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STUDY ON THE REMOVAL OF LEAD IONS BY PREPARED CELLULOSE ACETATE-RICE HUSK COMPOSITE FILMS

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Abstract

This research was aimed to study the characterization and adsorption properties of prepared cellulose acetate-rice husk composite films. Rice husk (Zeyar) was collected from a local rice mill in Hlegu Township, Yangon Region, Myanmar. The characterizations of prepared cellulose acetate and rice husk were determined according to physicochemical properties such as pH, moisture content, and bulk density. The polymer composite films were prepared by using cellulose acetate (CA), rice husk (RH), and glutaraldehyde as a cross-linker. The prepared CA-RH composite films were characterized by conventional methods such as swelling and modern techniques such as EDXRF and SEM. For the removal of lead ions by CA-RH composite films, the effects of various parameters such as pH, initial concentration, contact time, and dosage were investigated by batch method. The adsorption capacity decreased with the increase in the initial concentration of lead ions in the solution. In conclusion, CA-RH composite films should be used as an effective adsorbent for the removal of heavy metal ions from industrial wastewater.

Keywords: Cellulose acetate, rice husk, composite film, heavy metal ions, sorption

Introduction

Cellulose acetate membrane (CAM) is one of the good sorbents since it is low-cost and renewable (Hui *et al.*, 2006). Moreover, CAM has a comparatively high modulus, tensile strength, and adequate flexural and is a microdispersion sorbent, which enhances its capability to adsorb heavy metals (Tian *et al.*, 2011), as CAM is grafted with functional groups such as –$OCOCH_3$ and –OH groups, so that CAM can bond with heavy metal ions through surface complexation mechanisms (Kamaruzaman *et al.*, 2017). Cellulose is a polymer of glucose molecules. In turn, glucose, which is the primary source of energy for living cells, whether it is ingested (as in animals) or synthesized (as in plants), is a six-carbon molecule that includes a hexagonal ring. One of the six carbons lies above the ring and is attached to a hydroxyl group; two of the carbons within the ring itself are also attached to a hydroxyl group. These three -OH groups can readily react with other molecules to form hydrogen bonds. The hydrogen atom of the hydroxyl group, which is attached to the oxygen that is also attached to carbon on the other side, can be readily displaced by certain molecules that then take that hydrogen's spot in the parent glucose construct. One of these molecules is acetate. Acetate, the form of acetic acid that has lost its acidic hydrogen, is a two-carbon compound often written CH_3COO^-. Cellulose acetate, as the term is commonly used, actually refers to cellulose diacetate, in which two of the three available hydroxyl groups in each glucose monomer have been replaced by acetate. Cellulose acetate is the most important cellulose ester (Puls *et al.*, 2011).

Rice husk is a by-product of rice production during milling which can be used in agriculture activity in Asia and particularly Myanmar (Mahvi *et al*., 2005). The quantity of rice husk depends on the kinds of paddy, grain type, soil and climatic condition in which the paddy is cultivated, and type of rice mill used (Farook and Ismail, 2005). The production of rice, one of the major food crops in the world, generates one of the major wastes of the world, namely, rice husks (RHs). The abundant, cheap, regenerable RHs naturally have high contents of silica and the silica, has a high reactivity (xiong *et al*., 2009).

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Heavy metals such as cadmium, lead, zinc, nickel, copper, and chromium (III) or their compounds have been extensively used by various metal-finishing, mining, and chemical industries. This has led to a sharp increase in the contamination of water. Because of their toxicity, the presence of any of these metals in excessive quantities will interfere with many beneficial uses of the water (Srivastava and Majumder, 2008). The maximum limit under the standard is 0.02 mg L^{-1} for Cd, 0.50 mg L^{-1} for Pb, and 1.0 mg L^{-1} each for Zn, Ni, Cu, and Cr (III). Despite their potential toxicity, many of these metals are still widely used (Hamidi *et al*., 2008).

Lead is a gray-white, soft metal with a low melting point, a high resistance to corrosion, and poor electrical conducting capabilities. It is highly toxic. In addition to its highly concentrated ores, lead is naturally available in all environmental media in small concentrations. Lead is one of the industrial pollutants that may enter the ecosystem through soil, air, and water. Inorganic lead causes disturbances in the center nervous system by changing the characteristics of the early organism. According to the WHO, the maximum permissible limit (MPL) of lead in drinking water is 0.1 mg L^{-1}. Hence, the appropriate treatment of industrial wastewater, which releases lead into aquatic and terrestrial systems, is very important. At present, different methods have been utilized to remove heavy metals from the contaminated wastewater, such as filtration, adsorption, chemical precipitation, ion exchange, membrane separation methods, and electro-remediation methods (Naeema and Kandi, 2014). The aim of the research is to study the characterization and adsorption properties of prepared cellulose acetate-rice husk composite films.

Materials and Methods

Sampling

Rice husk from the species Zeyar was collected from a local rice mill in Hlegu Township, Yangon Region. A cellulose acetate was purchased from Academy Chemical Group in 28th Street, Pabedan Township, Yangon Region.

Preparation of Cellulose Acetate-Rice Husk Composite Films

The casting solution used in this work consisted of a mixture of cellulose acetate and rice husk. A cellulose acetate solution of (5 % w/v) was prepared by dissolving 5 g of cellulose acetate in 100 mL of formic acid using a magnetic stirrer for 5 h to get a clear, homogeneous casting solution. The solution was then added to rice husk powder in various ratios and stirred with a magnetic stirrer. A cellulose acetate-rice husk solution was then added with different weights of rice husk and 0.1 % v/v glutaraldehyde as a cross-linker. The polymer solutions were kept for sufficient time to remove any bubble formation and were cast onto a cleaned and dried glue tray at room temperature. Trays were left for about 5 days to obtain cellulose acetate-rice husk (CA-RH) composite films. The films after drying were easily removed from the glue tray and immersed in a 1 M NaOH solution to remove residual materials, then washed with distilled water several times to remove alkali and unreacted materials, and finally dried in the air at room temperature. Then, the various cellulose acetate-rice husk composite films were obtained.

Removal of Lead (II) Ions from Aqueous Solution

A stock solution containing 200 mg L^{-1} lead (II) nitrate was prepared. Working solutions were prepared from the stock solution by dilute appropriate aliquots with distilled water. Each 100 mL of this solution was mixed with 2 cm × 2 cm of prepared composite films in the flask. The flask was placed in an electric shaker at room temperature and shaken for 1 h. The sample was allowed to stand to settle out the solid particles, and the residual lead (II) ion solution was taken out and then diluted to a certain volume. It was followed by complexometric titration using EDTA and the xylenol orange indicator (Vogel, 1961). The effect of PH, contact time, dosage on the removal of Pb (II) ions by cellulose acetate-rice husk (CA-RH 4) composite film were investigated.

Characterization of Prepared Cellulose Acetate-Rice Husk Composite Film before and after Adsorption of Lead (II) Ions

The prepared cellulose acetate-rice husk composite films before and after adsorption of lead (II) ions were examined by SEM for a visual inspection of surface morphological porosity. The procedure of EDXRF procedure was done according to the recommended standard procedure as reported in the catalogue.

Application of Prepared Cellulose Acetate-Rice Husk Composite Film in the Treatment of Lead (II) Ions in Industrial Waste Water

The industrial wastewater sample was collected from the industrial zone of Thingangyun Township. The prepared cellulose acetate-rice husk composite film (2 cm × 2 cm) was suspended in 100 mL of industrial wastewater at pH 5. The sample was equilibrated in an electric shaker for 1 h at ambient temperature.

After 1 h shaking, the sample was allowed to stand to settle out the solid particles. The residue was then separated by filtration. The content of lead ions in decanted wastewater was determined by an atomic absorption spectrophotometer.

Results and Discussion

Cellulose Acetate-Rice Husk Composite Films

Cellulose acetate–rice husk composite films were prepared by solution-casting from cellulose acetate and rice husk at various compositional ratios. Figure 1 shows the cellulose acetate-rice husk composite films, which consist of a mixture of cellulose acetate (5% w/v), various weight percents of rice husk, and glutaraldehyde (0.1% v/v) as a cross-linker. The cellulose acetate-rice husk composite films were prepared by casting, evaporation, and annealing. The films differ in their preparation processes in accordance with the various amounts of rice husk content. The prepared CA-RH 4 composite film was chosen for the removal of lead ions from aqueous solutions.

CA-RH 1 **CA-RH 2** **CA-RH 3** **CA-RH 4** **CA-RH 5**

CA-RH-1 = Cellulose acetate-rice husk film (5:0.2 % w/w in 100 mL of formic acid)
CA-RH-2 = Cellulose acetate-rice husk film (5:0.4 % w/w in 100 mL of formic acid)
CA-RH-3 = Cellulose acetate-rice husk film (5:0.6 % w/w in 100 mL of formic acid)
CA-RH-4 = Cellulose acetate-rice husk film (5:0.8 % w/w in 100 mL of formic acid)
CA-RH-5 = Cellulose acetate-rice husk film (5:1.0 % w/w in 100 mL of formic acid)

Figure 1. Cellulose acetate-rice husk composite films

Removal of Lead (II) ions by Cellulose Acetate-Rice Husk Composite Films

The pH of an aqueous solution is an important parameter in the adsorption of Pb(II) ions from the aqueous solution onto the adsorbent. Figure 2 illustrates that the effect of pH obviously influences the adsorption of the Pb (II) ions from an aqueous solution by the CA-RH 4 composite film. The removal of the Pb (II) ion increased with increasing pH, and the maximum adsorption capacity was observed at pH 5.

Figure 3 represents the maximum adsorption that was reached at 20 min for the removal of Pb(II) ions. After the maximum contact time has been reached, the percent removal becomes independent of time due to the decrease in the number of adsorption sites.

The effects of the amount of cellulose acetate-rice husk composite films in the range of 0.065 g (4 cm^2), 0.118 g (9 cm^2), 0.158 g (16 cm^2), 0.225 g (25 cm^2), and 0.297 g (36 cm^2) on the removal of Pb(II) ions from a constant initial concentration of 200 mg L^{-1} at pH 5 were investigated. According to Figure 4, it can be seen that as the amount of cellulose acetate-rice husk composite films increases, the percent removal of Pb(II) ions increases. It can be observed that 96.5% of Pb(II) ions can be removed with 0.297 g (36 cm^2) of CA-RH 4 composite film in an initial concentration of 200 mg L^{-1} of Pb (II) ions at pH 5.

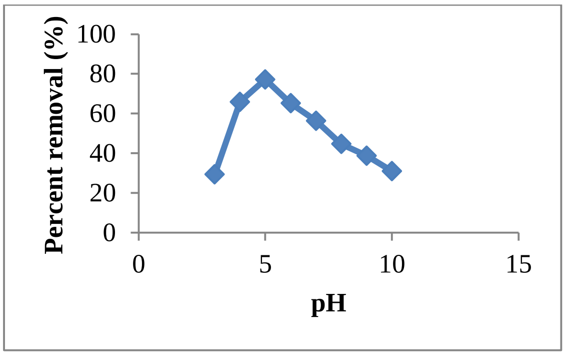

Figure 2. Effect of pH on the removal of Pb(II) ions by cellulose acetate-rice husk (CA-RH 4) composite film

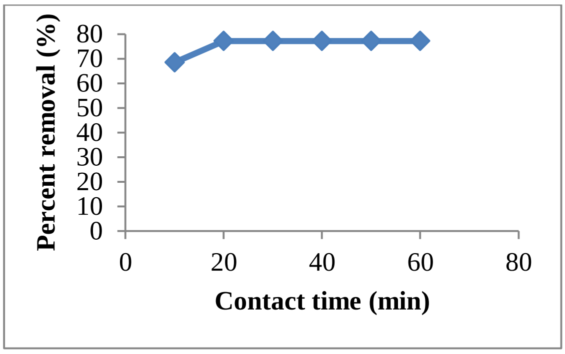

Figure 3. Effect of contact time on the removal of Pb(II) ions by cellulose acetate-rice husk (CA-RH 4) composite film

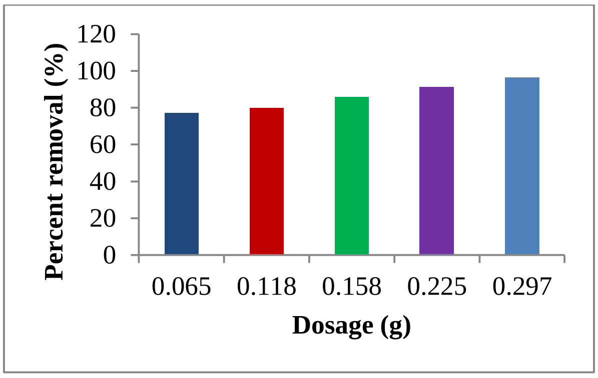

Figure 4. Effect of dosage on the removal of Pb(II) ions by cellulose acetate-rice husk (CA-RH4) composite film

Characterization by SEM Analysis

Figure 5 shows the surface morphology of the cellulose acetate-rice husk (CA-RH 4) composite film. The morphological features of the cellulose acetate-rice husk composite film, including the striated nature of the film, may be responsible for the enhanced specific sorption properties. Figure 6 shows the surface morphology of the Pb(II) ions loaded on the cellulose acetate-rice husk (CA-RH 4) composite film. It can be clearly seen that Pb(II) ions were sorbed in the voids of the composite films, suggesting that a large cluster of Pb(II) ions has been sorbed and precipitated onto the surface of composite films. A less rugged surface is observed, which can be due to the difference in the coordination sphere of Pb(II) ions.

Characterization by EDXRF analysis

Figure 7 shows the EDXRF spectrum of the cellulose acetate–rice husk composite film. The spectrum indicated that silica (ca. 80.454 %) is the major constituent in the film. It is a semi quantitative value measured on a matrix basis. The presence of Pb(II) ions sorbed on the cellulose acetate-rice husk composite film is shown by the EDXRF spectrum represented in Figure 8. The measurements made and values therein are more semiquantitative and on a matrix basis. It can be observed that each spectrum indicates that the relevant Pb(II) ions were sorbed on the composite films. An interesting observation is the alternation of spectra after Si(II) ions have been replaced by Pb(II) ions. It can be inferred from the pronounced peaks that each spectrum had represented. Figure 8 bears out the fact that from a mixture of Pb(II) ions was sorbed by the composite films.

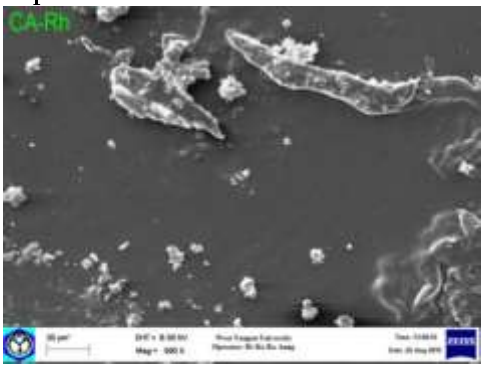

Figure 5. SEM micrograph of cellulose acetate-rice husk (CA- RH 4) composite film

Figure 6. SEM micrographs of cellulose acetate-rice husk (CA-RH 4) composite film after lead adsorption

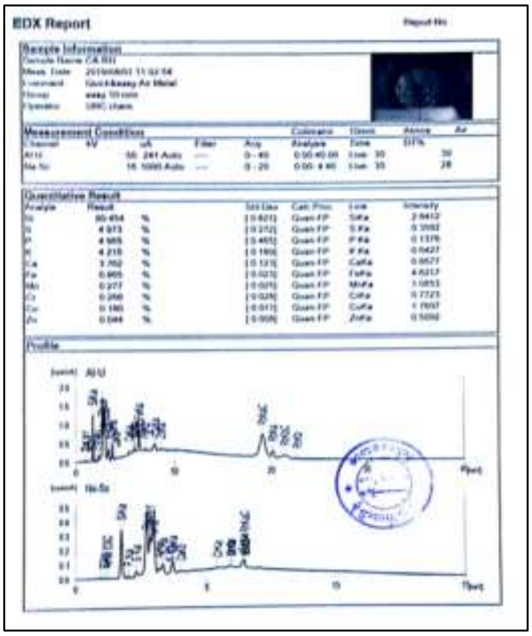

Figure 7. EDXRF spectrum of cellulose acetate-rice husk (CA-RH 4) composite film.

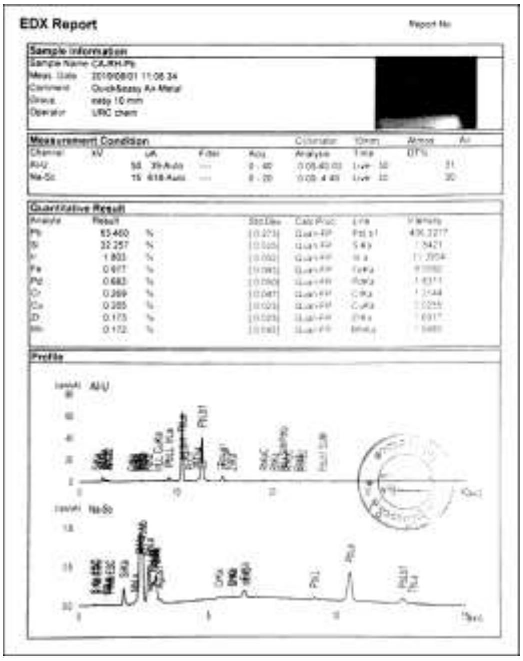

Figure 8. EDXRF spectrum of cellulos acetate-rice husk (CA-RH 4 composite film after lead adsorptio

AAS Analysis of Lead from Wastewater Treatment

The Lead(II) ion concentrations in industrial wastewater sample were determined by an atomic absorption spectrophotometer. The Lead(II) ion concentration was found to be 5.66 mg L^{-1} in industrial wastewater. It can be seen that the Lead(II) ion in wastewater sample was reduced significantly by the cellulose acetate-rice husk composite film. The results are shown in Table 1. On examination of the resulting data, removal efficiency was 87.6 %. The process of removing Lead(II) ions from wastewater sample by cellulose acetate-rice husk composite film can be used for the effective treatment of industrial effluents.

Table 1. Lead Removal Efficiency in Battery Wastewater by using Cellulose Acetate-Rice Husk (CA-RH-4) Composite Film

Metal Ions	Before treatment (mg L^{-1})	After treatment (mg L^{-1})	Removal efficiency (%)
Pb	5.66	0.7018	87.6

Conclusion

In the research, the ability of a cellulose acetate-rice husk composite film to adsorb Pb(II) ions from aqueous solutions has been explored. The maximum adsorption capacity of the Pb(II) ions by the cellulose acetate-rice husk composite film was about pH5. The percent removal increased with decreasing initial concentrations of Pb(II) ions. It was observed that 77.2 % of Pb(II) ions was removed with a dosage of 0.065 g of cellulose acetate-rice husk composite film in 100 mL of 200 mg L^{-1} Pb(II) ion solutions. The data obtained from all experiments for the removal of Pb(II) ions from aqueous solutions showed that with increasing, contact time, the removal percent also increased. After 20 min, the removal of Lead(II) ions became independent of time. As the amount of sorbent increased, the percent removal increased was 96.5 % of Pb(II) ions was removed with a dosage of 0.297 g (36 cm^2) of cellulose acetate-rice husk composite film in an initial concentration of 200 mg L^{-1} of Pb(II) ions. The lead concentration of 5.66 mg L^{-1} was found in industrial wastewater, which was removed by using cellulose acetate-rice husk composite film. On examination of the resulting data, 87.6% removal efficiency was observed. The cellulose acetate-rice husk composite film can be used as an effective and efficient sorbent for the treatment of industrial effluents. Therefore, cellulose acetate-rice husk composite film should be used as an ecofriendly and environmental-friendly adsorbent material for wastewater treatment.

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