantages, such as good sorption efficiency towards phenols, good compatibly with various kinds of solvents, good repeatability, with no impact on sorbent drying (Raoov, Mohamad, Bin Abas, et al., 2014). As reported (Bakheet et al., 2016), direct method of trace analyte determination at ultra-trace concentration is difficult to achieve in complex systems through UV–visible spectrometry due to its low sensitivity and selectivity. An effective separation step is often needed prior to the analyte determination (Bakheet et al., 2016). A magnetic solid-phase extractor based on magnetic carboxymethyl-hydroxypropyl-β-cyclodextrin polymer-Fe_3O_4 functionalized with imidazolium IL (Fe_3O_4@IL-CM-HP-β-CDCP) has been developed (Bakheet et al., 2016) for a selective separation of linuron prior to its determination via UV–visible spectrometry, and the successful fabrication was confirmed by FTIR,

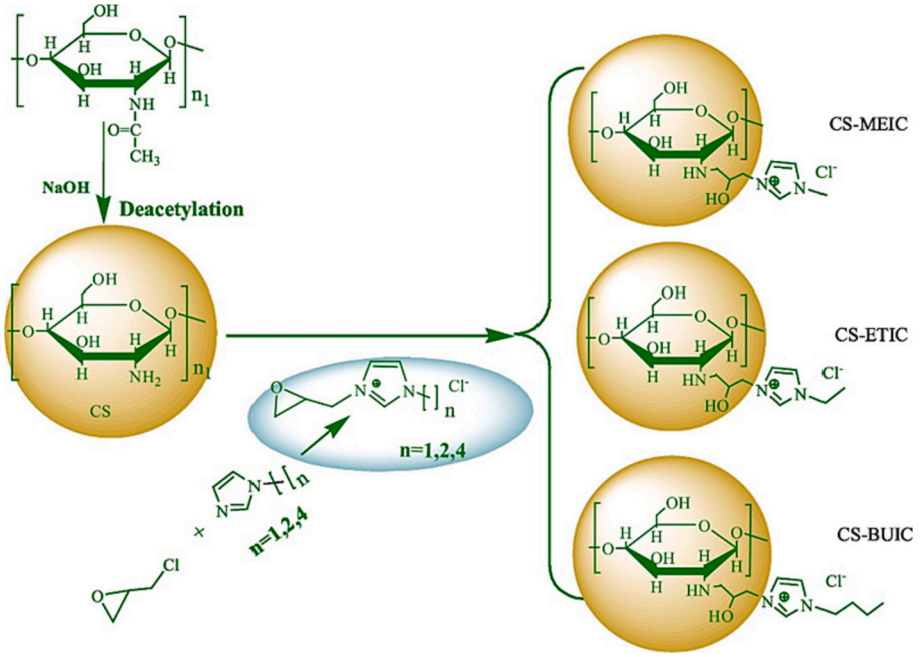


Fig. 8. Preparation route of chitosan-based adsorbents modified by imidazolium-based ILs (Lou et al., 2018) (with permission Elsevier B.V.).

Table 3
Summary of some literature work on imidazolium-based IL-modified adsorbent for solid-phase extraction.

Solid-phase adsorbent	ILs incorporated	Surface area (m^2/g)	Contaminant	Detection limit	Recovery	References
Macroporous β-Cyclodextrin-ionic liquid polymer	1-Benzylimidazole	1.254	Phenol	0.23–0.35 mg/L	87–116 %	(Raoov, Mohamad, Bin Abas, et al., 2014)
ILs-modified polymer	EmimBr	3.468	Cyanazine and triazine	0.51 and 0.35 ng/mL	72.0–95.1 %	(Han et al., 2013)
IL-modified phenolic resin	Imidazolium-based		Thidiazuron and forchlorfenuron	1.69–1.95 ng/g	91.4–100.7	(Li et al., 2020)
Cyclodextrin-ionic liquid polymer	1-Benzylimidazole	1.254	2,4-Dichlorophenol			(Raoov et al., 2013)
β-Cyclodextrin polymer/Fe_3O_4 composites	$[C_8mim]PF_6$		linuron	7.0 gL^{-1}		(Bakheet et al., 2016)
ILs modified cationic starch	BmimBr		Th(IV)		98.0–100 %	(Bursali et al., 2016)

SEM and XRD. The uptake behavior of the new Fe_3O_4@IL-CM-HP-β-CDCP MNPs adsorbent towards linuron was studied. Adsorption study revealed the Fe_3O_4@IL-CM-HP-β-CDCP MNPs for a selective separation of linuron prior to its determination by UV–visible spectrometry. Rapid uptake of linuron onto Fe_3O_4@IL-CM-HP-β-CDCP MNPs was reported with elution by 4.0 mL ethanol in 15 min. The limit of detection, limit of quantification, correlation coefficient and preconcentration factor were 7.0 g/L, 70.0 g/L, 0.9987 and 15 respectively (Bakheet et al., 2016).

Imidazolium-based ILs have also utilised as additives in polymerization process in order to improve the performance of molecular imprinted polymers (Liu et al., 2021). For instance, He et al. prepared imprinted membrane of cellulose acetate blend with BmimCl as an additive for the selective adsorption of salicylic acid from industrial wastewater. It was presented that the blend showed better hydrophilicity and permeation selectivity compare to membrane because the IL used as additive made the membrane to form more ordered and denser porous structure (He et al., 2015).

A highly selective polymer imprinted membranes of cellulose acetate (CA) blend was prepared by He et al. for selective adsorption of salicylic acid (SA) by using phase inversion technique. The sulfonated polysulfone (SPS) was used as a functional polymer, polyethylene glycol-4000 (PEG 4000) and BmimCl as the additives. The SEM imaging revealed the cross-sectional morphology of CA membranes with polymer blend composition and additives influences the morphology. The fabricated BmimCl-modified membranes showed low contact angle, high membrane flux, strong adsorption capacity and high permeation selectivity. The adsorption kinetic studies fitted to the pseudo-second-order kinetic model using multiple regression analysis. The selectivity coefficients of CA/SPS(90/10) + BmimCl-MIM for SA in relation to competition analogs p-hydroxybenzoic acid and phenol were 5.8549 and 5.9062, respectively, which suggested that CA/SPS(90/10) + BmimCl-MIM had high selectivity and binding affinity for the template SA. The overall results suggest that BmimCl can be considered as an effective additive for CA imprinted membranes in the treatment of SA-contained (He et al., 2015).

Imidazolium ILs were impregnated into cationic starch by Bursali et al. to fabricate adsorbents for extraction of Th(IV). Cationic starch (CS) was prepared by mixing potato starch with epichlorohydrin (EPI) and 3-chloro-2-hydroxypropyltrimethyl-ammonium chloride (CHPTMA) in alkali medium of NH_4OH (25 % solution) and NaOH. Thereafter, 1-butyl-3-methylimidazolium ILs with different anionic groups BF_4^-, Br^-, PF_6^-, TF_2N^- were impregnated onto CS. Th(IV) were preconcentrated using the various ILs impregnated CS. Th(IV) was preconcentrated with ~73 % sorption capacity by CS and was found to increase up to 98 %–100 % for butyl-3-methylimidazolium ILs impregnated sorbents at pH 7.0. The sorption capacities of Th(IV) were 0.453, 0.399, 0.281, and 0.183 mmol/g for CS–BmimBr, CS–BmimTF_2N, CS–BmimPF_6^- and CS–BmimBF_4^-, respectively, and the elution occurred with NaOH and HCl solutions at pH 7.0 (Bursali et al., 2016).

2.4. Structure of ILs modified polysaccharides and adsorption performance

Investigation into the structural, morphological and thermal properties of the ILs modified polysaccharides adsorbents have been assessed (Li et al., 2016; Peng et al., 2021; Stanton et al., 2018; Stefanescu et al., 2020). Findings have revealed that ILs have strong influence on the structure of polysaccharides adsorbents, and could be modified into amorphous or semicrystalline structures (Stanton et al., 2018). The thermal properties of ILs modified polysaccharides adsorbents are independent of the type of cation of ILs, but the levels of the β-sheet configuration are dependents on the type of anion, and could change the bio-composite thermal properties (Stanton et al., 2018). Considering the use of imidazolium ILs as solvent for the modification of polysaccharides, the thermal stability of the polysaccharide derivatives have also proven to depends mainly on the anion of the IL. Stefanescu et al. revealed through the modification of chitosan in BmimAc that the phthalated chitosan exhibited a lower thermal stability than that of chitosan, meanwhile when the BmimCl was used as solvent, the thermal stability of the phthalated chitosan increased, indicating an interference of the ionic solvents in the mechanisms of reaction (Stefanescu et al., 2020). FTIR spectra of various imidazolium ILs modified polysaccharides often shows O—H stretching within 3700–3100, as certain hydroxyl groups of the polysaccharide are retained after modification with imidazolium based IL, which are useful for electrostatic interactions and hydrogen bonding with contaminants containing polar functional group (Chen et al., 2011; Raoov, Mohamad, & Abas, 2014; Wang et al., 2019; Xu et al., 2015).

There is a correlation between the structures of imidazolium-based ILs with the adsorption performance of imidazolium ILs modified polysaccharides. The length of the carbon chain and isomers of ILs has influence on the capture ability of the modified polysaccharides adsorbents. Huang et al reported that the alkyl chain length substituents 4, 6, 8, 10 and 12 carbons of the imidazolium IL modified adsorbent exhibit good adsorption performance at pH 3–7 for adsorption Re(VII), with that of 8 carbon length chain having highest adsorption percentage in a wider pH range 1–7 (Huang et al., 2021). Hydrophobicity of the imidazolium modified adsorbents and their contact angle increases with increase in the alkyl chain length (Huang et al., 2021) which influences their electrostatic interactions with either polar and non-polar adsorbate molecules.

The effect of conjugation in the imidazolium based IL-modified polysaccharides has been investigated, and the conjugation could be confirmed using ^1H NMR and FT-IR analysis (Wei et al., 2013). Modified polysaccharides conjugation prepared through amidation reaction of chitosan with carboxylic acid-functionalized imidazolium ILs revealed good anion adsorption performance (adsorption capacities of 0.422 mmol/g and 0.840 mmol/g for $Cr_2O_7^{2-}$ and PF_6^- respectively), which were related to degree of substitution. Higher degree of substitution degree leads to better adsorption, and could be ascribed to adsorption of IL. The anion adsorption may also be improved at low pH as a result of

protonation of amino group of chitosan. The modified chitosan based polysaccharides would aggregate in the water after the adsorption for separation. As reported, these characteristics would enable conjugated imidazolium based-IL polysaccharides to be utilised as a novel anion adsorbent for wastewater treatment (Wei et al., 2013)..

The amount of polysaccharide in imidazolium-ILs modified polysaccharide has been shown to have effect on their adsorption performance. For instance, adsorption of Re(VII) onto imidazolium-ILs modified chitosan had been explored (Lou et al., 2018). As the amount of chitosan in the adsorbent matrix increases, the adsorption efficiency was found to decreases despite the increased nitrogen content. Therefore, it was suggested that the nitrogen on the chitosan was not a good binding site for Re(VII). The variation in the amount of imidazolium and epichlorohydrin (ECH) under a fix amount chitosan (0.3 g) gave highest adsorption efficiency (99.03 %) at pH 3 when the volume ratio of imidazole to ECH was 1:2. It was revealed that an increase in imidazolium content which corresponds to a nitrogen content increment from 7.32 % to 7.58 % resulted into increased adsorption efficiency from 60.01 % to 99.03 %. This could be attributed to higher content of imidazolium-based IL grafted onto chitosan, and an indication that the nitrogen on the imidazolium group of the modified chitosan possess affinity for Re(VII) (Lou et al., 2018).

3. Conclusion and future trends

3.1. Conclusion

Recent trends in the use of ILs for the fabrication of polysaccharides-based adsorbents involved the use of the ILs as either solvent or as a component of the adsorbent. The polysaccharides that have been extensively modified as adsorbent using ILs in the past few decades are cellulose and chitosan. Their respective adsorbents have shown good adsorptive features such as high surface area and good porous system after modification with ILs. The imidazolium based-ILs are the most applied type of the ILs for polysaccharides modification into various adsorbents, with more attention on hydrophilic imidazolium-based (such as EmimCl and BmimCl) due to their good solvent properties link to thermal stability and solvation capability; and also their ease of preparation and cost effectiveness. The mechanism of separation of ILs-based materials often entails multiple interactions like electrostatic, H-bonding, π–π interaction and ion exchange. The fabrication of polysaccharides into beads, films, microspheres, sponges, hydrogel and aerogels have also been possible using imidazolium based-ILs. The imidazolium based ILs-modified polysaccharides often show good thermally stability and their fabricated adsorbents characteristics are influenced by the cation and anion group of the imidazolium-based ILs. Literature surveys revealed that, incorporation of imidazolium based-ILs into polysaccharides to fabricate adsorbents with enhanced adsorptive characters proceeds via covalent linkages.

3.2. Future trend

It has been established in the literature that ILs are “green chemicals”, and researchers have intensified effort on the use of ILs for the modification of polysaccharides-based adsorbents including their hybrid adsorbents prepared via incorporation of inorganic materials. However, biodegradability and biocompatibility studies of polysaccharides-based adsorbents, most especially the hybrid adsorbents involving polysaccharides/inorganic material composites have not been exclusively investigated. Further investigation of the biodegradability and biocompatibility studies of polysaccharides-based adsorbent could give further information of the minimizing secondary pollutants generated from spent adsorbents.

Polysaccharides-based adsorbent fabricated from biopolymer such as cellulose and chitosan have been prepared in imidazolium-based ILs with cation and anion group. Further investigations into the influence of various anion and cation of imidazolium-based ILs on the surface characteristics of adsorbents as regards to its adsorptive features are critically required. Investigation into the potentials of ILs modified natural polymer-based adsorbents with improved surface characteristics for the removal of body fluid from wound could be thoroughly studied. In recent time also, imidazolium-based poly (ILs) are being prepared as novel adsorbent. However, applications of imidazolium-based poly (ILs) into modification of polysaccharides based adsorbent have not been extensively studied and could be investigated.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

Acknowledgements

Ismaila O. Saheed wishes to acknowledge the financial Support from Tertiary Education Trust Fund (TETfund), Nigeria. In addition, University Sains Malaysia's Graduate Assistant Scheme is as well acknowledged.

References

Ahmad, M., Manzoor, K., & Ikram, S. (2017). Versatile nature of hetero-chitosan based derivatives as biodegradable adsorbent for heavy metal ions; A review. *International Journal of Biological Macromolecules, 105*, 190–203. https://doi.org/10.1016/j.ijbiomac.2017.07.008

Akpomie, K. G., & Conradie, J. (2020). Advances in application of cotton-based adsorbents for heavy metals trapping, surface modifications and future perspectives. *Ecotoxicology and Environmental Safety, 201*, Article 110825. https://doi.org/10.1016/j.ecoenv.2020.110825

Alexandra, S. M. W., Bohler, H., Kayali, A. L., & Mathias, U. (2020). One-step preparation of porous cellulose / chitosan macro- spheres from ionic liquid-based solutions. *Cellulose, 27*, 5689–5705. https://doi.org/10.1007/s10570-020-03165-y

Alzaydien, A. S., & Manasreh, W. (2009). Equilibrium, kinetic and thermodynamic studies on the adsorption of phenol onto activated phosphate rock. *International Journal of Physical Sciences, 4*(4), 172–181. http://www.academicjournals.org/IJPS.

Arora, R. (2019). Adsorption of heavy metals-a review. *Materials Today: Proceedings, 18*, 4745–4750. https://doi.org/10.1016/j.matpr.2019.07.462

Awang, N. A., Norharyati, W., & Salleh, W. (2019). Adsorption of cesium from aqueous solution using chitosan beads. *Journal Teknologi, 2*, 135–140. https://doi.org/10.11113/jt.v81.11514

Bakheet, A., Liu, J., & Zhu, X. (2016). New magnetic solid phase extractor based on ionic liquid modified β-cyclodextrin polymer/Fe3O4 nanocomposites for selective separation and determination of linuron. *Journal of Analytical Science and Technology, 7*(4). https://doi.org/10.1186/s40543-016-0082-9

Batool, F., Akbar, J., Iqbal, S., Noreen, S., Nasir, S., & Bukhari, A. (2018). Study of isothermal, kinetic, and thermodynamic parameters for adsorption of cadmium : An overview of linear and nonlinear approach and error analysis. *Bioinorganic Chemistry and Applications, 2018*(3463724), 11. https://doi.org/10.1155/2018/3463724

Bhatnagar, A., & Sillanpää, M. (2009). Applications of chitin- and chitosan-derivatives for the detoxi fi cation of water and wastewater — A short review. *Advances in Colloid and Interface Science, 152*(1–2), 26–38. https://doi.org/10.1016/j.cis.2009.09.003

Bursali, E. A., Bozkurt, S. S., & Yurdakoc, M. (2016). Impregnation of different ionic liquids onto cationic starch and their comparison in the extraction of Th(IV). *Turkish Journal of Chemistry, 40*, 364–372. https://doi.org/10.3906/kim-1506-65

Chen, Q., Xu, A., Li, Z., Wang, J., & Zhang, S. (2011). Influence of anionic structure on the dissolution of chitosan in 1-butyl-3-methylimidazolium-based ionic liquids. *Green Chemistry, 13*, 3446–3452. https://doi.org/10.1039/c1gc15703e

Chen, S., Fu, J., Fu, Z., Li, Y., Su, X., Zou, L., He, L., Liu, S., Ao, X., & Yang, Y. (2020). Preparation and characterization of magnetic molecular imprinted polymers with ionic liquid for the extraction of carbaryl in food. *Analytical and Bioanalytical Chemistry, 412*(5), 1049–1062. https://doi.org/10.1007/s00216-019-02330-y

Cho, C. W., Pham, T. P. T., Zhao, Y., Stolte, S., & Yun, Y. S. (2021). Review of the toxic effects of ionic liquids. *Science of the Total Environment, 786*, Article 147309. https://doi.org/10.1016/j.scitotenv.2021.147309

Clough, M. T., Kuzmina, O., & Welton, T. (2016). Enhancing the stability of ionic liquid media for cellulose processing : Acetal protection. *Green Chemistry, 18*, 3758–3766. https://doi.org/10.1039/c6gc00027d

Correia, D. M., Fernandes, L. C., Martins, P. M., García-astrain, C., Costa, C. M., Reguera, J., & Lanceros-méndez, S. (2020). Ionic liquid – polymer composites : A new platform for multifunctional applications. *Advanced Functional Materials, 1909736*, 1–43. https://doi.org/10.1002/adfm.201909736

Crini, G. (2006). Non-conventional low-cost adsorbents for dye removal : A review. *Bioresource Technology, 97*, 1061–1085. https://doi.org/10.1016/j.biortech.2005.05.001

Crini, G. (2005). Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. *Progress in Polymer Science, 30*, 38–70. https://doi.org/10.1016/j.progpolymsci.2004.11.002

Cvjetko Bubalo, M., Radošević, K., Radojčić Redovniković, I., Halambek, J., & Gaurina Srček, V. (2014). A brief overview of the potential environmental hazards of ionic liquids. *Ecotoxicology and Environmental Safety, 99*, 1–12. https://doi.org/10.1016/j.ecoenv.2013.10.019

Dai, Q., Ren, J., Kong, W., Peng, F., & Meng, L. (2015). Adsorption kinetics and thermodynamics of cellulose dinitrobenzoate prepared in ionic liquid for the removal of creatinine. *Bioresources, 10*, 3666–3681.

Dong, Z., Wen, D., Zhang, M., Xie, K., Hua, R., & Zhao, L. (2020). Recovery of rhenium (VII) from synthetic leaching solutions of uranium ore using ionic liquid modified cellulose microsphere adsorbents. *Hydrometallurgy, 197*, Article 105457. https://doi.org/10.1016/j.hydromet.2020.105457

Dong, Z., & Zhao, L. (2018). Covalently bonded ionic liquid onto cellulose for fast adsorption and efficient separation of Cr(VI): Batch, column and mechanism investigation. *Carbohydrate Polymers, 189*(February), 190–197. https://doi.org/10.1016/j.carbpol.2018.02.038

Fallah, Z., Nazarzadeh, E., Ali, M., Iftekhar, S., Ghomi, M., Sharifi, E., Tajbakhsh, M., Nikfarjam, N., Makvandi, P., Lichtfouse, E., Sillanpaa, M., & Varma, R. S. (2021). Ionic liquid-based antimicrobial materials for water treatment, air filtration, food packaging and anticorrosion coatings. *Advances in Colloid and Interface Science, 294*, Article 102454. https://doi.org/10.1016/j.cis.2021.102454

Ferreira, T. A., Rodriguez, J. A., Paez-Hernandez, M. E., Guevara-Lara, A., Barrado, E., & Hernandez, P. (2017). Chromium(VI) removal from aqueous solution by magnetite coated by a polymeric ionic liquid-based adsorbent. *Materials, 10*(5). https://doi.org/10.3390/ma10050502

Gao, H., Kan, T., Zhao, S., Qian, Y., Cheng, X., Wu, W., Wang, X., & Zheng, L. (2013). Removal of anionic azo dyes from aqueous solution by functional ionic liquid cross-linked polymer. *Journal of Hazardous Materials, 261*, 83–90. https://doi.org/10.1016/j.jhazmat.2013.07.001

Gomez-maldonado, D., Erramuspe, I. B. V., & Peresin, M. S. (2019). Natural polymers as alternative adsorbents and treatment agents for water remediation. *Bioresources, 14*, 10093–10160.

Han, D., Tang, B., & Row, K. H. (2013). Dispersive solid phase extraction with an ionic liquid modified polymer for determination of cyanazine and atrazine in tomatoes. *Analytical Letters, 46*(15), 2359–2371. https://doi.org/10.1080/00032719.2013.800533

Haque, A. N. M. A., Remadevi, R., Wang, X., & Naebe, M. (2020). Adsorption of anionic acid blue 25 on chitosan-modified cotton gin trash film. *Cellulose.* , Article 0123456789. https://doi.org/10.1007/s10570-020-03409-x

He, Z., Meng, M., Yan, L., Zhu, W., Sun, F., Yan, Y., & Liu, Y. (2015). Fabrication of new cellulose acetate blend imprinted membrane assisted with ionic liquid ([BMIM] Cl) for selective adsorption of salicylic acid from industrial wastewater. *Separation and Purification Technology, 145*, 63–74. https://doi.org/10.1016/j.seppur.2015.03.005

Huang, M., Kan, L., Zhao, W., Wang, Y., Xiong, Y., Shan, W., & Lou, Z. (2021). Highly efficient and selective capture of TcO4− or ReO4− by imidazolium-based ionic liquid polymers. *Chemical Engineering Journal, 421*, Article 127763. https://doi.org/10.1016/j.cej.2020.127763

Isosaari, P., Srivastava, V., & Sillanpää, M. (2019). Ionic liquid-based water treatment technologies for organic pollutants: Current status and future prospects of ionic liquid mediated technologies. *Science of the Total Environment, 690*, 604–619. https://doi.org/10.1016/j.scitotenv.2019.06.421

Jiang, Y., Li, F., Ding, G., Chen, Y., Liu, Y., Hong, Y., Liu, P., Qi, X., & Ni, L. (2015). Synthesis of a novel ionic liquid modified copolymer hydrogel and its rapid removal of cr (VI) from aqueous solution. *Journal of Colloid and Interface Science, 455*, 125–133. https://doi.org/10.1016/j.jcis.2015.05.030

Kaur, G., Kumar, H., & Singla, M. (2022). Diverse applications of ionic liquids : A comprehensive review. *Journal of Molecular Liquids, 351*, Article 118556. https://doi.org/10.1016/j.molliq.2022.118556

Kenawy, I. M. M., Eldefrawy, M. M., Eltabey, R. M., & Zaki, E. G. (2019). Melamine grafted chitosan-montmorillonite nanocomposite for ferric ions adsorption: Central composite design optimization study. *Journal of Cleaner Production, 241*, Article 118189. https://doi.org/10.1016/j.jclepro.2019.118189

Khurana, L., & Balasubramanian, K. (2016). Adsorption potency of imprinted Starch/PVA polymers confined ionic liquid with molecular simulation framework. *Journal of Environmental Chemical Engineering, 4*(2), 2147–2154. https://doi.org/10.1016/j.jece.2016.03.032

Kou, X., Ma, B., Zhang, R., Cai, M., Huang, Y., & Yang, Y. (2020). Properties and mechanism for selective adsorption of Au(iii) on an ionic liquid adsorbent by graftingN-methyl imidazole onto chloromethylated polystyrene beads. *RSC Advances, 10*, 20338–20348. https://doi.org/10.1039/d0ra03504a

Kyzas, G. Z., & Bikiaris, D. N. (2015). Recent modifications of chitosan for adsorption applications: A critical and systematic review. *Marine Drugs, 13*(1), 312–337. https://doi.org/10.3390/md13010312

Lemus, J., Palomar, J., Heras, F., Gilarranz, M. A., & Rodriguez, J. J. (2012). Developing criteria for the recovery of ionic liquids from aqueous phase by adsorption with activated carbon. *Separation and Purification Technology, 97*, 11–19. https://doi.org/10.1016/j.seppur.2012.02.027

Li, L., Luo, C., Li, X., Duan, H., & Wang, X. (2014). Preparation of magnetic ionic liquid/chitosan/graphene oxide composite and application for water treatment. *International Journal of Biological Macromolecules, 66*, 172–178. https://doi.org/10.1016/j.ijbiomac.2014.02.031

Li, M., Wang, Z., & Li, B. (2016). Adsorption behaviour of Congo red by cellulose/chitosan hydrogel beads regenerated from ionic liquid. *Desalination and Water Treatment, 57*(36), 16970–16980. https://doi.org/10.1080/19443994.2015.1082945

Li, J., Zuo, G., Qi, X., Wei, W., Pan, X., Su, T., Zhang, J., & Dong, W. (2017). Selective determination of Ag+ using Salecan derived nitrogen doped carbon dots as a fluorescent probe. *Materials Science and Engineering C, 77*, 508–512. https://doi.org/10.1016/j.msec.2017.04.007

Li, P., Lu, Y., Cao, J., Li, M., Yang, C., & Yan, H. (2020). Imidazolium ionic-liquid-modified phenolic resin for solid-phase extraction of thidiazuron and forchlorfenuron from cucumbers. *Journal of Chromatography A, 1623*, 33–36. https://doi.org/10.1016/j.chroma.2020.461192

Liu, H., Jin, P., Zhu, F., Nie, L., & Qiu, H. (2021). A review on the use of ionic liquids in preparation of molecularly imprinted polymers for applications in solid-phase extraction. *Trends in Analytical Chemistry, 134*, Article 116132. https://doi.org/10.1016/j.trac.2020.116132

Liu, Y., Liu, Y., Huo, T., Wu, X., Wei, J., Pei, D., Di, D., Wang, J., & Sun, Y. (2015). Effect of the ionic liquid group in novel interpenetrating polymer networks on the adsorption properties for oleuropein from aqueous solutions. *New Journal of Chemistry, 39*(12), 9181–9190. https://doi.org/10.1039/c5nj01475a

Liu, Z., Wang, H., Liu, C., Jiang, Y., Yu, G., Mu, X., & Wang, X. (2012). Magnetic cellulose-chitosan hydrogels prepared from ionic liquids as reusable adsorbent for removal of heavy metal ions. *Chemical Communications, 48*, 7350–7352. https://doi.org/10.1039/c2cc17795a

Lou, Z., Xing, S., Xiao, X., Shan, W., Xiong, Y., & Fan, Y. (2018). Selective adsorption of re (VII) by chitosan modified with imidazolium-based ionic liquid. *Hydrometallurgy, 179*, 141–148. https://doi.org/10.1016/j.hydromet.2018.05.025

Ma, W., & Row, K. H. (2018). Solid-phase extraction of chlorophenols in seawater using a magnetic ionic liquid molecularly imprinted polymer with incorporated silicon dioxide as a sorbent. *Journal of Chromatography A, 1559*, 78–85. https://doi.org/10.1016/j.chroma.2018.01.013

Ma, X., Liu, C., Anderson, D. P., & Chang, P. R. (2016). Porous cellulose spheres: Preparation, modification and adsorption properties. *Chemosphere, 165*, 399–408. https://doi.org/10.1016/j.chemosphere.2016.09.033

Meenatchi, B., Renuga, V., & Manikandan, A. (2017). Cellulose dissolution and regeneration using various imidazolium based protic ionic liquids. *Journal of Molecular Liquids, 238*, 582–588. https://doi.org/10.1016/j.molliq.2016.05.008

Mhemeed, A. H. (2018). A general overview on the adsorption. *Indian Journal of Natural Sciences, 9*(51), 16127–16131.

Mittal, H., Ray, S. S., Kaith, B. S., Bhatia, J. K., Sukriti, Sharma, J., & Alhassan, S. M. (2018). Recent progress in the structural modification of chitosan for applications in diversified biomedical fields. *European Polymer Journal, 109*(October), 402–434. https://doi.org/10.1016/j.eurpolymj.2018.10.013

Mittal, H., Ray, S. S., & Okamoto, M. (2016). Recent Progress on the design and applications of polysaccharide-based graft copolymer hydrogels as adsorbents for wastewater purification. *Macromolecular Materials and Engineering, 301*, 496–522. https://doi.org/10.1002/mame.201500399

Monir, T., Shahr El-Din, A., El-Nadi, Y., & Ali, A. (2020). A novel ionic liquid-impregnated chitosan application for separation and purification of fission 99Mo from alkaline solution. *Radiochimica Acta*, 1–11. https://doi.org/10.1515/ract-2019-3202

Musarurwa, H., & Tavengwa, N. T. (2020). Application of carboxymethyl polysaccharides as bio-sorbents for the sequestration of heavy metals in aquatic environments. *Carbohydrate Polymers, 237*, Article 116142. https://doi.org/10.1016/j.carbpol.2020.116142

Nayebi, R., Daneshvar Tarigh, G., & Shemirani, F. (2019). Porous ionic liquid polymer: A reusable adsorbent with broad operating pH range for speciation of nitrate and nitrite. *Scientific Reports, 9*(1), 11130. https://doi.org/10.1038/s41598-019-47648-w

Noorhisham, N. A., Amri, D., Mohamed, A. H., Yahaya, N., Ahmad, M. N., Mohamad, S., Kamaruzaman, S., & Osman, H. (2021). Characterisation techniques for analysis of imidazolium-based ionic liquids and application in polymer preparation : A review. *Journal of Molecular Liquids, 326*, Article 115340. https://doi.org/10.1016/j.molliq.2021.115340

Nurazzi, N. M., Asyraf, M. R. M., Rayung, M., Norrrahim, M. N. F., Shazleen, S. S., Rani, M. S. A., Shafi, A. R., Aisyah, H. A., Radzi, M. H. M., Sabaruddin, F. A., Ilyas, R. A., Zainudin, E. S., & Abdan, K. (2021). Thermogravimetric analysis properties of cellulosic natural fiber polymer composites : A review on influence of chemical treatments. *Polymers, 13*, 2710. https://doi.org/10.3390/polym13162710

Oshima, T., Sakamoto, T., Ohe, K., & Baba, Y. (2014). Cellulose aerogel regenerated from ionic liquid solution for immobilized metal affinity adsorption. *Carbohydrate Polymers, 103*(1), 62–69. https://doi.org/10.1016/j.carbpol.2013.12.021

Özge, G., & Asgar, K. (2021). Composite of natural polymers and their adsorbent properties on the dyes and heavy metal ions. *Journal of Polymers and the Environment.* , Article 0123456789. https://doi.org/10.1007/s10924-021-02154-x

Patil, C. M., Borse, A. U., & Meshram, J. S. (2018). Ionic liquid: Green solvent for the synthesis of cellulose/guar gum/PVA biocomposite. *Green Materials, 6*(1), 23–29. https://doi.org/10.1680/jgrma.17.00029

Peng, X., Chen, L., Liu, S., Hu, L., Zhang, J., Wang, A., Yu, X., & Yan, Z. (2021). Insights into the interfacial interaction mechanisms of p-arsanilic acid adsorption on ionic liquid modified porous cellulose. *Journal of Environmental Chemical Engineering, 9*, Article 105225. https://doi.org/10.1016/j.jece.2021.105225

Pourjavadi, A., & Doulabi, M. (2014). Preparation and evaluation of a polymeric gel containing ionic liquid-functionalized MWCNTs as a novel class of organic solvent absorbent. *Journal of Polymer Science, Part A: Polymer Chemistry, 52*(22), 3166–3172. https://doi.org/10.1002/pola.27372

Prasad, K., Mondal, D., Sharma, M., Freire, M. G., Mukesh, C., & Bhatt, J. (2018). Stimuli responsive ion gels based on polysaccharides and other polymers prepared using ionic liquids and deep eutectic solvents. *Carbohydrate Polymers, 180*, 328–336. https://doi.org/10.1016/j.carbpol.2017.10.020

Prasad, V., Kale, R. R., Kumar, V., & Tiwari, V. K. (2010). Carbohydrate chemistry and room temperature ionic liquids (RTILs): Recent trends, opportunities, challenges and future perspectives. *Current Organic Synthesis, 7*, 506–531.

Ptak, S., Zarski, A., & Kapusniak, J. (2020). The importance of ionic liquids in the modification of starch and processing of starch-based materials. *Materials, 13*, 4479. https://doi.org/10.3390/ma13204479

Qi, X., Tong, X., Pan, W., Zeng, Q., You, S., & Shen, J. (2021). Recent advances in polysaccharide-based adsorbents for wastewater treatment. *Journal of Cleaner Production, 315*, Article 128221. https://doi.org/10.1016/j.jclepro.2021.128221

Raghav, S., & Kumar, D. (2018). Adsorption equilibrium, kinetics, and thermodynamic studies of fluoride adsorbed by tetrametallic oxide adsorbent. *Journal of Chemical & Engineering Data, 63*, 1682–1697. https://doi.org/10.1021/acs.jced.8b00024

Raoov, M., Mohamad, S., & Abas, M. R. (2013). Removal of 2,4-dichlorophenol using cyclodextrin-ionic liquid polymer as a macroporous material: Characterization, adsorption isotherm, kinetic study, thermodynamics. *Journal of Hazardous Materials, 263*, 501–516. https://doi.org/10.1016/j.jhazmat.2013.10.003

Raoov, M., Mohamad, S., & Abas, M. R. (2014). Synthesis and characterization of β-cyclodextrin functionalized ionic liquid polymer as a macroporous material for the removal of phenols and As(V). *International Journal of Molecular Sciences, 15*, 100–119. https://doi.org/10.3390/ijms15010100

Raoov, M., Mohamad, S., Bin Abas, M. R., & Surikumaran, H. (2014). New macroporous β-cyclodextrin functionalized ionic liquid polymer as an adsorbent for solid phase extraction with phenols. *Talanta, 130*, 155–163. https://doi.org/10.1016/j.talanta.2014.06.067

Riedel, S. L., & Brigham, C. (2019). Polymers and adsorbents from agricultural waste. In *Byproducts from agriculture and fisheries: Adding value for food, feed, pharma and fuels* (pp. 523–544). https://doi.org/10.1002/9781119383956.ch22

Rufato, B. K., Almeida, V. C., Kipper, M. J., Rubira, A. F., Martins, A. F., & Muniz, E. C. (2019). Polysaccharide-based adsorbents prepared in ionic liquid with high performance for removing Pb(II) from aqueous systems. *Carbohydrate Polymers, 215*, 272–279. https://doi.org/10.1016/j.carbpol.2019.03.095

Saheed, I. O., Oh, W. D., & Suah, F. M. B. (2021a). Chitosan modifications for adsorption of pollutants – A review. *Journal of Hazardous Materials, 408*, Article 124889. https://doi.org/10.1016/j.jhazmat.2020.124889

Saheed, I. O., Oh, W., Latip, A. F. A., & Suah, F. B. M. (2022). Mesoporous chitosan/activated charcoal powder and bead modified in 1-butyl-3-methylimidazolium acetate for the adsorption of acid blue 25 from an aqueous solution. *Journal Chemical Technology and Biotechnology, 97*, 1315–1325. https://doi.org/10.1002/jctb.7027

Saheed, I. O., Oh, W., & Suah, F. M. B. (2021b). Enhanced adsorption of acid Blue-25 dye onto chitosan/porous carbon composite modified in 1-allyl-3-methyl imidazolium bromide ionic liquid. *International Journal of Biological Macromolecules, 183*, 1026–1033. https://doi.org/10.1016/j.ijbiomac.2021.05.042

Saheed, I. O., Oh, W., & Suah, F. M. B. (2021c). Removal of 1-Butyl-3-methylimidazolium bromide from an aqueous solution by using a spongy chitosan-activated carbon composite. *Colloid and Interface Science Communications, 42*, Article 100393. https://doi.org/10.1016/j.colcom.2021.100393

Sajid, M., Nazal, M. K., Ihsanullah, Baig, N., & Osman, A. M. (2018). Removal of heavy metals and organic pollutants from water using dendritic polymers based adsorbents: A critical review. *Separation and Purification Technology, 191*(June 2017), 400–423. https://doi.org/10.1016/j.seppur.2017.09.011

Samiey, B., Cheng, C. H., & Wu, J. (2014). Organic-inorganic hybrid polymers as adsorbents for removal of heavy metal ions from solutions: A review. *Materials, 7*(2), 673–726. https://doi.org/10.3390/ma7020673

Shamsuri, A. A., Abdan, K., & Kaneko, T. (2021). A concise review on the physicochemical properties of biopolymer blends prepared in ionic liquids. *Molecules, 26*(1). https://doi.org/10.3390/molecules26010216

Shamsuri, A. A., Jamil, S. N. A. M., & Abdan, K. (2021). A brief review on the influence of ionic liquids on the mechanical, thermal, and chemical properties of biodegradable polymer composites. *Polymers, 13*, 2597. https://doi.org/10.3390/polym13162597

Sharififard, H., Shahraki, Z. H., Rezvanpanah, E., & Rad, S. H. (2018). A novel natural chitosan/activated carbon/iron bio-nanocomposite: Sonochemical synthesis, characterization, and application for cadmium removal in batch and continuous adsorption process. *Bioresource Technology, 270*(August), 562–569. https://doi.org/10.1016/j.biortech.2018.09.094

Sheibani, E., Hosseini, A., Sobhani Nasab, A., Adib, K., Ganjali, M. R., Pourmortazavi, S. M., Ahmadi, F., Marzi Khosrowshahi, E., Mirsadeghi, S., Rahimi-Nasrabadi, M., & Ehrlich, H. (2021). Application of polysaccharide biopolymers as natural adsorbent in sample preparation. *Critical Reviews in Food Science and Nutrition*. https://doi.org/10.1080/10408398.2021.1978385

Silva, S. S., Mano, J. F., & Reis, R. L. (2017). Ionic liquids in the processing and chemical modification of chitin and chitosan for biomedical applications. *Green Chemistry, 19*(5), 1208–1220. https://doi.org/10.1039/C6GC02827F

Singh, S. K., & Savoy, A. W. (2020). Ionic liquids synthesis and applications : An overview. *Journal of Molecular Liquids, 297*, Article 112038. https://doi.org/10.1016/j.molliq.2019.112038

Song, M. H., Phuong, T., Pham, T., & Yun, Y. S. (2020). Ionic liquid - assisted cellulose coating of chitosan hydrogel beads and their application as drug carriers. *Scientific Reports, 10*, 13905. https://doi.org/10.1038/s41598-020-70900-7

Stanton, J., Xue, Y., Pandher, P., Malek, L., Brown, T., Hu, X., & Salas-de la Cruz, D. (2018). Impact of ionic liquid type on the structure, morphology and properties of silk-cellulose biocomposite materials. *International Journal of Biological Macromolecules, 108*, 333–341. https://doi.org/10.1016/j.ijbiomac.2017.11.137

Stefanescu, C., Daly, W. H., & Negulescu, I. I. (2012). Biocomposite films prepared from ionic liquid solutions of chitosan and cellulose. *Carbohydrate Polymers, 87*, 435–443. https://doi.org/10.1016/j.carbpol.2011.08.003

Stefanescu, C., Daly, W. H., & Negulescu, I. I. (2020). Functionalization of cellulose and chitosan in ionic liquids. *Cellulose Chemistry and Technology, 54*, 857–868.

Swatloski, R. P., Spear, S. K., Holbrey, J. D., & Rogers, R. D. (2002). Dissolution of celllulose [correction of Cellose] with ionic liquids. *Journal of the American Chemical Society, 124*(18), 4974–4975.

Tang, B., Tian, M., & Row, K. H. (2013). Adsorption of lactic acid onto three ionic liquid-modified porous polymers. *Journal of Applied Polymer Science, 129*(3), 1306–1313. https://doi.org/10.1002/app.38813

Tang, S., Yang, J., Lin, L., Peng, K., Chen, Y., Jin, S., & Yao, W. (2020). Construction of physically crosslinked chitosan/sodium alginate/calcium ion double-network hydrogel and its application to heavy metal ions removal. *Chemical Engineering Journal, 393*, Article 124728. https://doi.org/10.1016/j.cej.2020.124728

Tang, T., Cao, S., Xi, C., & Chen, Z. (2021). Multifunctional magnetic chitosan-graphene oxide-ionic liquid ternary nanohybrid: An efficient adsorbent of alkaloids. *Carbohydrate Polymers, 255*, Article 117338. https://doi.org/10.1016/j.carbpol.2020.117338

Therattil, J., & Kumar, A. (2020). Transport of organic solvents through ionic liquid modified natural rubber / MWCNT composites. *International Journal of Scientific & Technology Research, 9*(4), 3055–3064.

Tran, C. D., Duri, S., Delneri, A., & Franko, M. (2013). Chitosan-cellulose composite materials: Preparation, characterization and application for removal of microcystin. *Journal of Hazardous Materials, 252–253*, 355–366. https://doi.org/10.1016/j.jhazmat.2013.02.046

Vakili, M., Deng, S., Cagnetta, G., Wang, W., Meng, P., Liu, D., & Yu, G. (2019). Regeneration of chitosan-based adsorbents used in heavy metal adsorption: A review. *Separation and Purification Technology, 224*, 373–387. https://doi.org/10.1016/j.seppur.2019.05.040

Vidal, L., Riekkola, M. L., & Canals, A. (2012). Ionic liquid-modified materials for solid-phase extraction and separation: A review. *Analytica Chimica Acta, 715*, 19–41. https://doi.org/10.1016/j.aca.2011.11.050

Wang, F., Xie, C., Qian, L., He, B., & Li, J. (2019). Study on the preparation of ionic liquid doped chitosan/cellulose-based electroactive composites. *International Journal of Molecular Sciences, 20*, 6198. https://doi.org/10.3390/ijms20246198

Wang, J., & Zhuang, S. (2017). Removal of various pollutants from water and wastewater by modified chitosan adsorbents. *Critical Reviews in Environmental Science and Technology, 47*(23), 2331–2386. https://doi.org/10.1080/10643389.2017.1421845

Wang, J., Wei, L., Ma, Y., Li, K., Li, M., Yu, Y., Wang, L., & Qiu, H. (2013). Collagen/cellulose hydrogel beads reconstituted from ionic liquid solution for Cu(II) adsorption. *Carbohydrate Polymers, 98*(1), 736–743. https://doi.org/10.1016/j.carbpol.2013.06.001

Wang, L., Chen, J., Li, X., Chen, L., Zhang, K., Wang, X., & Zhu, G. (2021). Eco-friendly ionic liquid imprinted polymer based on a green synthesis strategy for highly selective adsorption tylosin in animal muscle samples. *Environmental Science and Pollution Research, 28*, 16470–16479.

Wang, M., & You, X. Y. (2021). Critical review of magnetic polysaccharide-based adsorbents for water treatment: Synthesis, application and regeneration. *Journal of Cleaner Production, 323*, Article 129118. https://doi.org/10.1016/j.jclepro.2021.129118

Wang, X., Zheng, Y., & Wang, A. (2009). Fast removal of copper ions from aqueous solution by chitosan-g-poly (acrylic acid)/attapulgite composites. *Journal of Hazardous Materials, 168*, 970–977. https://doi.org/10.1016/j.jhazmat.2009.02.120

Webb, P. A. (2003). *Introduction to chemical adsorption analytical techniques and their applications to catalysis*. MIC Technical Publications.

Wei, Y., Huang, W., Zhou, Y., & Zhang, S. (2013). Modification of chitosan with carboxyl-functionalized ionic liquid for anion adsorption. *International Journal of Biological Macromolecules, 62*, 365–369. https://doi.org/10.1016/j.ijbiomac.2013.09.020

Wieszczycka, K., Filipowiak, K., Wojciechowska, I., & Aksamitowski, P. (2020). Novel ionic liquid-modified polymers for highly effective adsorption of heavy metals ions. *Separation and Purification Technology, 236*, Article 116313. https://doi.org/10.1016/j.seppur.2019.116313

Wu, X., Liu, Y., Liu, Y., & Di, D. (2015). Evaluation on the adsorption capability of chemically modified macroporous adsorption resin with ionic liquid. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 469*, 141–149. https://doi.org/10.1016/j.colsurfa.2015.01.001

Xia, Z., Li, J., Zhang, J., & Zhang, X. (2020). Processing and valorization of cellulose, lignin and lignocellulose using ionic liquids. *Journal of Bioresources and Bioproducts, 5*(2), 79–95. https://doi.org/10.1016/j.jobab.2020.04.001

Xie, H., Zhang, S., & Li, S. (2006). Chitin and chitosan dissolved in ionic liquids as reversible sorbents of CO2. *Green Chemistry, 8*, 630–633. https://doi.org/10.1039/b517297g

Xu, L., Lu, X., & Cheng, X. (2015). Preparation of modified cotton cellulose in ionic liquid and its adsorption of Cu(II) and Ni(II) from aqueous solutions. *RSC Advances, 5*, 79022–79030. https://doi.org/10.1039/C5RA08265J

Yadaei, H., Hossein, M., Shemirani, F., & Nouroozi, S. (2018). Ferrofluid mediated chitosan@mesoporous carbon nanohybrid for green adsorption/preconcentration of toxic Cd(II): Modeling, kinetic and isotherm study. *Reactive and Functional Polymers, 122*, 85–97. https://doi.org/10.1016/j.reactfunctpolym.2017.10.011

Yan, H., Gao, M., Yang, C., & Qiu, M. (2014). Ionic liquid-modified magnetic polymeric microspheres as dispersive solid phase extraction adsorbent: A separation strategy

applied to the screening of sulfamonomethoxine and sulfachloropyrazine from urine. *Analytical and Bioanalytical Chemistry, 406*(11), 2669–2677. https://doi.org/10.1007/s00216-014-7665-3

Yan, H., Yang, C., Sun, Y., & Row, K. H. (2014). Ionic liquid molecularly imprinted polymers for application in pipette-tip solid-phase extraction coupled with gas chromatography for rapid screening of dicofol in celery. *Journal of Chromatography A, 1361*, 53–59. https://doi.org/10.1016/j.chroma.2014.07.102

Yong, C., Bond, Y., Hui, C., & Talib, A. (2018). Extraction and physicochemical characterization of chitin and chitosan from zophobas morio larvae in varying sodium hydroxide concentration. *International Journal of Biological Macromolecules, 108*, 135–142. https://doi.org/10.1016/j.ijbiomac.2017.11.138

Yusoff, M. M., Yahaya, N., Saleh, N. M., & Raoov, M. (2018). A study on the removal of propyl, butyl, and benzyl parabens: Via newly synthesised ionic liquid loaded magnetically confined polymeric mesoporous adsorbent. *RSC Advances, 8*(45), 25617–25635. https://doi.org/10.1039/c8ra03408g

Zhang, H., Wu, J., Zhang, J., & He, J. (2005). 1-Allyl-3-methylimidazolium chloride room temperature ionic liquid : A new and powerful nonderivatizing solvent for cellulose. *Macromolecules, 38*, 8272–8277. https://doi.org/10.1021/ma0505676

Zhang, J., Wu, J., Yu, J., Zhang, X., He, J., & Zhang, J. (2017). Application of ionic liquids for dissolving cellulose and fabricating cellulose-based materials : State of the art and future trends. *Materials Chemistry Frontiers, 1*, 1273–1290. https://doi.org/10.1039/c6qm00348f

Zhang, L., Xia, W., Liu, X., & Zhang, W. (2015). Synthesis of titanium cross-linked chitosan composite for efficient adsorption and detoxification of hexavalent chromium from water. *Journal of Materials Chemistry A, 3*(1), 331–340. https://doi.org/10.1039/c4ta05194g

Zhang, P., Hu, L., Lu, R., Zhou, W., & Gao, H. (2013). Application of ionic liquids for liquid – liquid microextraction. *Analytical Methods, 5*, 5376–5385. https://doi.org/10.1039/c3ay40597d

Zhang, S. F., Yang, M. X., Qian, L. W., Hou, C., Tang, R. H., Yang, J. F., & Wang, X. C. (2018). Design and preparation of a cellulose-based adsorbent modified by imidazolium ionic liquid functional groups and their studies on anionic dye adsorption. *Cellulose, 25*(6), 3557–3569. https://doi.org/10.1007/s10570-018-1815-2

Zhao, D., Liao, Y., & Zhang, Z. D. (2007). Toxicity of ionic liquids. *Clean, 35*(1), 42–48. https://doi.org/10.1002/clen.200600015

Zhao, F., Repo, E., Yin, D., Chen, L., Kalliola, S., Tang, J., Iakovleva, E., Tam, K. C., & Sillanpää, M. (2017). One-pot synthesis of trifunctional chitosan-EDTA-β-cyclodextrin polymer for simultaneous removal of metals and organic micropollutants. *Scientific Reports, 7*(1), 1–14. https://doi.org/10.1038/s41598-017-16222-7

Zheng, X., Ni, C., Xiao, W., Liang, Y., & Li, Y. (2022). Ionic liquid grafted polyethersulfone nanofibrous membrane as recyclable adsorbent with simultaneous dye, heavy metal removal and antibacterial property. *Chemical Engineering Journal, 428*, Article 132111. https://doi.org/10.1016/j.cej.2021.132111

Zhu, G., Cheng, G., Lu, T., Cao, Z., Wang, L., Li, Q., & Fan, J. (2019). An ionic liquid functionalized polymer for simultaneous removal of four phenolic pollutants in real environmental samples. *Journal of Hazardous Materials, 373*, 347–358. https://doi.org/10.1016/j.jhazmat.2019.03.101