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Preparation of Green Biosorbent using Rice Hull to Preconcentrate, Remove and Recover Heavy Metal and Other Metal Elements from Water

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Preparation of green biosorbent using rice hull to preconcentrate, remove and recover heavy metal and other metal elements from water

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HIGHLIGHTS

- Sodium hydroxide treated rice exhibited higher removal of multiple metal ions.
- Electrostatic attraction was determined to be main removal mechanism.
- Acidic circumstances facilitated the removal of metal ions.
- Processed rice hulls provide an economic alternative to costly resins.

GRAPHICAL ABSTRACT
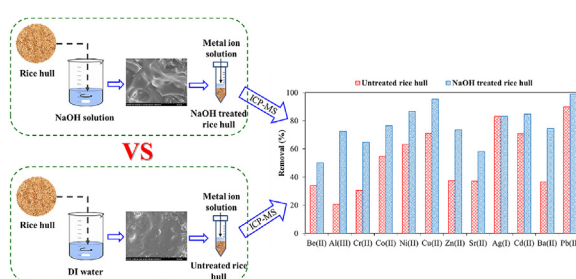
ABSTRACT

Sodium hydroxide treated rice hulls were investigated to preconcentrate, remove, and recover metal ions including Be^{2+}, Al^{3+}, Cr^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Sr^{2+}, Ag^+, Cd^{2+}, Ba^{2+}, and Pb^{2+} in both batch mode and column mode. Sodium hydroxide treatment significantly improved the removal efficiency for all metal ions of interest compared to the untreated rice hull. The removal kinetics were extremely fast for Co, Ni, Cu, Zn, Sr, Cd, and Ba, which made the treated rice hull a promising economic green adsorbent to preconcentrate, remove, and recover low-level metal ions in column mode at relatively high throughput. The principal removal mechanism is believed to be the electrostatic attraction between the negatively charged rice hulls and the positively charged metal ions. pH had a drastic impact on the removal for different metal ions and a pH of 5 worked best for most of the metal ions of interest. Processed rice hulls provide an economic alternative to costly resins that are currently commercially available products designed for metal ion preconcentration for trace metal analysis, and more importantly, for toxic heavy metal removal and recovery from the environment.

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1. Introduction

The contamination of water by heavy metals originating from through the discharge of industrial wastewater is a worldwide environmental problem and threat to human health (Abdolali et al., 2017; Ajmal et al., 2003; Das et al., 2008). Unlike organic pollutants

which are generally susceptible to biological degradation, heavy metals do not normally degrade into harmless end products (Gupta et al., 2001). In the US EPA's national primary drinking water regulations, the maximum contaminant levels (MCLs) of Sb, As, Ba, Be, Cd, total Cr, Cu, Pb, Se, and Tl are set to 0.006 mg/L, 0.01 mg/L, 2 mg/L, 0.004 mg/L, 0.005 mg/L, 0.1 mg/L, 1.3 mg/L, 0.015 mg/L, 0.05 mg/L, and 0.002 mg/L, respectively. The World Health Organization (WHO) also has similar regulations on the metal concentrations permitted in drinking water. Conventional methods for heavy metal pollution treatment include precipitation, electrochemical treatment, ion exchange, adsorption, and membrane process (Basso et al., 2002; Das et al., 2008; Li et al., 2015). Adsorptive removal of heavy metal ions in wastewater is usually achieved by using activated carbon or activated alumina (Faust and Aly, 2013; Sun and Shi, 1998). Though these are efficient techniques, the major disadvantages of these methods compared to widely available agricultural byproducts (ABPs) include the high cost, high energy requirement, and production of toxic sludge (Bulgariu and Bulgariu, 2018).

Readily available and inexpensive ABPs such as rice hull, soybean hull, sugarcane bagasse, and sunflower stalk have shown promising efficiency in heavy metal ions removal (Abdolali et al., 2016; Das et al., 2008; Khan et al., 2004; Okoro et al., 2011). Rice is cultivated as an essential food source in more than 75 countries, especially in Asia (Khan et al., 2004), and the world produces about 80 million tons of rice hull each year (Acharya et al., 2018). Because of its abundance, local availability, granular structure, low cost, insolubility in water, high chemical stability, and high mechanical strength, rice hulls were selected as a potential biosorbent (Abdelwahab et al., 2005; Acharya et al., 2018; Chuah et al., 2005; Ngah and Hanifah, 2008).

The major composition of rice hulls is ~32% wt. Cellulose, ~21% wt. Lignin, ~21% wt. Hemicellulose/pentosane, and ~15% wt. Ash in which 96% is silica (Chuah et al., 2005; Govindarao, 1980; Ngah and Hanifah, 2008). The content of each component is also source-dependent. The acidic nature of cellulose has been understood since the 1920s. Helen Masters reported that the neutral sodium chloride solution became acidic after being filtered through cotton wool (Masters, 1922). Heymann and his colleagues systematically studied the acidic nature of cellulose and they found that the acidity is mainly a result of the dissociation of the stray carboxyl groups on cellulose (Heymann and Rabinov, 1941; Rabinov and Heymann, 1941). Fras et al. found that the charge of cotton is due to the dissociation of two types of acidic groups, one with pKa = 3.5 and another one with pKa = 5.5. The pKa value of the stronger one typically corresponds to the carboxyl group (Fras et al., 2004). The dissociation of cellulose or lignocellulose under certain pH is very important for their absorption character and reactivity (Kreze et al., 2001, 2002).

Most publications that use rice hulls to remove heavy metal/metalloid ions were carried out in batch mode, whereas the continuous column mode is more efficient for real application (Bhatnagar et al., 2015). Even though there are some publications in column mode, the concentrations studied were generally at a high mg/L range and no more than 5 metal ions were studied (Bhatnagar et al., 2015; Low et al., 1999; Luo et al., 2011). For some samples, metal concentrations can be very low (μg/L and sub μg/L level) and are difficult to quantify even with the most sensitive inductively coupled plasma-mass spectrometer (ICP-MS). It is also important to be able to screen many different metals in a sample simultaneously to find the correlation between metal concentration and other factors, such as diseases status. For instance, the metallomics represents a promising biomarker discovery approach, which is exemplified in our recent study of correlating urinary metal to breast cancer (Burton et al., 2016).

Preconcentration is one way to analyze the low concentration of metals and it may also enable the use of atomic adsorption or inductively coupled plasma-optical emission spectrometry (ICP-OES) as the quantification technique rather than the expensive ICP-MS method. An economic sorbent capable of preconcentrating low levels of different metal ions with relatively high throughput, holds great significance. In this study, 12 common metal ions including Be^{2+}, Al^{3+}, Cr^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Sr^{2+}, Ag^+, Cd^{2+}, Ba^{2+}, and Pb^{2+}, are selected. Therefore, the objectives of this research are: 1) To probe the removal kinetics for these different metal ions in batch mode by processed rice hulls at the μg/L level, and 2) to study the performance of processed rice hulls in column mode for preconcentration, removal, and recovery of different metal ions at the μg/L level, and to evaluate the potential of a rice hull packed column to serve as an alternative to expensive ion exchange resins.

2. Materials and methods

2.1. Materials and chemicals

The rice hulls were purchased from HomeBrew4Less (Chambersburg, PA, USA). Ultrapure water (18.2 MΩ cm at 25 °C) was produced in-house using Advantage A10 Milli-Q system (Millipore, Billerica, MA, USA). The instrument calibration standard, containing all 12 metal ions of this study was purchased from PerkinElmer (Waltham, MA, USA) as a stock solution. Certified ACS grade sodium acetate trihydrate, glacial acetic acid, sodium hydroxide, trace metal grade nitric acid and hydrochloric acid were purchased from ThermoFisher (Pittsburg, PA, USA). Empty polypropylene solid phase extraction (SPE) tubes (6 mL size) with PE frits used as a packing column was purchased from Sigma/Supelco (St. Louis, MO, USA).

An Eberbach 6010 shaker was used to mix the samples continuously for removal tests in batch mode. An Accumet AB 15 pH meter coupled with an Accumet glass body a standard size combination electrode was used to measure the sample pH. A Supelco solid phase extraction manifold VISIPREP was used to conduct the column experiment.

2.2. Rice hull treatment

The rice hull was washed three times using DI water to rinse off the readily soluble material on the surface. The washed rice hall was then completely dried in an oven at 90 °C for overnight. Twenty grams of this rice hulls were added to 200 mL of a 1 M sodium hydroxide aqueous solution and were magnetically stirred in a 500-mL plastic beaker for 3 h at an ambient temperature. After stirring, the supernatant was decanted and the rice hulls were further washed with DI water to obtain a pH between 7 and 8. Lastly, the processed rice hull was dried in the oven at 90 °C until it maintained a constant weight.

2.3. ICP-MS analysis of metal concentrations

All plastic wares used in this study were pre-cleaned by soaking in 3% (v/v) nitric acid for overnight or longer prior to use. A working solution was prepared by diluting 100 mg/L stock solution which contains all the metal ions of interest to 100 μg/L using 10 mM sodium acetate-acetic acid buffer (pH = 5). In the pH effect study, different pHs of 10 mM sodium acetate-acetic acid buffer were used as a diluent.

The metal concentrations in samples were analyzed by following EPA method 200.8 (US EPA, 1994) using an Elan DRC-e inductively coupled plasma-mass spectrometer (ICP-MS) from PerkinElmer (Waltham, MA, USA) under the same operation

conditions of a published study (Shi et al., 2010). The US EPA quality control guidelines were closely followed for each analysis. Regular instrument calibrations were performed for each analyzed batch or more frequently as it became necessary. The method detection limits were also checked periodically. Reagent blanks, duplicated samples, sample spike recoveries were all analyzed for every 10 samples during each batch of analysis. The certified criteria were set for 80–120% spiked recovery and 10% of relative percent difference of duplicated samples.

2.4. Comparison of untreated and treated rice hulls

2.4.1. Physical characterization

A Nova 2000e surface area analyzer (Quantachrome Instruments, FL, USA) was used to measure the specific areas of rice hulls before and after the sodium hydroxide treatments. A FEI Helios NanoLab 600 FIB/FESEM scanning electron microscope (SEM) (Hillsboro, OR, USA) was used to characterize the microstructure of both untreated and treated rice hull.

2.4.2. Removal experiment in batch mode

One hundred milligrams of rice hulls were weighed and transferred to a pre-cleaned 19-mL propylene tube. Ten mL of 100 μg/L metal ion solution (pH = 5) was then added to the tube. The samples were shaken for 24 h with a speed of 180 strokes/min at ambient temperature. After shaking, 2.5 mL of the supernatant was transferred directly to a pre-cleaned auto-sampler tube followed by the acidification the sample. The acidification was carried out by adding 2.5 mL of 2% (v/v) nitric acid for ICP-MS analysis. The leftover solution was transferred to another clean tube for pH measurement and this pH was recorded as the final pH.

2.5. The effect of pH on removal

Different portions of 10 mM sodium acetate solution and 10 mM acetic acid solution were mixed to obtain different pHs. The 100 mg/L stock solution was diluted to 100 μg/L by using different pH sodium acetate-acetic acid buffers. The procedures described in *2.4.2* and *2.3* were used to conduct the removal experiment and ICP-MS analysis. All pHs were measured after shaking.

2.6. Rice hull dosage study

Dosage effect was systematically studied by using rice hull to working solution ratios of 1, 5, 10, 20, 50, 100, 150, 200, 300, and 500 mg/10 mL. The procedures used in the removal experiment and ICP-MS analysis were the same as those described in *2.4.2* and *2.3*. The pH was measured after 24 h shaking.

2.7. Effect of sodium hydroxide concentration on the rice hull treatment

Different sodium hydroxide concentrations, 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0 M, were used to process the rice hulls. Five grams of DI water washed rice hulls were mixed with 60 mL of different sodium hydroxide solutions in a 125-mL plastic bottle and the bottles were shaken for 3 h at ambient temperature on the shaker. After shaking, the supernatant was decanted and DI water was applied to wash the sodium hydroxide treated rice hull until the pH reached between 7 and 8. The treated rice hull was completely dried in the oven at 90 °C for overnight. The procedures described in *2.4.2* with a rice hull dosage of 100 mg/10 mL were used for removal experiments to evaluate the effect of sodium hydroxide concentration on the treatment. All pHs were measured after shaking.

2.8. Study of removal kinetics in batch mode

Based on results from the separate studies examining the effects of pH and dosages, pH = 5 and 100 mg/10 mL were selected to carry out the kinetics study. The experiment procedures were the same as the procedures described in *2.4.2* with the exception that the shaking times were set to 10 min, 20 min, 30 min, 1 h, 2 h, 5 h, 12 h, and 24 h. All pHs were measured after shaking.

2.9. Metal ion preconcentration, removal, and recovery in column mode

2.9.1. Column test procedures

In the column test, 500 mg of sodium hydroxide treated rice hull was packed into an SPE cartridge with a bottom frit. Another frit was placed on the top to secure the rice hull and to create a relatively dense "column bed". The same empty SPE cartridge with both top and bottom frits, but without the sodium hydroxide treated rice hull served as a control. The SPE cartridges were then put onto the SPE manifold. The SPE cartridge and solution bottle were connected through transfer tubing. Firstly, 10 mM sodium acetate-acetic acid buffer (pH = 5) was applied to wet and condition the rice hull until there were no bubbles coming out of the cartridge. Secondly, the sodium acetate-acetic acid buffer was replaced by the metal ion solution (pH = 5, 100 μg/L for each metal ion). The solution level in the cartridge was always kept above the top frit to avoid drying the cartridge. The vacuum applied to each port/cartridge was adjusted to make the solution pass through the SPE cartridge drop by drop. A pre-acid cleaned tube was put in the rack to collect the eluent from each SPE cartridge. Each tube collected 10 mL of eluent for each fraction and 14 fractions were collected in total. The pHs of the collected samples were measured and the metal concentrations were analyzed by ICP-MS using the procedures described in *2.3*.

2.9.2. Acid elution and metal ion recovery

After the preconcentration and removal experiments described in *2.9.1* were completed, the SPE cartridge was dried under a vacuum until no liquid came out. Three mL of 0.2 M trace metal grade hydrochloric acid was added to soak the rice hull packed cartridge for approximately 5 min. The vacuum was then turned on and adjusted to make the flow rate approximately 1 drop/sec and a total of 15 mL of acid was applied to each cartridge. The eluent was collected in a clean auto-sampler tube and analyzed by ICP-MS.

2.9.3. Column regeneration and reuse

After acid washing, the rice hull packed cartridge was rinsed by a sodium acetate-acetic acid buffer (pH = 5, 10 mM, without metal ions of interest) until the pH of the eluent reached 5. The procedures described in *2.9.1* were used for the column's second use and third use. However, instead of collecting separate 10-mL fractions in the first and second uses, a single 100 mL eluent was collected in a 125-mL plastic. The column's third use was utilized for ICP-MS analysis and pH measurement.

2.10. Application for real drinking water sample

To evaluate the applicability of the rice hull green adsorbent in real drinking water matrix, the experiments were performed for real drinking water from river water as resource. A 0.5 mL portion of 100 mg/L stock solution was spiked into each 500 mL drinking water sample. The pH of the water was adjusted to pH = 5 by 0.1 M acetic acid. The column test procedures described in *2.9.1* were used in the subsequent experimental processes with the only change of collecting a single 100 mL of eluent in a 125 mL plastic

bottle for each column instead of 14 different fractions. The pH of each collected sample was then measured, and the metal concentrations were analyzed by ICP-MS.

3. Results and discussion

3.1. Metal removal efficiency of untreated and sodium hydroxide treated rice hull

Fig. 1 shows the comparison of metal ion removal efficiencies by untreated (DI water washed) and sodium hydroxide treated rice hulls. The final pHs of untreated rice hull samples and sodium hydroxide treated rice hull samples, 4.9 and 5.0, respectively, did not change significantly at the end of the removal experiment. Untreated rice hull showed high removals for Pb, Cd, Cu, and Ag ions (about 70%–80%). However, for other metal ions tested, the removal was relatively low (from 20% to 60%). After the sodium hydroxide treatment, the removal efficiency increased significantly. All the metals tested were removed at percentages over 60% except Be(II) with about 50% removal. The removal of Pb(II) almost reached 100% and the removal of Cu(II) was more than 95%.

The major composition of rice hulls consists of cellulose, hemicellulose, lignin, and silica (Govindarao, 1980). During sodium hydroxide treatment, silica can be removed by the following reaction with sodium hydroxide:

$$2NaOH + SiO_2 \rightarrow Na_2SiO_3 + H_2O \tag{1}$$
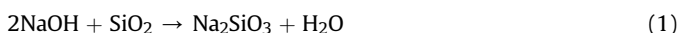
This was confirmed by measuring silicon levels in the solution after sodium hydroxide treatment by ICP-OES (data not shown). The specific surface areas for untreated rice hulls and sodium hydroxide treated rice hulls were 0.561 m^2/g and 1.574 m^2/g, respectively. After sodium hydroxide treatment, the specific surface area increased approximately 2 times. SEM images in Fig. 2 show that some porous structure was created on the surface the rice hull following the sodium hydroxide treatment, which made the rice hull more accessible for metal ions. It is reported that the surface area (porosity) of cellulosic materials is an important factor that affects the adsorption capacity (Sun and Xu, 1997; Wartelle et al., 2000). The more porous the rice hull, the more negative charges available on the surface for positively charged metal ions to react with. The removal capacity has a direct relationship with the total negative charge on the surface (Wartelle et al., 2000). Due to the high content of silica in rice hulls, the solution after sodium hydroxide contains a high content of sodium silicate and the by-

product can also potentially be used to produce pure silica (Kalapathy et al., 2000a, 2000b), which is economically beneficial and environmentally friendly.

3.2. Effect of pH

pH is an important factor in the removal study. It affects the surface charge of rice hull and the degree of ionization and speciation of metal ions in solution. Fig. 3 summarizes the pH effect on metal removal by processed rice hulls and it shows that the removal efficiency increases as pH increases, with the exception of Pb and Cr. The higher the pH, the more deprotonation of dissociable groups on the rice hull's surface, and therefore the more sites available for these positively charged ions to react with. This deprotonation is caused by groups such as the hydroxyl, carboxyl, and phenol groups. Pb was completely removed in the pH range from 3.67 to 4.50, then its removal rate decreased as the pH continued to increase. The removal efficiency of Cr increased at first and then started decreasing when the pH levels were higher than 5. This might be due to the formation of several hydroxyl low-soluble species, such as $Pb(OH)_2$ and $Cr(OH)_3$, which form at higher pH values. This formation may have resulted in the decreased electrostatic attraction since this occurrence is proportional to the number of charges (Feng et al., 2011). Considering both the pH-removal efficiency curve and potential metal ion precipitation at high pHs, a pH of 5 was optimal for most of the selected metal ions and thus was selected for the subsequent removal experiments.

3.3. Effect of processed rice hull dosage

Fig. 4 shows the dosage curve of processed rice hulls. The pH was measured after 24 h of shaking for each sample, until all of them were close to a pH of 4.9. At a fixed metal ion concentration, the higher the dosage, the more negative charges available on the rice hull surface, which resulted in a higher removal efficiency. At a lower dosage range of 1 mg/10 mL to 100 mg/10 mL, the removal efficiency increased drastically as the dosage increasing. However, from 100 mg/10 mL to 500 mg/10 mL, the removal efficiency either did not change or slightly increases as the dosage increases. Therefore, 100 mg/10 mL was chosen for the removal experiment.

3.4. Effect of sodium hydroxide concentration on treatment

Sodium hydroxide is believed to mainly remove the silica in rice hull and make it more porous and accessible. The silica is approximately 20% (w/w) of total weight of rice hulls, though this percentage is source-dependent (Govindarao, 1980). In the sodium hydroxide treatment, the ratio of rice hull to sodium hydroxide solution used was 1:10 (20 g of rice hull in 200 mL of sodium hydroxide solution). From the stoichiometry of the silica and sodium hydroxide reaction, sodium hydroxide was in excess. Moreover, if a 1 M sodium hydroxide solution was used, it would take a large amount of water to wash the rice hull to a pH between 7 and 8 after treatment. Therefore, sodium hydroxide concentration for the rice hull treatment was optimized. Fig. S1 shows the removal efficiency of rice hulls treated by different sodium hydroxide concentrations. The pHs were measured after shaking and all of them were very close to a pH of 5. Only the 0.1 M sodium hydroxide solution treated rice hull showed a slight decrease in removal efficiency. From the 0.2 M to the 1.0 M sodium hydroxide treated rice hull, there was no significant difference in removal efficiency. Therefore 0.2 M sodium hydroxide solution is sufficient for the treatment. During the experiment, the lower the sodium hydroxide concentration, the easier it was to wash off the residual sodium hydroxide on the rice hull.
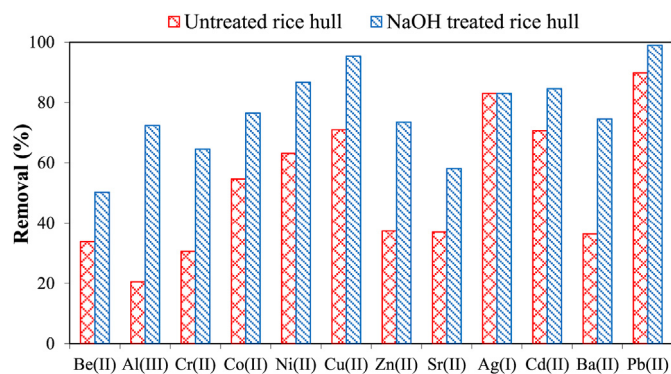

Fig. 1. Comparison of metal ion removal efficiencies by untreated (DI water washed) and sodium hydroxide treated rice hull in batch mode. Experiment conditions: rice hull = 100 mg, metal ion solution = 10 mL (100 μg/L), pH$_o$ = 5, reaction time = 24 h, T = 25 °C.
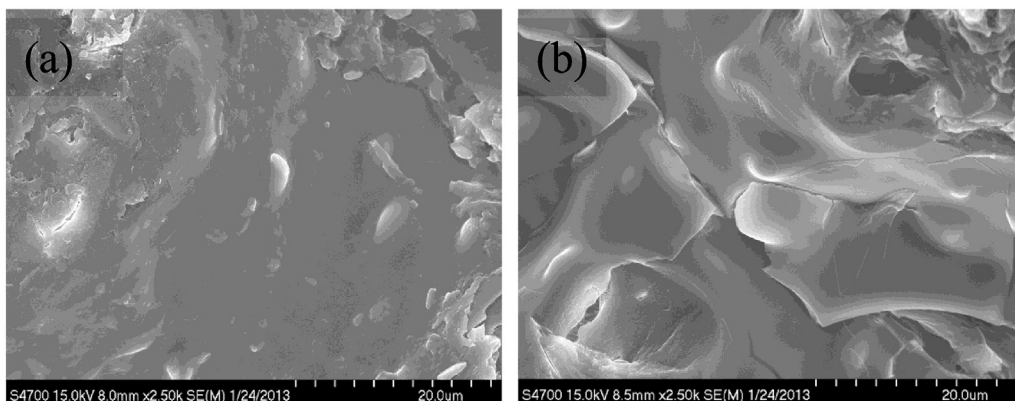
Fig. 2. SEM images of untreated rice hull and sodium hydroxide treated rice hull. The bottom of each panel shows the instrumental parameters. (a) and (b) are untreated and 1 M sodium hydroxide treated rice hulls, respectively.
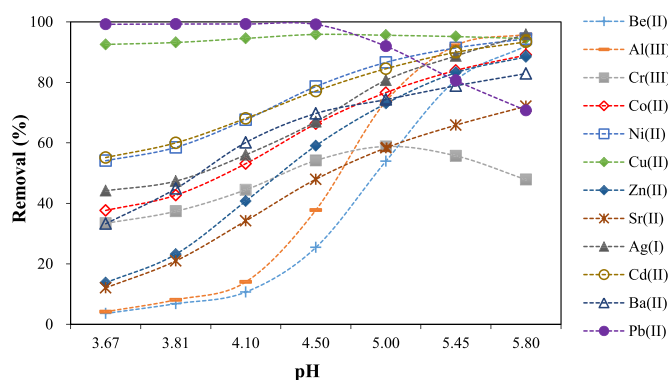

Fig. 3. Effect of pH for metal removal by sodium hydroxide treated rice hull. Experiment conditions: rice hull = 100 mg, metal ion solution = 10 mL (100 μg/L), reaction time = 24 h, T = 25 °C.

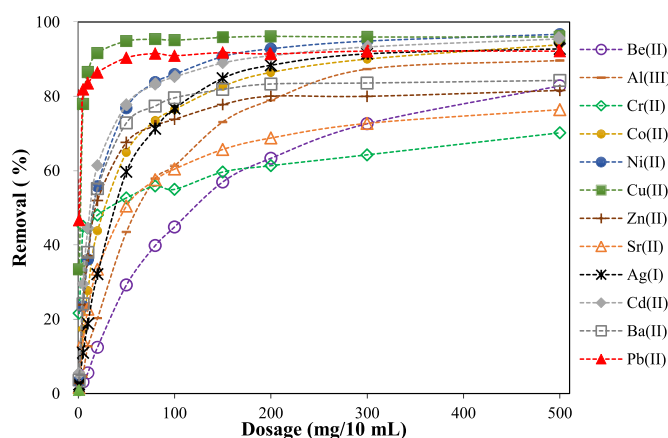**Fig. 4.** Effect of processed rice hull dosage on metal elements removal efficiencies. Experiment conditions: metal ion solution = 10 mL (100 μg/L), pH$_o$ = 5, reaction time = 24 h, T = 25 °C.

3.5. Kinetics study

Fig. S2 shows the kinetics data of all metal ions at a pH of 5 and 100 mg/10 mL dosage. Fig. S2(a) shows that the kinetics of Co, Ni, Cu, Zn, Sr, Cd, and Ba ions were extremely fast and the equilibrium could be reached in 10−20 min. These seven metal ions were classified as fast kinetics metals (Group 1). Fig. S2(b) shows that the

kinetics of Be, Al, Cr, Ag, and Pb ions were relatively slower than that of the first group, but most of them still reached equilibrium in 5 h. They were classified as slow kinetics metals (Group 2). Removal kinetics for Cr was much slower as 12 or more hours of contact time were needed to reach equilibrium. The result is also in agreement with Sun's research using a lignocellulosic sunflower stalk as an adsorbent for the removal of Zn, Cu, Cd, and Cr ions in wastewater (Sun and Shi, 1998). The overall fast kinetics also indicates that the principal removal mechanism was electrostatic attraction between the rice hull and the metal ions. Along with this, the electrostatic force normally yields rapid attraction between the opposite charges. The adsorption-dominated removal process usually involves an adsorbent material with an extremely high specific area, such as active carbon with several hundred m^2/g as its specific area. Even after sodium hydroxide treatment, the specific surface area of a rice hull was only 1.574 m^2/g, which is much lower than that of active carbon. Therefore, given the extremely fast kinetics and low specific surface area of a rice hull, electrostatic attraction rather than adsorption was believed to be the principal force for metal ion removal.

3.6. Column test

3.6.1. Removal efficiency in column test

Fig. 5(a) and (b) show the concentration profiles of 14 collected fractions from column tests. The negatively charged sites preferentially reacted with Group 1 metal ions (fast kinetics metals) over Group 2 metal ions (slow kinetics metals) in column mode. Therefore, in Fig. 5(a) the concentrations of Group 1 metal ions in the collected fractions were much lower than those of Group 2 metal ions shown in Fig. 5(b). In column mode, the metal ions passed through the rice hull column bed very quickly and thus the contact time between the rice hull and the metal ions was very short. In this situation, kinetics became the determining factor controlling the removal efficiency. Metal ions of fast kinetics occupied the attraction sites first. There was not enough time for metal ions with slow kinetics to all interact with the rice hulls and therefore they flew out of the column without being removed. As a consequence, most of them were still in the solution and the removal efficiency was relatively low.

3.6.2. Removal comparison between column mode and batch mode

The removal efficiency in column mode was calculated in the following manner to compare with batch mode removal efficiency. In column mode, 500 mg of rice hulls was packed in the cartridge and thus the equivalent volume of metal solution was 50 mL
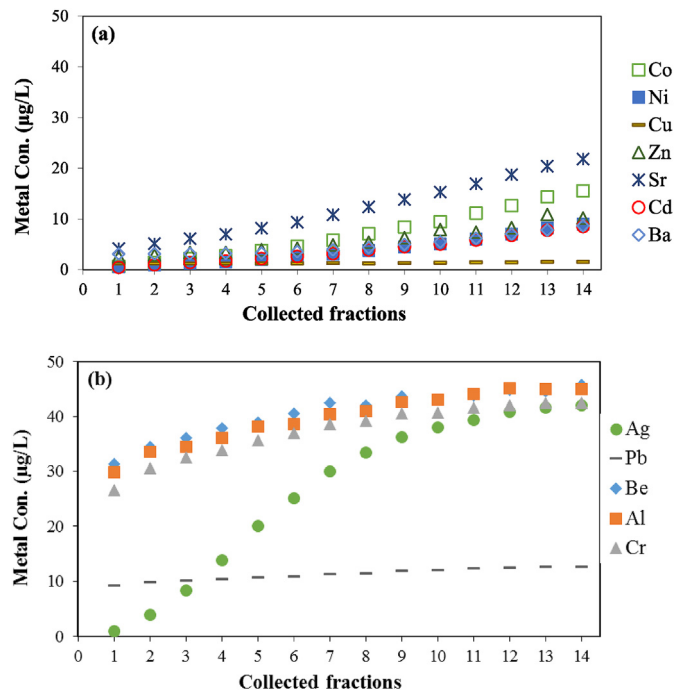
Fig. 5. Concentration profiles of 14 collected fractions in column tests. (a): Fast kinetics metals; (b) Slow kinetics metals. Experiment conditions: rice hull = 500 mg, [metal ion solution]$_o$ = 100 μg/L, pH$_o$ = 5, T = 25 °C.

compared to batch mode in which a 100 mg/10 mL dosage was used. Therefore, concentrations of the first five fractions were used to calculate the removal efficiency in column mode.

$$C_{average} = (C_1 V_1 + C_1 V_1 + ... + C_5 V_5) / 50 \qquad (2)$$

$$Removal\ Efficiency, \% = 100 \times (C_0 - C_{average}) / C_0 \qquad (3)$$

$C_{average}$, the average concentration of metal ions in the first five fractions.

C_1, C_2, C_3, C_4, C_5, the metal concentration in the first, second, third, fourth, fifth fraction, respectively.

$v_1 = v_2 = v_3 = v_4 = v_5 = 10$ mL.

C_0, metal concentration after passing empty SPE cartridge.

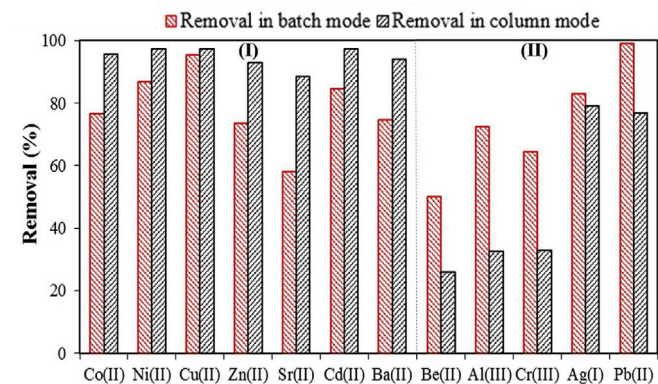Fig. 6 shows the comparison of metal removal efficiency in column and batch modes. The removal efficiencies were different in two modes for Group 1 and Group 2 metal ions. For the fast kinetics metal ions (Group 1), the removal efficiencies in the column test were better than those in batch test. For the slower kinetics metal ions (Group 2), the removal efficiencies in batch mode were better than those in column mode due to the longer contact time in the batch test.

3.6.3. Desorption efficiency in column mode

Fig. S3 shows the desorption of metal ions adsorbed on treated rice hulls by using 15 mL of 0.2 M hydrochloric acid. Except for Al ions, all other metal ions can be eluted with 70% efficiency or better. One hundred and forty mL (10 mL × 14 = 140 mL) of water sample was "extracted" using the rice hull column and only 15 mL of 0.2 M hydrochloric acid can elute 70% or more adsorbed metal ions. This means that this method can be used as a preconcentration technique to preconcentrate low-level metal ions in water for AA and ICP-OES analysis.

3.6.4. Column reuse

The rice hull packed cartridge was used three times to test its reusability. The removal efficiency was calculated using a 500 mg rice hull packed column to extract 100 mL of a 100 μg/L metal ion working solution. Fig. S4 shows that after using a column for three times, the removal efficiencies were still kept about same for most of the metal elements except Ag(I), which displayed some decrease during the third usage (15%). These results indicate that the rice hull column was stable and reusable.

3.7. Removal of metal elements from drinking water

Fig. 7 shows the results of a real drinking water sample application. The removal efficiencies for Cu(II) and Pb(II) in the drinking water were high (92.0% and 85.8%, respectively), which were only slightly difference from their efficiencies in the reagent water. The removal efficiencies of the fast kinetics elements Be, Al, Cr, Ag, and Pb were higher in the drinking water than the removal efficiencies in reagent water. The removal efficiencies of slow kinetics elements Co, Ni, Cu, Zn, Sr, Cd, and Ba were lower in the drinking water than the removal efficiencies in the reagent water. The differences of the removal efficiencies in the real drinking water and in the reagent water could be attributed to the matrices of water samples. Some major mineral ions, such as Ca^{2+} and Mg^{2+}, are present in drinking water. As we mentioned above, the electrostatic adsorption is the dominant process to remove metal ions. The presentence of these

Fig. 6. Comparison of metal removal efficiencies in column and batch modes. (I): Fast kinetics metals; (II): Slow kinetics metals. Experiment conditions: rice hull = 500 mg, [metal ion solution]$_o$ = 100 μg/L, pH$_o$ = 5, T = 25 °C.
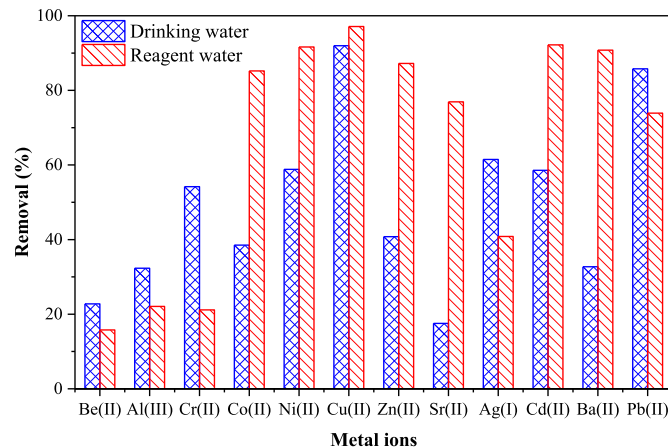

Fig. 7. Comparison of metal elements removal efficiencies for DI water and drinking water sample. Experiment conditions: rice hull = 500 mg, [metal ion solution]$_o$ = 100 μg/L, pH$_o$ = 5, T = 25 °C.

mineral ions can completely deprotonated negatively charged sites on treated rice hulls with the targeted metal ions. Due to its high electrostatic accumulation and greater affinity for the binding site of a rice hull, these divalent cations may have a greater effect on metal adsorption (Lodeiro et al., 2006; Volesky, 2003). Previous studies also showed that the anions such as nitrate, chloride, and sulfate can decrease metal biosorption, which maybe another potential cause for these removal efficiency changes (Ahuja et al., 1999; Diniz and Volesky, 2005). The presences of these cations and anions in the real drinking water may also affect the adsorption kinetics of metal elements by the treated rice hulls. Subsequently, this may affect the removal efficiencies of different metal elements, especially those in the column test for which that contact time is a critical factor. Further studies of the mechanism are valuable, but beyond the scope of this study. Nevertheless, these real application test results indicate that the treated rice hulls have a high practical potential in field application of water treatment.

4. Conclusions

Sodium hydroxide treated rice hulls display excellent removal efficiencies for most heavy metal ions. The principal removal mechanism is believed to be the electrostatic attraction between the negatively charged rice hulls and the positively charged metal ions. pH had a drastic impact on the removal for different metal ions and a pH of 5 worked best for most of the metal ions of interest. The fast removal kinetics made the processed rice hull a promising SPE-type material to preconcentrate and recover metal ions at low concentration levels, thus less expensive analysis methods can be used for subsequent detection. This type of green biosorbent, if upgraded to a large scale process, may be applied to remove and recover heavy metals from the environment.

Credit author statement

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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.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.chemosphere.2020.127940.

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