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Adsorption of lead(II) onto organic acid modified rubber leaf powder: Batch and column studies

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ABSTRACT

This study evaluated the Pb(II) sorption capacities of two chemically modified biosorbents which are citric acid modified rubber leaf powder (CARL) and monosodium glutamate modified rubber leaf powder (MGRL). The raw rubber leaf powder (RLP) was modified to improve its effectiveness in removing the Pb(II) ions in an aqueous solution. CARL was prepared by esterification of citric acid onto the cellulose structure while MGRL was prepared by functionalising monosodium glutamate onto the epoxy activated rubber leaf powder. The sorption performance of the sorbents was examined by pH, kinetics and isotherm experiments. The adsorption of Pb(II) was much more favourable at higher pH. The rate limiting step in the adsorption process for both adsorbents was chemisorption and both adsorbents had a better fitting to the pseudo-second order kinetic model. The maximum capacities of Pb(II) calculated by the Langmuir isotherm by CARL and MGRL were 97.19 and 109.95 mg/g, respectively. In column experiments, the breakthrough time was found to decrease from 25 to 5 min for CARL and 37.5 to 10 min for MGRL with an increase in Pb (II) concentration from 20 to 60 mg/L. The Thomas and Yoon–Nelson models had a good fit with the fixed bed column data. Different column parameters such as column adsorption capacity and 50% adsorbate breakthrough were calculated. It was found that the adsorption capacity and performance of MGRL was superior to CARL in both batch and fixed bed column studies.

1. Introduction

Water is a source of life and energy. However, millions of people worldwide are suffering from the shortage of fresh and clean drinking water. The rapid pace of industrialization, population expansion, and unplanned urbanization have largely contributed to the severe water pollution and surrounding soils. The main sources of freshwater pollution can be attributed to a discharge of untreated sanitary and toxic industrial wastes, the dumping of industrial effluent as well runoff from agricultural fields. It is well known that 70–80% of all illnesses in developing countries are related to water contamination, particularly susceptible for women and children (Yola et al., 2012; Bhatnagar and Sillanpää, 2010). Among the sources of release of heavy metals into the aquatic environment are oil and gas, plastic, pharmaceutical, storage-battery manufacture, paper and pulp, mining, electroplating, lead smelting, other metallurgical finishing, automobile industry, agricultural runoff, chemical spills and municipal wastewaters (Gilbert et al., 2011). The deleterious effects of heavy metal species on ecosystems and human health are well known, and numerous studies on industrial treatment methods to prevent or limit discharges have been done (Çolak et al., 2013).

There are various treatment methods in treating heavy metals from aqueous solutions. For example, chemical precipitation, evaporation, coagulation–flocculation, floatation, ion

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exchange, membrane filtration, electrochemical means and adsorption (Amini et al., 2009). Adsorption technology is being used extensively for the removal of heavy metals from aqueous solutions due to benefits such as cleaner process, more efficient and cost effective technology (Pintor et al., 2015; Atar et al., 2012). Numerous adsorbents have been studied, either inorganic adsorbent such as boron waste (Atar and Olgun, 2009; Atar et al., 2011) or organic based adsorbent like barley straw (Ibrahim et al., 2010). A review on some recent low cost organic based adsorbents has been done by Wan Ngah and Hanafiah (2008a).

Various advantages of utilising plant wastes for wastewater treatment include simple technique, requires less processing, good adsorption capacity, selective adsorption of heavy metal ions, low cost, free availability and the ease of regeneration. However, the use of untreated plant wastes as adsorbents present several problems such as low adsorption capacity, high chemical oxygen demand (COD) and biological chemical demand (BOD) as well as total organic carbon (TOC) due to the release of soluble organic compounds from the plant materials (Gaballah et al., 1997). The downside of the increased COD, BOD and TOC is related to the depletion of dissolved oxygen content in water and consequently threaten aquatic life. Therefore, there is a need for plant based adsorbents to be modified or treated prior to being applied for the decontamination of heavy metals.

As of late, modified cellulose is regarded as a cheaper and more effective adsorbent and is commonly investigated. Cellulose is not only renewable, biodegradable, and inexpensive, but also has many primary active hydroxyls which are easy to trigger many reactions, such as free radical reaction, esterification, halogenation, oxidation, and etherification (Zhou et al., 2011). In this study, Pb(II) adsorption behavior on citric acid and monosodium glutamate modified rubber leaf powder was studied and compared. The new adsorbents which contain functional groups such as hydroxyl and carboxylic groups were expected to remove Pb(II) from aqueous solutions under batch and fixed bed column modes.

2. Methods

2.1. *Adsorbents and Pb(II) solution*

Freshly fallen mature rubber leaves (light brown in color) were collected from Universiti Teknologi MARA Pahang rubber plantation, Malaysia. The leaves were washed with water to remove dust and soluble impurities. The washed rubber leaves were then dried overnight in an oven at 105 °C followed by grinding and sieving to obtain a powder with a particle size of less than 180 μm. This powder is labeled as a rubber leaf powder (RLP).

The preparation of the CARL adopts the method described by Altundogan et al. (2007) with some modifications. A measured amount of RLP powder was stirred with 0.2 M citric acid for 2 h followed by extensive rinsing with distilled water. It was then put inside an oven overnight at 50 °C. The thermochemical reaction is continued by raising the oven temperature to 120 °C for 90 min. The adsorbent was then washed with 0.1 M NaOH by stirring for two h. Then, the adsorbent was rinsed with excess distilled water and then dried in the oven until constant weight at 50 °C and was stored. The modified adsorbent is labeled as citric acid modified rubber leaf (CARL).

The preparation method for monosodium glutamate functionalised rubber leaf powder follows the method reported by Gong et al. (2009). First, 20 g grams of rubber leaf powder was suspended in 240 mL dioxane. The suspension was then added with 24 mL of 20% (w/v) NaOH. Then, 40 mL of epichlorohydrin was added and the reaction suspension was stirred for 5 h at 65 °C. After leaving it overnight at room temperature, the epoxy-activated rubber leaf powder was collected using suction filtration, washed thoroughly with dioxane followed by pH 10.1 buffers. For the coupling of the functional ligand, the activated rubber leaf powder was immediately suspended in dioxane containing 12 g of monosodium glutamate. A drop of phenolphthalein was added followed by drop wise addition of 20% (w/v) NaOH while stirring until the monosodium glutamate totally dissolved. The mixture was stirred at 55 °C for 4 h and was then left overnight at ambient temperature. The final product was recovered by suction filtration and washed extensively with distilled water. Finally, it was dried at 50 °C for 24 h in a forced air oven and was stored. The adsorbent is referred to as monosodium glutamate modified rubber leaf powder (MGRL).

2.2. *Characterisation of the adsorbents*

Characterizations of the adsorbents were carried out to understand the physicochemical properties of the adsorbent. The carbon and nitrogen percentage was performed using the Thermo Finnigan Elemental Analyzer 2000, Italy. The analysis of the functional groups in CARL and MGRL was performed by using a Fourier transform infrared spectrophotometer (FT-IR, Spectrum One, PerkinElmer, USA). The pH of the aqueous slurry was carried out according to the method described by Wan Ngah and Hanafiah (2008b). The surface morphology of the adsorbents was observed by using the scanning electron microscope (SEM; LeoSupra VP50, Carl-Zeiss SMT, Germany) coupled with an X-ray energy dispersive spectrometer (EDX).

2.3. *Pb(II) sorption experiment*

The batch adsorption experiments were carried out in duplicates and the results were reported as the average. All chemicals used were of analytical reagent grade. The standard solution of Pb(II) (1000 mg/L) was purchased from Merck (Germany). Experimental solutions of the desired lead concentrations were obtained by successive dilutions from the standard Pb(II) solution. For adsorption experiments, a known weight of the adsorbent was mixed with 50 mL lead solutions in a conical flask at room temperature (24.0 ± 0.5) °C, shaken at 480 rpm for a set period of time. The initial pH of lead solution was adjusted to the desired pH by adding 1 mol HCl or NaOH solutions. The effect of pH on the adsorption was carried out over a pH range of 2–5 to avoid the precipitation of Pb(OH)2. This is because the precipitation of Pb(II) starts at pH 5.8 (Tiwari et al., 2007). To study the effect of adsorbent dosage, the weight of adsorbent was varied from 0.4 to 2 g/L. The effects of lead concentration and contact time were conducted by shaking the adsorbent with Pb(II) solutions (20, 40 and 60 mg/L) at various time intervals (0–120 min). The isotherm study was conducted by equilibrating Pb(II) solutions of 20–100 mg/L with 0.02 g of adsorbents. After adsorption, the mixtures were filtered and the filtrates were analyzed for Pb content using an atomic absorption spectrophotometer (Perkin Elmer, Analyst 400 AA, USA). The adsorption capacity, q, (mg/g) and