

Communication

Simple Preparation of a Unique Ionic Liquid/Deep Eutectic Solvent and β -Cyclodextrin Composite Discs and Its Use to Capture Hazardous Substances from Water

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Abstract: With the development of health service, animal husbandry, aquaculture and the chemical industry, more and more pollutants are discharged into the water environment, including antibiotics and heavy-metal ions. These hazardous substances pose a great threat to environmental safety and human health. Two new kinds of green solvents, ionic liquids (ILs) and deep eutectic solvents (DESs), are widely utilized in various fields, including separation and environmental engineering, and are attracting much attention from academia and industry. In this study, an optimal ionic liquid and a deep eutectic solvent were selected, and their complex with β -cyclodextrin (β -CD) was first prepared by a process of simple and effective inclusion. After necessary characterization and analysis, two kinds of complexes were applied to prepare a special two-sided sorbent disc by adding a diluent (excipient) and pressing the substance under 5~15 MPa. As a result, the IL and DES were stably immobilized on the disc to play a key role in the selective adsorption of targets. Moreover, the experiments with different hazardous substances achieved the expected results. This study demonstrates that the complex disc, with its easy preparation, good stability, and simple operation, exhibited many merits in its separation performance. We believe it to be a useful tool for water purification and detection of noxious substances.

Keywords: ionic liquid; deep eutectic solvent; cyclodextrin; sorbent disc; water environment



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1. Introduction

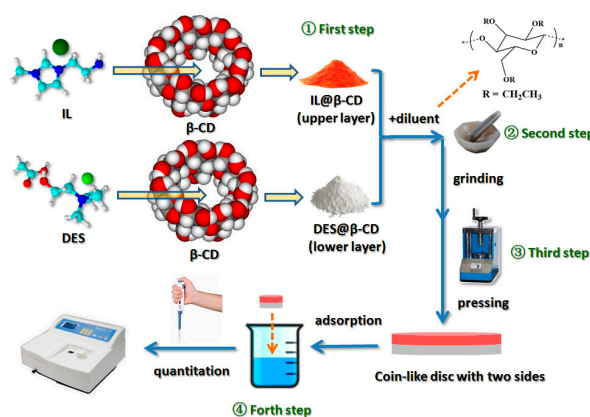
With the rapid development of society and the economy, the impact of industry, agriculture, and urban life on the environment has become increasingly prominent, and water pollution problems of different types and degrees are widespread [1,2]. In industry, harmful substances such as heavy metals, dyes, phenols, and various saline wastewaters are discharged. For agricultural production, pesticides are widely used and only 20% is absorbed by crops; the rest either gasifies into the atmosphere or penetrates into the soil and groundwater through the earth surface. Furthermore, urban life produces a large amount of garbage and drug residues. All these hazardous substances pose a serious threat to human health and sustainable development, and the incidence of tumors, skin diseases, allergies, malformations, and nervous system diseases has greatly increased in the past decade [3].

Two new kinds of green solvents, ionic liquids (ILs) and deep eutectic solvents (DESs), are attracting major attention in academic and industrial circles [4]. Of the two, ionic liquids are the salts completely composed of cation and anion that appear liquid at or near room temperature. Their low melting point is ascribed to the asymmetry of some substituents in their structure that make the ions unable to regularly accumulate into crystals. The most common cations are imidazole salts, while the frequently applied anions include halogen,

tetrafluoroborate, and hexafluorophosphate ions, etc. DESs, on the other hand, are composed of hydrogen bond acceptors and hydrogen bond donors with a certain stoichiometric ratio (commonly molar ratio = 1:1). Most DESs are two-component mixtures, but a few eutectic solvents have three components. Water molecules can be one of the components of some eutectic solvents. The most common hydrogen bond acceptor is choline chloride, alongside hydrogen-bond donors such as urea, carboxylic acid, polyol, amino acid, sugar, etc. In separation science, more and more ILs and DESs are being successfully applied for their advantages of good selectivity, designability, stability, recyclability, etc. [5].

At present, researchers focus their major attention on the detection and removal of hazardous substances in various forms and ways. Among them, adsorption methods based on various innovative sorbents are the most prominent [6,7]. From theoretical, mechanistic, and practical perspectives, green solvents have enormous potential for application in this field. In particular, immobilized ILs or DESs, modified with some supports or related sorbents to make their utilization more convenient, thus saving on consumption and avoiding residues, [8,9] are of major importance. For instance, a modified IL clay was prepared to remove Pb(II), Co(II) and Zn(II) ions from water [10], and its catalytic activity after treatment with heavy-metal ion solutions was proved in the reduction of its nitroarenes to its corresponding amines. Various metal organic frameworks combined with imidazolium, quinolinium and benzothiazolium ILs were developed for the removal of three antibiotics from water [11]. Moreover, a series of natural and low-cost menthol-based hydrophobic DESs was synthesized to extract triphenylmethane (TPM) dye micropollutants from dilute aqueous solution [12]. DES-modified mixed-iron hydroxide–silica was successively used in magnetic solid-phase extraction for enrichment of organochlorine pesticides [13]. In summary, ILs and DESs have achieved great success as extractants and sorbents together with their immobilized forms for treating related targets. However, no investigations address employing the appropriate IL and DES simultaneously in the same sorbent, and the procedures of immobilizing and utilizing them for separation can be further simplified.

Therefore, a unique composite sorbent disc was invented to achieve the above goals as a contribution to sustainable development. In the following study, the optimal ionic liquid and deep eutectic solvent were selected, and their complex with β -cyclodextrin (β -CD) was first prepared by a simple and effective method of inclusion, and the related immobilization process was observed by infrared spectrum and conductivity methods. After the necessary characterization and analysis, the two kinds of complex were applied to prepare the designed two-sided sorbent disc by adding a diluent (excipient) and pressing the disc under 5~15 MPa. After the investigation under key preparation conditions, we explored whether the components could be stably immobilized on the disc to play the key role in the selective adsorption of the targets. Adsorption experiments for different hazardous substances were carried out to achieve the expected goals. The technical route of the investigation is summarized in Scheme 1.



Scheme 1. The preparation and application of immobilized IL and DES on β -CD and related two-sided composite sorbent disc.

2. Materials and Methods

2.1. Reagents and Materials

Choline chloride, glacial acetic acid, methanol, absolute ethanol, potassium hydroxide, acetonitrile, standard metal salts, and pigment were all purchased from the Kelong chemical factory (Chengdu, China). β -CD (molecular weight: 1135 g/mol), N-methylimidazole, 2-bromoethylamine hydrobromate, methyl, ethyl and carboxymethyl cellulose were purchased from the Aladdin chemical reagent factory (Shanghai, China). Except for the chromatographic grade methanol used for quantitative analysis, all reagents and solvents were analytical pure grade and were used without further purification if not stated otherwise. All the standard hazardous substances with a purity not lower than 98.0% were purchased from the Aladdin and Aike chemical reagent factory (Shanghai, China). The experimental water was prepared with a Milli-Q water purification system (Millipore, Bedford, MA, USA). Actual water samples were locally collected.

2.2. Instruments

Conductivity was detected with a DDSJ-319L conductivity meter (0.000 μ S/cm–3000 mS/cm, \pm 0.5% FS, Leici Instrumental, Shanghai, China). NMR spectra of the IL and DES were performed on an AV II-400 MHz spectrometer (Bruker, Basel, Switzerland). A Spectrum Two L1600300 Spectrometer (Perkin Elmer, Waltham, MA, USA) was applied to record the Fourier transform infrared spectra (FT-IR) in the range of 4000–450 cm^{-1} . Thermogravimetric analysis (TGA) was performed on a TGA/DSC 2-type instrument (Mettler Toledo, ImLangacher, Switzerland) with a heating rate of 10 $^{\circ}\text{C}/\text{min}$ from 30 $^{\circ}\text{C}$ to 600 $^{\circ}\text{C}$ in a nitrogen atmosphere. The contents of hazardous inorganic ions and alkaline red were determined by an AOE380 UV spectrometer (Aoyi Instrument Co., Ltd., Shanghai, China). Quantitative determination of alkaline red in the actual water sample was performed by UltiMate3000 high performance liquid chromatography (DIONEX Co., Sunnyvale, CA, USA).

2.3. Preparation of IL and DES

According to current reports and our pilot experimental screening, the IL of 1-aminoethyl-3-methylimidazole bromide ($[\text{NH}_2\text{emim}][\text{Br}]$) and DES of choline chloride-acetic acid (1:2) were chosen for the current study. The former was synthesized through the reported method [14] as follows: 0.15 mol of 2-bromoethylamine hydrobromate and equimolar N-methylimidazole were mixed and stirred with 30 mL absolute ethanol as the solvent for 10 min. After thorough stirring, the radiation power of the XH-300UL multifunctional microwave synthesizer (Xianghu Technologies, Beijing, China) was set to 300 W, and the reactive duration was 20 s. The three-round reaction was completed at an interval of 5 min. After that, 15 mL of 0.01 mol/mL KOH aqueous solution was added to the synthesized product and stirred in an ice water bath for 5 min. Finally, the system was kept at 0 $^{\circ}\text{C}$ until no more sediment formed, and it was then filtered. The filtrate was concentrated and dried and further mixed with enough absolute ethanol to precipitate KBr. Yellow viscous $[\text{NH}_2\text{emim}][\text{Br}]$ was successfully obtained after final filtration and drying in a vacuum, and the yield of the IL was 91%.

Second, with choline chloride as the hydrogen bond acceptor and acetic acid as the hydrogen bond donor, the molar ratio was set at 1:2. In an operation moderately modified the previous [15], solid choline chloride was added to the liquid acetic acid, and the mixture was thoroughly stirred at 60 $^{\circ}\text{C}$ for 80 min to form a colorless, uniform and transparent liquid. No solid precipitation occurred after long-term storage at room temperature, which indicated the final formation of a stable DES (yield near 100%).

2.4. Preparation of IL/DES@ β -CD

It was reported that inclusion and encapsulation of an ionic liquid with β -CD [16] can immobilize the former and then make it more convenient and stable during application. The solubility of β -CD in 60 $^{\circ}\text{C}$ water was 7.29 mg/g, and its saturated solution at 60 $^{\circ}\text{C}$ was first prepared according to these data. Next, the DES of choline chloride-acetic acid

with five times the amount of β -CD was added to the solution and stirred thoroughly at 60 °C for 2 h. After the loading was completed, the system was placed in the freezer for 24 h. It could be observed that much crystal had been precipitated. After suction filtration, the complex of IL and CD was dried in a vacuum to obtain a white granular solid (DES@ β -CD) for further disc pressing. Similarly, the saturation β -CD solution at 60 °C was prepared, and then the IL of [NH₂emim][Br] with five times the amount of β -CD was used to form the IL@ β -CD complex under stirring for 4 h. After crystallization and drying, a white granular solid (IL@ β -CD) was obtained. For comparison, ultrasound assistance and a grinding method were chosen here. After a 40/60 °C β -CD saturated aqueous solution had been prepared, the IL/DES with five times the amount of β -CD was added to the solution and ultrasonicated (300/600 W) at 40/60 °C for 1 h. After the loading was completed, the system was put into the freezer for 24 h. When there was no more crystallization, the solid complex was collected for comparison. Unlike in the ultrasonic method, the grinding was carried out as follows: a certain amount of dry β -CD was added to distilled water with 2 times the mass of β -CD, and the mixture was evenly ground in the mortar. Then the equimolar IL/DES was added to the components and continuously ground for 30 min to obtain a uniform paste. After that, the mixture was placed in the freezer for 24 h.

2.5. Preparation of IL/DES@ β -CD Discs

After thorough drying and primary sieving, the complex of IL/DES@ β -CD was evenly mixed with the diluent (substituted celluloses) with a mass ratio of 0.15:0, 0.125:0.025, 0.1:0.05, 0.075:0.075, 0.05:0.1, 0.025:0.125 (diluent: IL/DES@ β -CD, g/g). After passing through a 200-mesh sieve, the powders were pressed in a stainless steel mold with a diameter of 13 mm under the pressure of 5~20 MPa for 0~3 h. With the increasing dosage of the complex of IL/DES@ β -CD and diluents at a fixed mass ratio, various tablet weights of 0.1 g, 0.15 g, 0.2 g and 0.3 g and a thickness ratio of 1:1.5:2:3 were obtained. Furthermore, to make a coin-like double-face sorbent disc, the mixture powders of 1.5 g DES@ β -CD and ethyl cellulose was first spread in the mold as a thin layer (bottom side), and the same amount of IL@ β -CD and ethyl cellulose mixed powders was spread on the top side. After the two layers were pressed at 15 MPa for 5 min to obtain white double-faced discs, they would play their respective roles of selective adsorption for different targets in the following experiment.

2.6. Removal of Hazardous Substances from Water

After the stable sorbent discs based on IL/DES@ β -CD were obtained, they were placed in the aqueous solution of hazardous substances at the preset concentration (1 mg/mL). Locally collected water samples were employed. During the adsorption process, the whole system was continuously shaken in the constant temperature shaker at R.T. After the preset adsorption time, the appropriate volume of the supernatant was taken out and analyzed (1 mL or 30 μ L for UV or HPLC analysis of inorganic ions and alkaline red, respectively). The adsorption efficiency (%) was determined by the ratio with the target concentration before and after adsorption, which was utilized to evaluate the removal performance of the new sorbent discs. The actual water sample had been collected from the environment by employing a specialized hard sampling bottle immediately sealed after collection. The water sample was centrifuged (500 rpm) it had settled for 12 h at room temperature; the supernatant was filtered under a vacuum in a glass sand-core funnel to obtain the experimental water sample to be utilized for this study within 24 h. After adsorption was completed, the water sample was further filtered with a 0.45 μ m microporous membrane for the following quantitation.

3. Results and Discussion

3.1. Structural Identification of the IL and DES

To identify the synthesized IL and DES before their applications, ¹H-NMR (400 MHz, DMSO-d₆) was first applied to determine their structures. For [NH₂emim][Br], the sig-

nals included 9.24 ppm (s, -N-CH=N=), 7.82 ppm (d, =N-CH=CH-N≡), 7.75 ppm (d, =N-CH=CH-N≡), 4.22 ppm (t, ≡N-CH₂-), 3.84 ppm (s, =N-CH₃) and 2.72 ppm (m, NH₂-CH₂-). For choline chloride-acetic acid, the signals at 5.64 ppm (t, -CH₂-Cl), 3.77 ppm (t, -CH₂-N⁺) and 3.39 ppm (s, -CH₃ × 3) originate from the hydrogen bond acceptor of choline chloride, and those at 11.90 ppm (s, -COOH) and 1.86 ppm (s, -CH₃) result from acetic acid. Compared with those before forming DES, their chemical shift was a little increased for the intermolecular hydrogen bonds. The above results proved the structures of [NH₂emim][Br] and choline chloride-acetic acid as well as their successful preparation [14,15,17].

3.2. Loading of IL/DES on β-CD

To achieve a better loading performance and kinetics, various loading methods were compared to supplement the procedure for preparing the β-CD saturation solution utilized in this section. Based on current studies [18,19], the other two methods selected were ultrasound assistance and adopting the grinding method as a control, respectively. An ultrasonic wave was utilized for strengthening the loading in the former method, which resulted in a more uniform system; the IL/DES and β-CD were mixed in the solution and ultrasonicated for a sufficient duration. After the loading and cooling were completed, the solid complex was collected as a crystallization for comparison. However, the grinding method is mainly carried out in the semidry state, and the loading process involves squeezing, shearing, and friction effects. The IL/DES and β-CD were continuously ground with the assistance of water to obtain a uniform paste which was then frozen. In the solid phase, the mixture was white (see Figure 1a). The above three methods enabled us to observe for the first time the complex of DES/IL-β-CD as the white semi-transparent solid phase appearing in the liquid system, and its color together with its status allowed us to judge whether the immobilization by inclusion had been successful. After suction filtration and drying, the complex of IL/DES on β-CD was obtained. Through comparison on corresponding IR spectra of different products obtained by the above three ways, the example of IL@β-CD illustrates (see Figure 1b,c, the error of wavenumber: ±0.2 cm⁻¹) that the saturation-solution method resulted in the expected complex because the IR absorbance peak of IL around 1570 cm⁻¹ in Figure 1b was observed in a related product. Therefore, this method was finally applied for loading both IL and DES on β-CD. In particular, the featured peak around 1570 cm⁻¹ showed the common characteristic absorbance of ILs for the stretching vibration of C=N in the imidazole ring, and its peak intensity can be effectively adopted to judge the IL content in related systems [20]. Moreover, the shift of this peak was in the range from -10 to -20 cm⁻¹ after the IL was bound in the complex. Meanwhile, the intensity decreased; both the results are related in their limited stretching vibration. Similarly, in Figure 1c, the great absorbance peak around 3370~3390 cm⁻¹ results from the O-H stretching vibration in β-CD and DES. The typical signal of C-H stretching vibration appears around 2920 cm⁻¹; concurrently, the featured absorbance of C=O with the stretching vibration from HAC in the DES will shift from 1731.9 to 1709.0 cm⁻¹ for the similar vibration limitation after inclusion as the IL. Finally, the peak cluster between 1020~1160 cm⁻¹ corresponds to the C-O stretching vibration in the inner cavity and the C-O-C stretching vibration of β-CD [21].

Based on the online measurement of conductivity, the loading process (complex formation process) is as follows:

$$y = -4851.4x + 1974.8 \text{ (for the IL, } R^2 = 0.9887) \quad (1)$$

$$y = -4520.1x + 2075.4 \text{ (for the DES, } R^2 = 0.9953) \quad (2)$$

where x is the concentration of β-CD (mol/L), and y is the system conductivity (μS/cm). As a result, the conductivity decreases remarkably with increasing β-CD concentration, which proves the inclusion-complex formation between β-CD and IL/DES. Moreover, the conductivity curve shows a good linear relationship ($R^2 > 0.98$) at a concentration range

of 0~0.025/0.050 mol/L β -CD (see Figure 1d,e). Compared with the loading process in the tunnels (inner diameter: 10~30 nm) of carbon nanotubes in our previous study [22], the inner cavity size of β -cyclodextrin is in the range of 0.5~0.8 nm. The immobilization method in this study is based on supramolecular interactions and an inclusion effect instead of loading. Both modes can result in enough stability of the IL and the DES and are easier to perform than the chemical modification.

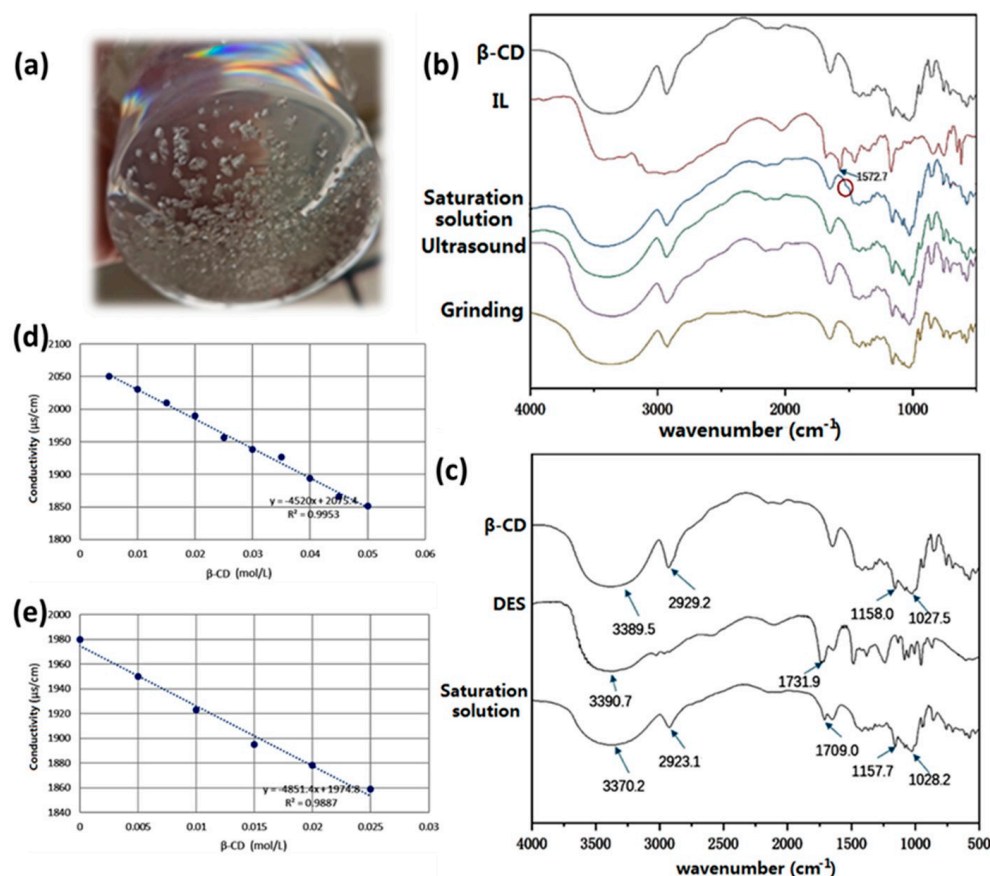


Figure 1. (a) Complex of DES/IL- β -CD; (b) IR spectra (KBr) of β -CD, IL and their complex from the saturation solution, ultrasound, and grinding methods; (c) IR spectra (KBr disc) of β -CD, DES and their complex from the saturation-solution method; (d) curve of conductivity and β -CD concentration for IL immobilization; (e) curve of conductivity and β -CD concentration for DES immobilization.

3.3. Preparation of IL/DES@ β -CD Sorbent Discs

In the first round of screening through pre-experiments, it was found that ethyl cellulose could obtain a more ideal mechanical strength of the sorbent disc than methyl cellulose and carboxymethyl cellulose at the same dose. A single complex of IL or DES@ β -CD was ground into a powder and mixed with the diluents of ethyl cellulose in different proportions. Here the pressure of 15 MPa was selected according to the pilot experiments, a figure lower than that of common pressed tablets (20~410 MPa) [23]. After being sieved with a 200-mesh sieve and pressed under 15 MPa for 30 min to obtain a white tablet (0.15 g), the relationship between hardness and the diluent dose was explored. As shown in Figure 2a, the hardness of the IL@ β -CD disc increases slowly when the diluent dosage is in the range of 0~0.1 g and reaches the ordinary disc hardness (around 100 N) at 0.1 g. When the diluant dosage exceeds 0.1 g, the hardness increases rapidly. In comparison, the DES@ β -CD disc shows a more stable growth in strength after the diluent dose is around 0.1 g (Figure 2b); its hardness is a little higher than that of the IL@ β -CD disc below 0.1 g, which means a higher density and a tighter combination of involved components; after that it begins to lower.

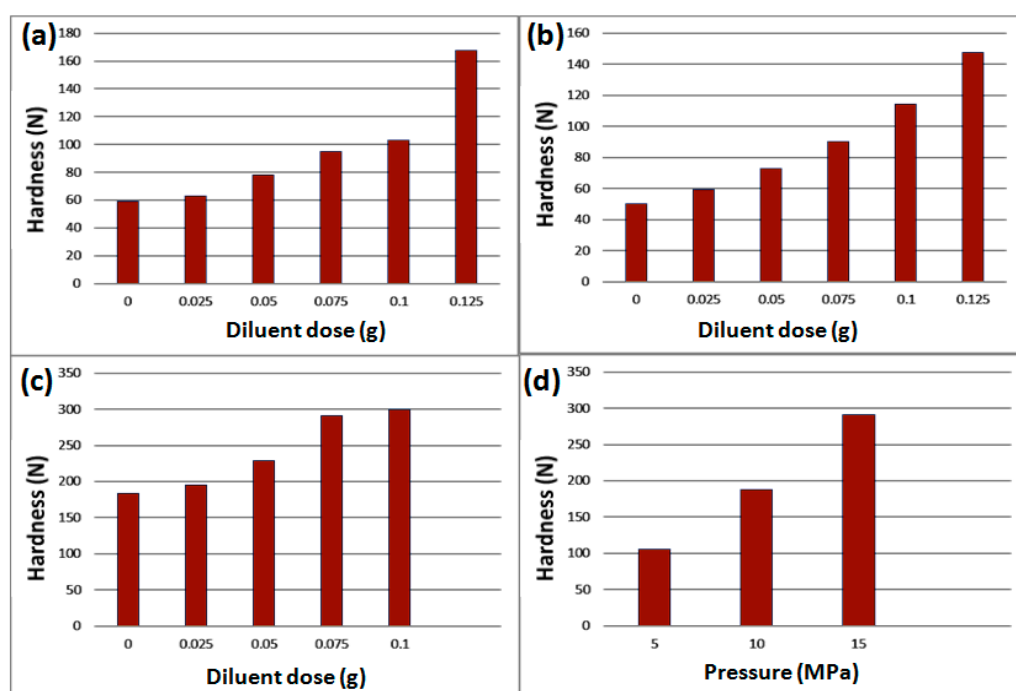


Figure 2. Relationship of diluent dose on hardness of (a) IL- β -CD disc, (b) DES- β -CD disc, and (c) double-sided disc, respectively; (d) relationship of pressure on hardness of double-sided disc.

According to the method in Section 2.5, the equivalent powders of IL@ β -CD and DES@ β -CD were successively spread in the mold to form two layers. After pressing, the faces of IL@ β -CD and DES@ β -CD were successfully formed, and then the relationship between their hardness and the dose of diluents was also explored (Figure 2c). Interestingly, the hardness of the double-sided disc formed by the combination of the two complexes is much greater than that of the single-component disc with the same amount of diluent. Above 0.075 g, the hardness increase will become very slow, and the obtained double-sided disc can be kept in the shaker (500 rpm) for more than 5 h without any disintegration, which ensures its stable functioning in the adsorption process. When the amount of diluent reaches 0.125 g, the force sensor is overloaded, indicating that the hardness is excessively high. In the investigation of the pressure on the hardness (see the results in Figure 2d), the mixture powders composed with the complex and diluents (1:1) were pressed under different pressures for 5 min, and the hardness of the discs was measured. It can be found that 15 MPa is enough for preparing a stable disc with a hardness near 300 N. When the pressure is higher than 15 MPa, the force sensor will be overloaded. Moreover, an excessively tight matrix is not beneficial for mass transfer [24] because the time to reach adsorption equilibrium is very long to.

Moreover, Figure 3a–c depict the micromorphology of the IL@ β -CD and DES@ β -CD layer sections together as a double-sided disc, respectively. No pores, cavities, and areas of uneven color are apparent; moreover, the DES@ β -CD layer shows fewer cracks at the same magnification, which accords with the previous strength measurement. Thus, a higher density and tighter combination of involved components were achieved in the DES@ β -CD layer than in the IL@ β -CD layer. As seen in Figure 3c, two layers can form a clear and smooth boundary through a simple stacking and pressurization process, which is easier to enlarge and repeat than other preparation methods of current sorbents. Finally, the current adsorption tablets were continuously stirred (300 rpm) in water for 72 h without any disintegration, indicating their good stability in possible working environments.

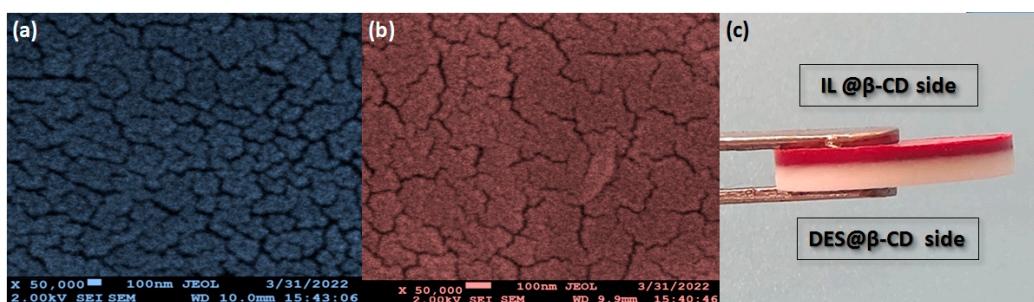


Figure 3. SEM photos of (a) IL-β-CD layer section and (b) curve of DES-β-CD layer section; (c) appearance of double-sided disc.

3.4. Performance Validation of the Sorbent Discs to Capture Hazardous Substances

Discharged water containing heavy metal is considered a form of industrial wastewater that causes serious environmental damage and poses significant harm to humans [25]. Unlike other organic compounds, heavy-metal elements in water cannot be degraded and have enrichment properties. Therefore, this was selected as our adsorption object. Because of the existence of $-NH_2$ in the structure of the IL, the single IL@β-CD disc showed a removal effect for heavy-metal ions, which included Cu^{2+} , Cd^{2+} , Ni^{2+} , As^{2+} , Co^{2+} , and Pb^{2+} . The amino groups can form stable chelates with these target ions, so the disc plays an adsorptive role. The removal efficiency of Cu^{2+} and Pb^{2+} was the highest (experimental conditions: a 0.15 g disc, 1 mg/mL ion concentration, 10 mL solution, 300 rpm, unadjusted pH, adsorption until the solution color no longer became lighter, R.T.), reaching 95.2 and 88.7 mg/g (see Figure 4a) according to the previous quantitative method [22,26]. Adsorption can be improved by adding the loading IL amount and optimizing the separation conditions. For the adsorption of the kinetics of Cu^{2+} , it was found that the pseudo second-order model has a higher correlation coefficient ($R^2 = 0.9902$, $k_2 = 3.09 \times 10^{-2}$ g/mg min) than the pseudo first-order kinetic models ($R^2 = 0.9712$, $k_1 = 0.028$ /min), indicating that the overall rate of the process is influenced by both intraparticle diffusion and external mass transfer. Moreover, chemisorption is the rate-limiting step during adsorption [27].

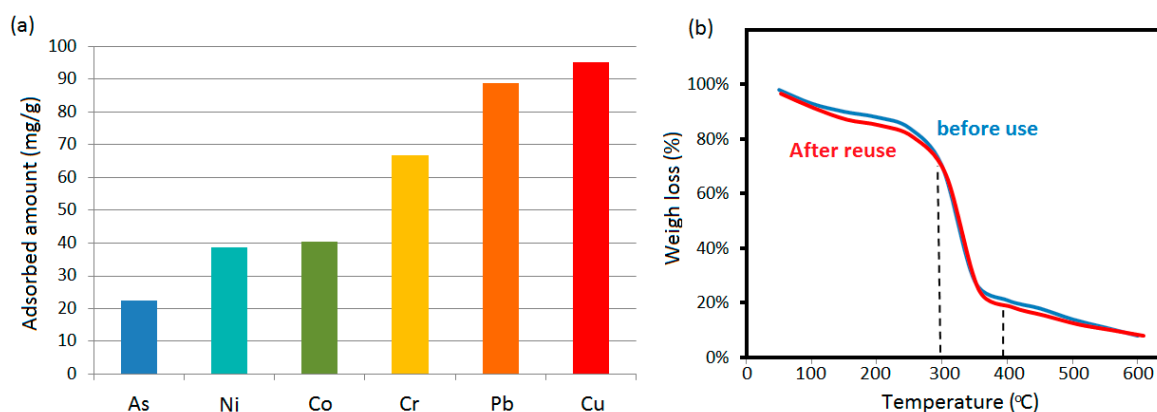


Figure 4. (a) Comparison of adsorbed amounts of metal ions and (b) thermogravimetric analysis (TGA) of double-sided disc before and after reuse.

On the other hand, cationic dyes are widely used in the textile, dyeing and finishing industries. Once these dyes appear in a water environment, they have a significant impact on the water chromaticity. Therefore, we chose alkaline red 18 (C.I.11085) as the target of the investigation for the single DES@β-CD disc in this section; although it is more easily adsorbed by acidic adsorbents because of its structure, we aimed to investigate whether the DES of choline chloride-acetic acid would also play a certain role. After the adsorption experiments (experimental conditions: a 0.15 g disc, 1 mg/mL, 10 mL solution,

300 rpm, unadjusted pH, 24 h, R.T.), the adsorption efficiency of alkaline red was 60.8 mg/g according to the developed quantitative method [28], and was thus in the reported range of over 10–100 mg in current studies of similar sorbents [29]. According to the verified mechanisms in recent reports, the interactions between the immobilized IL/DES and hazardous substances of the above inorganic ions together with pigment mainly include electronic interaction, π - π dispersion interaction, H-bonding, and ion-exchange etc. [22,30–32].

Based on the above performance, the double-faced disc of two complexes was used to simultaneously adsorb these substances on its two sides, and the actual water sample was collected from Mingyuan Lake in Jiangan campus of Sichuan University, Chengdu. Before the adsorption experiment, the water was spiked with standard Cu^{2+} and alkaline red 18 to the concentration of 100 $\mu\text{g/L}$ according to the previous method [33]. As a result, 96.5% Cu^{2+} and 94.9% pigment were adsorbed by the double-faced sorbent disc. After the desorption of the 0.12 M HCl solution, the disc can be reutilized. As shown in Figure 4b, the thermogravimetric analysis results indicate that there is no significant change in the composition of the double-layer composite disc before and after reuse. Because polysaccharides, including cyclodextrin and substituted cellulose, are the main components in the tablet, the main weight loss of around 300–400 °C corresponds to their decomposition [34,35]. The IL and DES are not as stable and begin to degrade before this temperature range. If there is a decrease in adsorption performance after multiple uses, it is suggested to crush the tablet and employ ethyl acetate to remove ethyl cellulose from the powders; then the remaining complexes of IL/DES and β -CD can be further washed with HCl and UP water. After they were dried, the resultant powders were mixed with clean diluent in a preset proportion for re-pressing the new tablet.

4. Conclusions

As two kinds of effective green solvents attracting great attention in recent years, ILs and DESs are widely used in various fields such as separation and environmental science and attracting major attention from academia and industry. However, they have not been simultaneously utilized in the same sorbent; furthermore, current forms of sorbents need to be extended and renewed. In the current study, the suitable ILs and DESs were selected with their potential targets. Together with β -CD, they were first prepared by a simple and effective inclusion method. After that, the two kinds of complex were applied to a special coin-like sorbent disc with two different sides by adding diluent and pressing the mixture for appropriate duration. As a result, the IL and DES were stably immobilized on the different sides of the disc for selective adsorption of possible pollutants in water in a simple, easy-to-perform operation. We expect that this procedure will be a useful tool for water purification and quality detection by feasibly combining green solvents and adsorption technologies.

Author Contributions: Conceptualization, N.L. and Y.G.; methodology, N.L.; software, Y.G.; validation, N.L. and Y.G.; formal analysis, H.C.; investigation, H.C.; data curation, A.A.; writing—original draft preparation, A.A.; writing—review and editing, S.T.; visualization, S.T.; supervision, S.Y.; project administration, S.Y.; funding acquisition, S.Y. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Juni, F.; Bashir, M.J.K.; Haider Jaffari, Z.; Sethupathi, S.; Wong, J.W.C.; Zhao, J. Recent advancements in the treatment of emerging contaminants using activated persulfate oxidation process. *Separations* **2023**, *10*, 154. [[CrossRef](#)]
2. Liu, X.; Lu, D.; Zhang, A.; Liu, Q.; Jiang, G. Data-driven machine learning in environmental pollution: Gains and problems. *Environ. Sci. Technol.* **2022**, *56*, 2124–2133. [[CrossRef](#)]
3. Nitin, R.; Prabhat, K.S.; Nityanand, S.M. Pharmaceuticals in water as emerging pollutants for river health: A critical review under Indian conditions. *Ecotoxicol. Environ. Saf.* **2022**, *247*, 114220.
4. Jaqueline, B.; João, H.Z.D.S. Chapter 3—Green Solvents for Remediation Technologies. In *Green Sustainable Process for Chemical and Environmental Engineering and Science*; Rajender, B.I., Abdullah, M.A., Eds.; Elsevier: Amsterdam, The Netherlands, 2021; pp. 23–30.
5. Feng, X.; Song, H.; Zhang, T.; Yao, S.; Wang, Y. Magnetic Technologies and green solvents in extraction and separation of bioactive molecules together with biochemical objects: Current opportunities and challenges. *Separations* **2022**, *9*, 346. [[CrossRef](#)]
6. Abu, H.N.; Abdul, S.N.; Siti, F.M.N.; Syafikah, H.P.; Muhammad, L.N.; Siti, M.N.H.; Rushdan, A.I.; Norzita, N.; Aznizam, A.B.; Zuliahani, A.; et al. Recent Advances in using adsorbent derived from agricultural waste for antibiotics and non-steroidal anti-inflammatory wastewater treatment: A review. *Separations* **2023**, *10*, 300.
7. Kopac, T. Research progress on process-intensified water treatment applications. *Separations* **2022**, *9*, 353. [[CrossRef](#)]
8. Wang, Y.; Li, W.; Luo, S.; Liu, S.; Li, J. Research advances on the applications of immobilized ionic liquids functional materials. *Acta Chim. Sin. Chin. Ed.* **2018**, *76*, 85–94. [[CrossRef](#)]
9. Dowlatshah, S.; Saraji, M.; Pedersen-Bjergaard, S.; Ramos-Payán, M. Microfluidic liquid-phase microextraction based on natural deep eutectic solvents immobilized in agarose membranes. *J. Chromatogr. A* **2021**, *1657*, 462580. [[CrossRef](#)] [[PubMed](#)]
10. Kakaei, S.; Khameneh, E.S.; Hosseini, M.H.; Moharreri, M.M. A modified ionic liquid clay to remove heavy metals from water: Investigating its catalytic activity. *Int. J. Environ. Sci. Technol.* **2019**, *17*, 2043–2058. [[CrossRef](#)]
11. Yohannes, A.; Li, J.; Yao, S. Various metal organic frameworks combined with imidazolium, quinolinium and benzothiazolium ionic liquids for removal of three antibiotics from water. *J. Mol. Liq.* **2020**, *318*, 114304. [[CrossRef](#)]
12. Fan, T.; Yan, Z.; Yang, C.; Qiu, S.; Peng, X.; Zhang, J.; Hu, L.; Chen, L. Preparation of menthol-based hydrophobic deep eutectic solvents for the extraction of triphenylmethane dyes: Quantitative properties and extraction mechanism. *Analyst* **2021**, *146*, 1996–2008. [[CrossRef](#)]
13. Phosiri, P.; Burakham, R. Deep eutectic solvent-modified mixed iron hydroxide–silica: Application in magnetic solid-phase extraction for enrichment of organochlorine pesticides prior to GC-MS analysis. *J. Sep. Sci.* **2022**, *44*, 3636–3645. [[CrossRef](#)] [[PubMed](#)]
14. Mao, X.; Liu, Y.; Chen, D.; Chen, Z.; Chunan, M.A. Electrochemical reduction of CO₂ in [NH₂-emim]Br/[Bmim]BF₄ ionic liquid composite. *CIESC J.* **2017**, *68*, 2027–2034.
15. Sethi, O.; Singh, M.; Kang, T.S.; Sood, A.K. Volumetric and compressibility studies on aqueous mixtures of deep eutectic solvents based on choline chloride and carboxylic acids at different temperatures: Experimental, theoretical and computational approach. *J. Mol. Liq.* **2021**, *340*, 117212. [[CrossRef](#)]
16. Das, K.; Datta, B.; Rajbanshi, B.; Roy, M.N. Evidences for inclusion and encapsulation of an ionic liquid with β-CD and 18-C-6 in aqueous environments by physicochemical investigation. *J. Phys. Chem. B* **2018**, *122*, 1679. [[CrossRef](#)] [[PubMed](#)]
17. Li, X.; Lee, Y.R.; Row, K.H. Synthesis of mesoporous siliceous materials in choline chloride deep eutectic solvents and the application of these materials to high-performance size exclusion chromatography. *Chromatographia* **2016**, *79*, 375–382. [[CrossRef](#)]
18. Pedro, A.Q.; Coutinho, J.A.P.; Freire, M.G. Immobilization of Ionic Liquids, Types of Materials, and Applications. In *Encyclopedia of Ionic Liquids*; Zhang, S., Ed.; Springer: Singapore, 2022.
19. Shah, R.V.; Pandey, A.K.; Kumar, S.J.; Paul, S.; Rao, R.M.; Jaison, P.G. One step sample treatment and loading using a deep eutectic solvent immobilized in a porous substrate for thermal ionization mass spectrometry of Pu(IV) ions. *J. Anal. Atom. Spectrom.* **2020**, *35*, 2315–2321. [[CrossRef](#)]
20. Liu, B.; Zhou, Y.; Luo, X.; Qin, H.; Cao, S. FTIR spectral analysis of ionic liquids 1-butyl 1-3-methylimidazolium bromine synthesis. *Adv. Meas. Lab. Manag.* **2007**, *2*, 13–14.
21. Bratu, I.; Veiga, F.; Fernandes, C.; Hernanz, A.; Gavira, J.M. Infrared spectroscopic study of triacetyl β-cyclodextrin and its inclusion complex with nifedipine. *Spectroscopy* **2015**, *18*, 459–467. [[CrossRef](#)]
22. Chen, C.; Feng, X.; Yao, S. Ionic liquid-multi walled carbon nanotubes composite tablet for continuous adsorption of tetracyclines and heavy metals. *J. Clean. Prod.* **2020**, *286*, 124937. [[CrossRef](#)]
23. Marten, K.; Jian, X.W.; Jukka, R.; Jens, M.C.; Thomas, R.; Claudia, S.L. Multispectral UV imaging for fast and non-destructive quality control of chemical and physical tablet attributes. *Eur. J. Pharm. Sci.* **2016**, *90*, 85–95.
24. Park, G.; Lee, J.H.; Kim, I.S.; Cho, J. Pharmaceutical rejection by membranes for wastewater reclamation and reuse. *Water Sci. Technol.* **2004**, *502*, 239–244. [[CrossRef](#)]
25. Dietzel, B.M. Novel green technology for wastewater treatment: Geo-material/geopolymer applications for heavy metal removal from aquatic media. *Int. J. Sediment Res.* **2023**, *38*, 33–48.
26. Zhang, T.; Jiang, W.; Cao, Y.; Zhu, C.; Toukouki, S.; Yao, S. A facile one-pot synthesis of ionic liquid@porous organic frameworks for rapid high-capacity removal of heavy metal ions, pesticides and aflatoxin from two non-food bioactive products. *Ind. Crops Prod.* **2022**, *181*, 114859. [[CrossRef](#)]

27. Lee, S.P.; Ali, G.; Algarni, H.; Chong, K.F. Flake size-dependent adsorption of graphene oxide aerogel. *J. Mol. Liq.* **2019**, *277*, 175–180. [[CrossRef](#)]
28. Wang, X.; Ying, C. UV-Vis detection-reversed- phase high performance liquid chromatography determination of basic red 1:1. *Text. Aux.* **1998**, *5*, 35–37.
29. Kopsidas, O. Pigment adsorption optimization in various low cost adsorbents. *J. Environ. Sci. Eng. A* **2021**, *10*, 20. [[CrossRef](#)]
30. Danner, M.C.; Robertson, A.; Behrends, V.; Reiss, J. Antibiotic pollution in surface fresh waters: Occurrence and effects. *Sci. Total Environ.* **2019**, *664*, 793–804. [[CrossRef](#)]
31. Kozonoi, N.; Ikeda, Y. Extraction mechanism of metal ion from aqueous solution to the hydrophobic ionic liquid, 1-butyl-3-methylimidazolium nonafluorobutanesulfonate. *Monatshfte Chemie-Chem. Mon.* **2007**, *138*, 1145–1151. [[CrossRef](#)]
32. Li, Z.; Tang, C.; Hu, S.; Wang, C. Preparation and dye-adsorption of ionic liquid loading molecular sieve. *Chin. J. Environ. Eng.* **2014**, *8*, 3848–3852.
33. Lakshmi, D.S.; Santoro, S.; Avruscio, E.; Tagarelli, A.; Figoli, A. Preparation of polymer inclusion membranes (PIMs) with ionic liquid and its application in dye adsorption process supported by statistical analysis. *Int. J. Membr. Sci. Technol.* **2015**, *2*, 65–77. [[CrossRef](#)]
34. Zhao, Y.; Zhang, L.; Zhai, X.; Liu, Q.; Sun, L.; Liu, M.; An, L.; Xian, L.; Zhang, P.; Chen, L. Study on adsorption performance of benzoic acid in cyclocarya paliurus extract by ethyl cellulose microspheres. *Chemistry* **2021**, *3*, 1113–1125. [[CrossRef](#)]
35. Wang, T.; Li, B.; Feng, Y.; Guo, Q. Preparation, quantitative analysis and bacteriostasis of solid state iodine inclusion complex with β -cyclodextrin. *J. Incl. Phenom. Macrocycl. Chem.* **2011**, *69*, 255–262. [[CrossRef](#)]

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