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SYNTHESIS AND CHARACTERIZATION OF PSYLLIUM HUSK GRAFTED COPOLYMERS FOR THE APPLICATION AS BIO-ADSORBENT OF HEAVY METALS

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Abstract

Heavy metal contamination in the environment and food chain is one of the largest concerns of the twenty-first century and a plant derived adsorbent might provide a sustainable solution to this problem. Psyllium Husk (Isobgul) is already consumed as a natural remedy for the treatment of constipation and other health purposes. The objective of the present study was to modify the surface morphology of Psyllium Husk and its use for the adsorption of heavy metals from aqueous solutions. A binary grafted co-polymer of Psyllium mucilage was successfully synthesized by grafting Acrylic Acid and Acrylonitrile monomers onto the polysaccharide chain under microwave irradiation. FTIR spectroscopy confirmed the formation of different functional groups on the polysaccharide chain. SEM analysis showed increased roughness in surface morphology on modified Psyllium Husk. Batch adsorption tests were conducted using this grafted polymer to analyze its adsorption efficiency of Pb (II), Cr (III) and Cd (II) ion. Atomic Absorption Spectroscopy confirmed up to 79% removal of the Lead (II) ion, 42% removal of Cadmium (II) and 45% removal of Chromium (III) ion from aqueous solutions using 0.1 g of adsorbent in 50 ml solution. The adsorption mechanism was studied by fitting the batch adsorption data against various known isotherms and kinetic models. Results showed that experimental data had a better fit against the Langmuir isotherm for Cd adsorption and against the Freundlich isotherm for Pb and Cr adsorption. The time-dependent lead adsorption data were fitted against the pseudo-first order and pseudo second-order model. R^2 values (0.7746 for pseudo first-order and 0.9979 for pseudo second-order) show that the adsorption mechanism closely followed the pseudo second-order model. The results of this study indicate that the grafting capabilities of Psyllium Husk can be leveraged to create Psyllium Husk-based adsorbent in raw water treatment and may have further applications as dietary supplement that can effectively remove heavy metals from the human body provided that this product does not have any level of toxicity for oral consumption.

Keywords: Psyllium Husk, Heavy metals, Bio-adsorbent, Contamination

1. Introduction

Heavy metals have been widely distributed in the natural environment and the overall eco-system of Bangladesh as a result of rapid industrialization, urbanization, and numerous anthropological activities. The concentration of Cd, Pb, and Cr metals are well above the safe limit in the rivers that surround Dhaka and Chittagong, including the Buriganga, Turag, Shitalakhya, and Karnaphuli rivers [1]. Agricultural soil irrigated with Shitalakhya river water in Narayangonj showed elevated levels of Pb (28.13 mg/kg), Cd (0.97 mg/kg), and Cr (69.75 mg/kg) [2]. Waste water from the Hazaribagh leather industrial area in Dhaka was found to be responsible for high Cr (976 ± 153 mg/kg) concentrations in the local soil [3]. Countrywide implementation of treatment plants for industrial effluent and ground water is thus required to effectively remove these metals from food chain.
Most of the residential filtration system and industrial adsorption technologies incorporate Activated Carbon (AC) for its low cost and high adsorption capacity. A recent report stated that typical commercial Activated carbon (4$/kg) has a capacity of 3.1 mg/g for Lead Adsorption at 0.05 ppm and adsorption capacity of 146.85 mg/g with a 60 mg/L initial Pb ion concentration [4]. However, the production process of AC has some environmental impacts. Study shows that the total energy consumption and GHG emissions of AC production varies (43.4 to 277 MJ/kg AC and 3.96 to 22.0 kg CO2-eq/kg AC) depending upon the characteristics of the feed stock [5]. In this regard, polysaccharide-based graft copolymers might prove to be more eco-friendly alternative of AC. P. Prapainainar et al (2017) reported that typical graft copolymer production via irradiation has an energy consumption of around 160 MJ/kg and zero GHG emission. These reports present a scope of research on commercialization of graft copolymer adsorbents by enhancing their adsorption efficiency and reducing energy consumption in the production process.
Extensive researches have been conducted towards enhancing metal adsorption properties of polysaccharides by grafting with various monomers.

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Chitosan grafted with Maleic anhydride and Ethylene dimethacrylate can effectively remove chromium and copper ions from the industrial waste water [6]. Hao et al. investigated the substantial improvement in copper (II) ion adsorption by PEI (Polyethylenimine) grafted cellulose. The grafting was achieved by free radical polymerization initiated by ceric ammonium nitrate (CAN). Czarnecka et al. (2020) utilized CAN initiated free radical reaction to synthesize a super adsorbent by modifying starch with acrylic acid side chains [7]. Sokker et al. (2011) developed a hydrogel grafting polyacrylamide onto polysaccharide chain of the chitosan by irradiation [8]. These polysaccharide-based copolymers also have numerous applications in the fields of drug delivery and pharmaceutical industry besides being utilized in ground water treatment [9]. Several toxicity studies have been carried out in recent years on graft copolymers and there has not been any published report confirming the presence of acute toxicity. T. K. Giri et al (2015) studied the characteristics of modified locust bean gum with polyacrylamide and did not find any toxicity associated with it [10]. These studies indicate that graft copolymerization might enable dietary polysaccharides to effectively remove heavy metals from human body. With this scope in mind, the primary objective of this study was to investigate the possibilities of introducing heavy metal adsorption properties in Psyllium Husk, a polysaccharide based dietary fibre, via grafting with suitable vinyl monomers. In this study, the target copolymer was achieved via microwave initiated grafting so as to eliminate the use of a chemical initiator.

Psyllium comes from a shrub-like herb called Plantago ovata that grows worldwide but is most common in Southeast Asia. It has been used as a home remedy for diarrhea, chronic constipation, ulcer, piles and many other diseases [11]. Polysaccharides are the backbone of the chemical structure of Psyllium husk. These polysaccharides are comprised of D-glucose, L-arabinose, D-xylose, D-galactose, and L-rhamnose [12]. Acrylic Acid (AA) and Acrylonitrile (AN) were chosen as monomers for our study of grafting process in order to introduce different functional groups onto the polysaccharide chain [13].

The target copolymer was achieved by microwave-initiated grafting. Characterization of synthesized copolymer was performed via FTIR and SEM analysis. Batch adsorption tests were performed at pH=7, average pH inside small intestine [14], using stock solutions of lead, Cadmium and Chromium. Adsorption data were collected via AAS and fitted against various isotherms and kinetic models.

2. Methodology

2.1 Synthesis

1 gram of psyllium husk was added in 100 ml distilled water. The mixture was left to settle for 1 hour to obtain a homogeneous mixture. Then 0.7 mol/L Acrylic acid (AA) and 0.027 mol/L Acrylonitrile (AN) were added in the mixture. The mixture was treated under the microwave irradiation to initiate the free radical reaction. Trace amount of Hydroquinone solution was added after 1 minute to stop the reaction. The grafted copolymer was precipitated with excess methanol and washed with Acetone. The precipitate was then dried in a freeze drier for 24 hours.

2.2 Characterization

The product was then powdered and stored. FTIR spectra of raw Isobgoul and grafted copolymer were recorded in the range of 4000–400 cm^{-1} in transmission mode using an FTIR-8400 (Shimadzu, Japan). Initially, the samples were freeze-dried and powdered to prepare for the analysis. Surface morphology of the synthesized particles was analyzed using a field mission scanning electron microscope (FESEM) model ZIESS EVO 18 at 10.0 kV operating voltage.

2.3 Batch adsorption test

Pb (II), Cr (II) and Cd (II) adsorption capabilities of newly synthesized copolymer were analyzed by varying- (a) The concentration of heavy metal ions for a fixed amount of adsorbent mass (b) The amount of adsorbent at a fixed concentration of 200 ppm of metal ions. For each test run, a specific amount of copolymer was introduced in a sample stock solution of 50 mL at pH=7. Then the solution was stirred for about 10 mins or higher so as to give the adsorption process enough time to reach equilibrium. After that the solution was filtered using a Whatman filter and a vacuum filter. the concentration of the filtrate was analyzed via AAS (Atomic Adsorption spectroscopy). Data collected from these tests were later used to generate adsorption isotherms.

2.4 Kinetic Modeling

200 ppm 0.5 L Pb (II) ion solution was prepared before the test. 0.5 gm of adsorbent polymer was added in the solution under constant stirring. Then a number of samples of 5 mL were drawn at short intervals. Sampling was continued for 1 hour and then the concentrations were analyzed through AAS. Data collected from this experiment were used to fit against kinetic adsorption models.

3. Results and Discussion

3.1 FTIR Spectroscopy

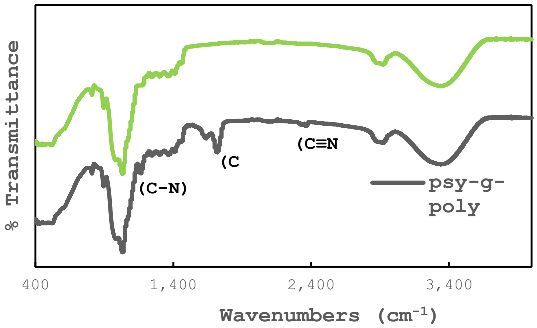


Fig.1 FTIR spectroscopy of psy-g-poly and raw psyllium husk.

According to figure 1, a number of new peaks were found in the spectrum of psy-g-poly by comparing it with that of raw psyllium husk. These peaks were found at 2300, 1750 and 1251 cm^{-1}. According to the literature, these peaks indicate the presence of C≡N nitrile stretching, C=O stretching of amide-I and C-N stretching of amide-III respectively [15]. These peaks were absent in the spectrum of raw psyllium husk. It can be assumed that these new functional groups were formed during the radiation assisted copolymerization reaction. Therefore, it confirmed that the grafting process was successful and psy-g-poly had new sites that would bond with the metal ion in the solution via co-ordination for all these groups contain lone pair electron.

3.2 SEM Analysis

The changes in surface morphology due to attempted graft polymerization were observed in SEM images of raw psyllium husk and psy-g-poly. A substantial change in surface properties after synthesis is illustrated by the SEM images in figure 2(a) and 2(b). The surface of pure psyllium husk in figure 2(a) seemed to be quite smooth. But the SEM image of the end product sample in figure 2(b) showed some definite roughness on the surface. This introduction of surface roughness through the attempted modification process can be attributed to the successful formation of new metal bonding sites.

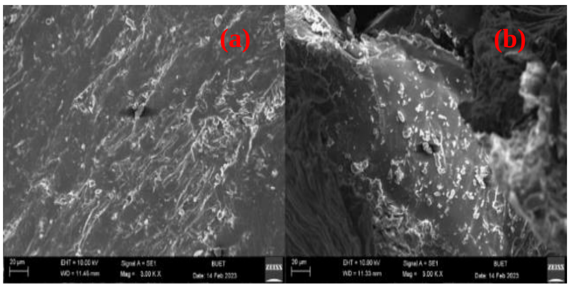


Fig.2 SEM image of (a) raw psyllium husk and (b) synthesized copolymer.

3.3 Batch adsorption test

From figure 3(a), it is evident that the percentage of adsorbed metal ion decreased with the increase in initial concentration of stock solution. As these data were taken using a fixed amount of adsorbent material, the surface area for adsorption or the number of adsorption sites were limited. Therefore, the amount of adsorbed metal ion could not increase infinitely. All three graphs in figure 3(a) shows that the percent adsorption reached a constant value when the initial concentration of the stock solution was increased indefinitely. It indicates that metal ions were adsorbed in the pores of the adsorbent at high concentration. It can be assumed that the newly synthesized copolymer has a highly porous structure and the surface of the copolymer has a limited number of binding sites for metal ion. The percent adsorptions were 60-80%, 35-45%, and 20-40% for concentrations ranging from 50 to 250 ppm of lead, chromium and cadmium respectively using 0.1 gm of adsorbent in 50 mL of stock solution. When the amount of adsorbent is increased, it generally leads to an increase in adsorption percentage. This can be attributed to several factors, such as increased surface area, enhanced contact, reduced competition and persistent concentration gradient between solid and liquid phase. According to figure 3(b), all three plots seemed to reach for a maximum limit as the dosage of adsorbent was increased. This can be attributed to the reduction in concentration gradient as that is the driving force of ion transport between phases.

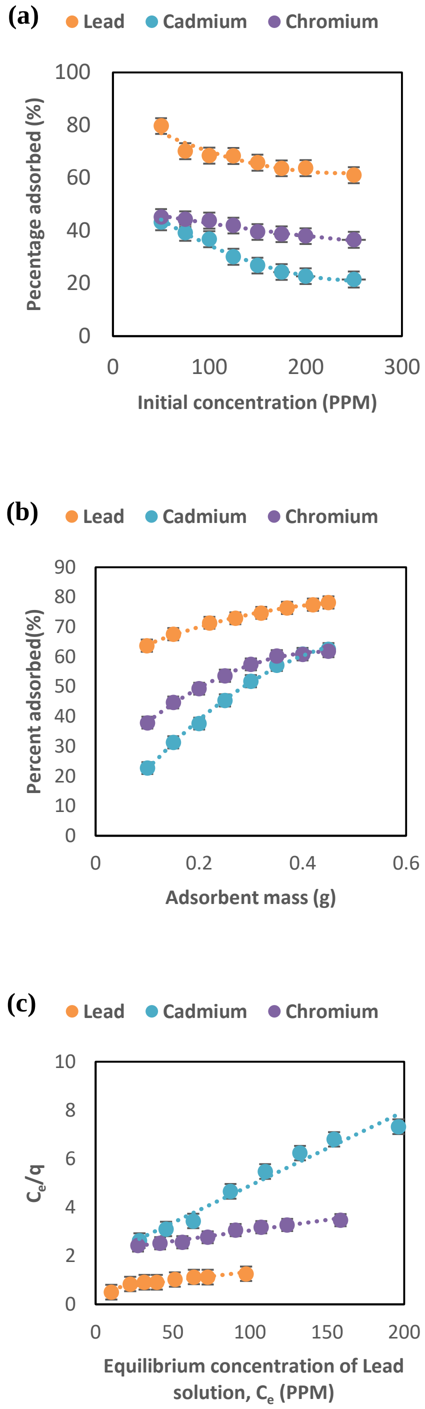
Two well-known isotherm models were fitted against the experimental data- (a) Langmuir isotherm and (b) Freundlich isotherm [16]. R^2 values from the isotherm graphs indicates that adsorption of Pb (II) and Cr (III) follows Freundlich isotherm model (0.9908 for Pb and 0.9899 for Cr) whereas adsorption of Cd (II) follows Langmuir model (0.9695 for Cd) more closely. Figure 3(c) and 3(d) illustrates the fit of Langmuir and Freundlich isotherm models for lead, cadmium and chromium adsorption.

3.4 Kinetic Modeling

The pseudo-first-order kinetic adsorption model is an empirical equation used to describe the rate of adsorption of solute molecules onto a solid adsorbent surface. The model assumes that the rate-limiting step is the adsorption of solute molecules onto the surface. It is denoted by, $\log(q_e - q_t) = \log(q_e) - \frac{k_1}{2.303}t$ [16] where, q_t is the amount of adsorbate adsorbed at time, t, q_e is the amount of adsorbate adsorbed at equilibrium k_1 is the rate constant of the pseudo-first-order model, and t is the time.The pseudo-second order model suggests that the adsorption mechanism is likely to involve chemical bonding or chemisorption between the solute and the adsorbent surface assuming that the adsorbent surface is heterogeneous containing different types of active sites with varying affinities for the solute.

It is denoted by, $\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$ [16]

where, k_2 is the rate constant of the pseudo-second-order model. The graphs 3(e) and 3(f) show that the adsorption followed the pseudo-second order model more closely (R^2 values of 0.7746 and 0.9979 for pseudo first-order and pseudo second-order respectively).



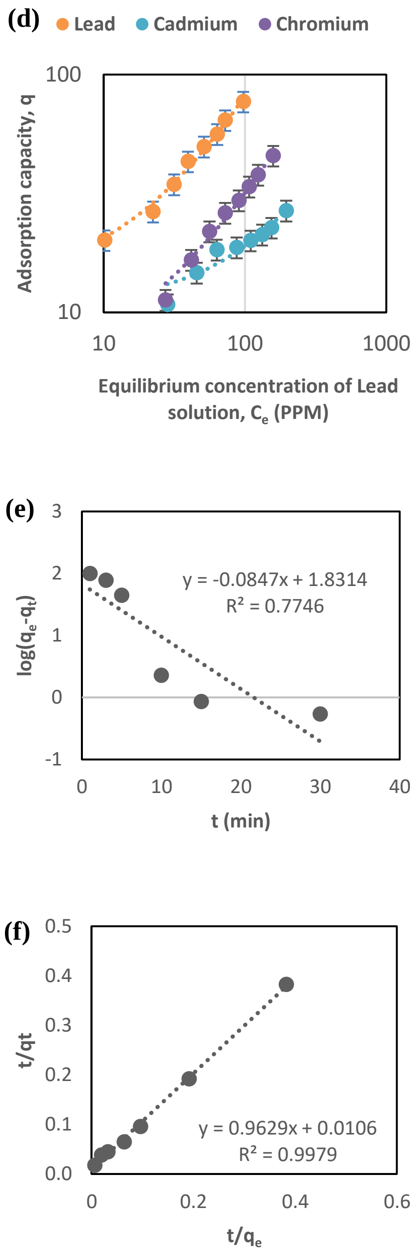


Fig.3 (a) Percent adsorption of different metals vs various concentration of stock solution using a fixed amount of absorbent (b) Percent adsorption for different amounts of adsorbent at a fixed concentration of stock solution (c) Langmuir Isotherm models for adsorption (d) Freundlich Isotherm models for adsorption (e) Pseudo first order model (f) Pseudo second order model

4. Conclusion

The study was conducted to investigate the heavy metal adsorbing capabilities of modified Psyllium Husk. The modification process, which involved grafting the Psyllium Husk with suitable monomers, enhanced its heavy metal adsorption properties. In batch adsorption tests, the adsorption percentage of lead (II) was higher than cadmium (II) and chromium (III) ions with the copolymer. The heavy metal adsorbing capabilities of modified psyllium husk make it a promising candidate for removing heavy metals from aqueous systems like groundwater. This can be particularly useful in areas where heavy metal contamination is common in food and water sources, as it can help prevent the absorption of toxic metals into the bloodstream and reduce the risk of adverse health effects. Further toxicological studies are required to determine the safety of oral consumption of this product as a fiber supplement. In conclusion, the results of this study indicate that modified Psyllium Husk can be utilized to remove lead, cadmium and chromium from aqueous solutions.

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