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FTIR spectrophotometry, kinetics and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding the mechanism of Cd^{2+} and Pb^{2+} removal by mango peel waste

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ABSTRACT

Mango peel waste (MPW) was evaluated as a new sorbent for the removal of Cd^{2+} and Pb^{2+} from aqueous solution. The maximum sorption capacity of Cd^{2+} and Pb^{2+} was found to be 68.92 and 99.05 mg g^{-1}, respectively. The kinetics of sorption of both metals was fast, reaching at equilibrium in 60 min. Sorption kinetics and equilibria followed pseudo-second order and Langmuir adsorption isotherm models. FTIR analysis revealed that carboxyl and hydroxyl functional groups were mainly responsible for the sorption of Cd^{2+} and Pb^{2+}. Chemical modification of MPW for blocking of carboxyl and hydroxyl groups showed that 72.46% and 76.26% removal of Cd^{2+} and Pb^{2+}, respectively, was due to the involvement of carboxylic group, whereas 26.64% and 23.74% was due to the hydroxyl group. EDX analysis of MPW before and after metal sorption and release of cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and proton H^{+} from MPW with the corresponding uptake of Cd^{2+} and Pb^{2+} revealed that the main mechanism of sorption was ion exchange. The regeneration experiments showed that the MPW could be reused for five cycles without significant loss in its initial sorption capacity. The study points to the potential of new use of MPW as an effective sorbent for the removal of Cd^{2+} and Pb^{2+} from aqueous solution.

1. Introduction

Cadmium and lead are among the heavy metals considered as most toxic to human and aquatic life [1,2]. There has been a sharp rise in the global use of cadmium and lead for batteries and other applications, such as in pigments, polyvinyl chloride stabilizers and electroplating [3]. Wastewaters generated by these and related industries contain high levels of these toxic metal ions, which are mandatory to be treated to safe limits before disposal into natural water bodies and open terrain spaces. Various treatment procedures, such as chemical precipitation and coagulation, ion exchange, reduction, osmosis and reverse osmosis, membrane processes, and electrolytic technologies are available for the removal of heavy metal contaminants in effluents and industrial wastewaters. Technoeconomic considerations, however, limit their wide scale application [4]. As a result of these shortcomings, considerable attention has been paid to the development of safe technologies that can reduce heavy metal concentrations to environmentally acceptable levels at affordable cost [5,6].

Many natural polymers, such as alginate, pectin, cellulose, chitosan and chitin are known to strongly bind heavy metal ions [5,7,8]. These polymers not only have excellent heavy metals sorption capability, but they are also environment-friendly due to their renewable, biocompatible, biodegradable and nontoxic nature. However, it is difficult to use such polymers for commercial applications because of their water solubility under some practical conditions, and technoeconomical considerations related with their isolation and stabilization [5]. This difficulty can be overcome by using raw biomass wastes generated in agriculture, forestry and fisheries, which are rich in biopolymeric materials [3,8,9]. The stability of these materials as metal biosorbents is also higher than isolated-stabilized natural polymers. From such a viewpoint, several studies have been devoted during recent decades to investigate metal-binding efficiency of several biowastes [6]. In continuation of these efforts, mango peel waste was evaluated to determine its potential as a metal biosorbent.

Mango (*Mangifera indica* L., family Anacardiaceae) is a delicious fruit grown in almost all tropical and subtropical regions of the world. Currently, with about 27 million ton production annually,

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mango ranks 5th in production among the major fruit crops [10]. The edible part (the pulp), which makes up to 33%–85% of the fresh fruit, is processed for products such as juices, nectars, concentrates, jam, jelly powders, fruit bars, and dried mango products [11]. During the processing of mango, peel, which is 7%–24% of the total fruit weight, is generated as a by-product/waste. The peel serves no commercial purpose, which is discarded as a waste thus becoming a source of pollution. Mango peel contains pectin, cellulose, hemicellulose, lipids, protein, polyphenols and carotenoids [12]. Among these, pectin and cellulose are the predominant types of polysaccharides present in mango peel. These polymers are rich in functional groups such as carboxylic (galacturonic acids in pectin) and hydroxyl (in cellulose), and are known to strongly bind metal cations in aqueous solution [3,8,9]. Therefore, mango peel, due to its high pectin and cellulose content, offers the potential of use as adsorbent for the removal of toxic metals, dyes, and other organic materials from industrial effluents. The present work was thus undertaken to evaluate the application potential of pectin- and cellulose-rich mango peel waste as a new, inexpensive and environment-friendly adsorbent material for treating wastewaters containing toxic metals. We understand that to date no study on the use of MPW as a metal sorbent to treat wastewaters has been reported. Metal ions, such as Cd^{2+} and Pb^{2+}, being most toxic to human and aquatic life, and commonly released in the environment via wastewaters of many industrial processes, were selected as sorbates for this investigation. The effect of principal operational parameters on metal sorption, such as sorbent quantity, contact time, pH, and metal ion concentration, were monitored to optimize the sorption process for its possible use as a low-cost adsorbent for wastewater treatment. Mechanistic aspects of metal biosorption by MPW were investigated using different experimental approaches, such as FTIR, chemical blocking of functional groups and concomitant release of cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) from MPW with metal (Cd^{2+}, Pb^{2+}) uptake, to determine the role of carboxyl, hydroxyl and alkaline and alkaline earth metals present in MPW in an ion exchange process.

2. Material and methods

2.1. Sorbent material

Mango peel waste (MPW) was obtained from the juice production pilot plant of Food and Biotechnology Research Centre, Pakistan Council of Scientific and Industrial Research Laboratories Complex, Lahore, Pakistan. After thorough washing with tap water, MPW was washed with double-distilled water, oven dried at 70 °C, ground and sieved. Powdered material of particle size 0.85–1.0 mm was used for metal sorption studies.

2.2. Metal solutions

Standard stock solutions of Cd^{2+} and Pb^{2+} ($1000 \pm 2\,mg\,l^{-1}$, as their respective nitrate salts, Merck Ltd., Poole, UK) were used to prepare appropriate concentrations of each metal for the sorption studies. pH of the working solutions was adjusted at 5.0, unless otherwise stated, using 0.1 M NaOH. Fresh dilutions were used for each sorption study.

2.3. Point of zero charge

The point of zero charge (pH_{PZC}) of the MPW was determined by the solid addition methods [13]. To a series of 100 ml Erlenmeyer flasks, 45 ml of KNO_3 solution of known strength was transferred. The initial pH (pH_i) values of the solutions were roughly adjusted from 2 to 12 by adding either 0.1 N HNO_3 or NaOH. The total volume of he solution in each flask was made exactly to 50 ml by adding the KNO_3 solution of the same strength. The pH_i values of the solutions were then accurately noted, and 0.1 g of MPW was added to each flask, which were securely capped immediately. The suspensions were then manually shaken and allowed to equilibrate for 48 h with intermittent manual shaking. The pH values of the supernatant liquid (pH_f) were noted. The difference between the initial and final pH values (ΔpH) was plotted against the pH_i.

2.4. Sorption studies

Sorption capacity of MPW was determined by contacting 250 mg ($2.5\,g\,l^{-1}$) with 100 ml metal solutions of known concentration ($10–600\,mg\,l^{-1}$) in 250 ml Erlenmeyer flasks, shaken on an orbital shaker at 100 rpm for 120 min at room temperature ($25 \pm 2\,°C$), followed by centrifugation at 5000 rpm for 5 min to separate MPW from the metal solution. Residual metal concentration in the supernatant metal solutions was determined by atomic absorption spectrophotometric analysis. Rate of metal sorption by MPW was determined by analyzing residual metal ions in the supernatant after contact periods of 15, 30, 45, 60, 90 and 120 min. The solid phase mass was varied between 0.5 and $10\,g\,MPW\,l^{-1}$ metal solution for determining the effect of sorbate to sorbent ratio for the percentage and unit metal sorbate sorption capacity of the MPW sorbent. For determining the effect of pH on metal sorption by MPW, initial pH of each metal solution was adjusted to the desired value (2–7) using 0.1 M HCl or 0.1 M NaOH. Final pH of the sorbate–sorbent sorption mixture was measured at sorption equilibrium. Metal-free and MPW-free blanks were used as the controls. All the experiments were performed in triplicate.

2.5. FTIR, SEM and EDX analysis

FTIR spectroscopy (Thermo Nicolet IR-100 Spectrometer, Thermo Nicole Corporation, Madison, USA) was done to identify the chemical functional groups present on native MPW and the metal (Cd^{2+}, Pb^{2+})-loaded MPW. IR absorbance data were obtained for wavenumbers in the range of $400–4000\,cm^{-1}$ and analyzed using software Encompass®. The surface structure of the MPW before and after Cd^{2+} and Pb^{2+} sorption was analyzed by scanning electron microscopy (SEM LEO DSM-982 Gemini, Cambridge, UK) and for electron dispersive X-ray analysis (EDX-System, INCA-Oxford, High Wycombe, UK). The EDX-system was coupled with SEM using mixed BSE (back scatter electron) + LSE (lateral secondary electron) signal detectors.

2.6. Major cations content of MPW biomass

Release of alkali and alkaline earth metals (Mg^{2+}, Ca^{2+}, K^+, Na^+) from acid-washed (0.1 M HCl) MPW was used to determine its approximate ion exchange capacity. Protonation of MPW was done to show that the exchangeable cations present on the native MPW could be released into solution after the uptake of protons. For this purpose, 1.0 g of MPW was treated with 100 ml of 0.1 M HCl. The suspension was stirred on magnetic stirrer for 60 min at room temperature, then separated by centrifugation at 5000 rpm for 5 min. The residue MPW was resuspended in fresh 0.1 M HCl solution and the treatment was repeated twice. MPW residue so obtained was analyzed for the release of Mg^{2+}, Ca^{2+}, K^+, and Na^+ using atomic absorption spectrophotometer (UNICAM 969, Unicam, Cambridge, UK). Replacement of HCl with deionized water in a similar procedure served as the control. Elemental composition of MPW was determined by the standard AOAC dry ashing method [14], followed by atomic absorption spectrophotometer metal analysis.