Research article

Removal of metals from industrial wastewater and urban runoff by mineral and bio-based sorbents

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A B S T R A C T

The study was performed to evaluate chemically modified biosorbents, hydrochloric acid treated peat (HCl-P) and citric acid treated sawdust (Citric acid-SD) for their metal removal capacity from dilute industrial wastewater and urban runoff and compare their efficiency with that of commercially available mineral sorbents (AQM PalPower M10 and AQM PalPower T5M5 magnetite). Batch and column experiments were conducted using real water samples to assess the sorbents' metal sorption capacity. AQM PalPower M10 (consisting mainly of magnesium, iron and silicon oxides) exhibited excellent Zn removal from both industrial wastewater and spiked runoff water samples even at low dosages (0.1 g/L and 0.05 g/L, respectively). The high degree of Zn removal was associated with the release of hydroxyl ions from the sorbent and subsequent precipitation of zinc hydroxide. The biosorbents removed Ni and Cr better than AQM PalPower M10 from industrial wastewater and performed well in removing Cr and Cu from spiked runoff water, although at higher dosages (0.3–0.75 g/L). The main mechanism of sorption by biosorbents was ion exchange. The sorbents required a short contact time to reach equilibrium (15 –30 min) in both tested water samples. AQM PalPower T5M5 magnetite was the worst performing sorbent, leaching Zn into both industrial and runoff water and Ni into runoff water. Column tests revealed that both HCl-P and AQM PalPower M10 were able to remove metals, although some leaching was witnessed, especially As from AQM PalPower M10. The low hydraulic conductivity observed for HCl-P may restrict the possibilities of using such small particle size peat material in a filter-type passive system.

1. Introduction

The release of untreated industrial wastewater and urban runoff into the environment has deteriorated the quality of water sources and has compromised not only the health of the aquatic ecosystem but has also caused harmful impacts on human health (Abdel-Raouf et al., 2012). Among a wide range of pollutants contained in wastewater systems, metals are one of the most toxic substances, as they do not degrade and tend to bioaccumulate in the environment (Barakat, 2011).

Conventional methods, including chemical precipitation, ion exchange, reverse osmosis, activated carbon, etc. (Araújo et al., 2013; Barakat, 2011; Fu and Wang, 2011), are commonly used for the treatment of wastewater that contains metals. However, these methods present drawbacks such as high operational costs, high chemical requirements and large volume of sludge produced, etc. (Araújo et al., 2013; Barakat, 2011; Fu and Wang, 2011). There is thus a need to explore purification methods that are not only cost-effective but also environment-friendly and viable for commercial-scale application. Over the last decade, bio-based water and wastewater treatment materials have received increased attention due to the advancement of bioeconomy principles and a worldwide effort to increase the sustainability of water and wastewater purification processes. The utilization of biosorbents, for example, has been identified as a sustainable alternative to methods conventionally applied for metal removal. Among several biosorbents

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investigated to date, sawdust and peat have emerged as viable options (Bulgariu et al., 2011; Šćiban et al., 2007) due to their abundance, low cost and sustainable nature.

Sawdust, a by-product of the timber industry, is mainly composed of cellulose and lignin, which contain functional groups such as phenols, carboxyls and hydroxyls in their structure. These groups provide sawdust with its metal binding capacity (Šćiban et al., 2007). The main sorption mechanism is ion exchange through the adhesion of positively charged metal ions on a sorbent surface consisting of negatively charged polymeric functional groups (Akunwa et al., 2014; Božić et al., 2009; Bulut and Tez, 2007). Peat is formed from the degradation of a wide range of plant and tree species in marshy, waterlogged lands (Brown et al., 2000). This biomass is composed of several organic acids (like humic and fulvic acids), salts of organic acids, minerals as well as polymeric compounds such as protein, cellulose and lignin which contain active functional groups (carboxyl, hydroxyl, sulphonic and phenolic) (Bartczak et al., in press). The polar characteristics imparted by the presence of these functional groups are responsible for binding metal to the peat surface (Bulgariu et al., 2011). A number of studies have identified sawdust and peat as promising products for wastewater purification; however, there are several factors which affect their metal removal efficiency. Good distribution of pore size, sufficient surface area for sorption and the presence of active functional groups have been identified as the most important characteristics of biosorbents required to achieve maximum sorption capacity (Gautam et al., 2014). Furthermore, the nature of the metal ions to be sorbed also plays a prominent role in the efficiency of the sorption process. Chemical treatment of biosorbents is normally used to enhance their physico-chemical properties and to improve their sorption capacity via the ionization of functional groups. Furthermore, this kind of treatment can improve the properties of sorbents such as wettability and homogeneity and help to address the challenge of treating dilute wastewater, which existing conventional treatment methods are unable to do.

The objective of this study was thus to evaluate the efficiency of chemically modified biosorbents for the removal of metals (e.g. zinc, chromium, nickel, copper) from an industrial wastewater flow (Outokumpu Chrome, Tornio, Finland), and from urban runoff (Oulu, Finland). Acidic modification for treatment of peat (hydrochloric acid) and sawdust (citric acid) was selected based on a literature research. Peat was modified using HCl and the treatment was selected with the aim of decreasing peat's natural hydrophobicity and improving its poor settling properties (Leiviskä et al., 2018). In addition, treatment with HCl acid would not have oxidised the organic content of peat as HCl is not an oxidising agent, thereby keeping its organic content intact (Batista et al., 2009). Furthermore, according to Gosset et al. (1986), modification with HCl can lead to the desorption of metals ions originally present in natural peat, thus increasing its metal uptake capacity. Regarding sawdust modification using citric acid, Zhou et al. (2015) stated that citric acid forms ester linkages with cellulosic materials due to its crosslinking properties. At high temperature (120 °C), citric acid is converted to citric acid anhydride, which is capable of readily reacting with the O-H groups present in the cellulosic structure, thus creating ester linkages and introducing carboxylic groups into the biomass structure (Salam et al., 2011) that act as ion exchange sites. As the aim was to provide information for the industry on more sustainable as well as commercially available materials, the metal removal efficiency of biosorbents was compared to some commercially available mineral sorbents (AQM Palpower T5M5 magnetite and AQM Palpower M10) developed by a local Finnish company for the removal of metals from wastewater streams.

2. Materials and methods

2.1. Chemicals and materials used

All the chemicals used were of analytical grade. Citric acid ($C_6H_8O_7$, 99% purity) and sodium hypophosphite ($NaPO_2H_2$, $\geq$99% purity) were purchased from Sigma-Aldrich, St. Louis, USA. Stock solutions of nickel nitrate ($Ni(NO_3)_2$, 1000 Ni mg/L) and HCl (0.2 M) were made by dissolving nickel nitrate (99.9% purity, Merck) and diluting concentrated HCl (37%, Merck) in Milli-Q water (Merck Millipore), respectively. The nickel nitrate solutions used during the batch sorption tests were obtained from dilutions of the stock solution to pre-selected concentrations. The pH values of the nickel nitrate solutions were adjusted using 0.1 M HCl and 0.1 M NaOH (solutions made using 99.1% purity pellets, Sigma-Aldrich). Nitric acid, 0.5% (HNO_3, 65%, Suprapur grade, 69.2% purity, Merck) was used in the preservation of water samples for metal analysis.

Scots pine sawdust (*Pinus sylvestris*) and peat obtained from Stora Enso Veitsiluoto pulp mill in Kemi, Finland, were the biomass materials used during experiments. Sawdust and peat were subjected to pre-treatment which involved drying at 80 °C for 24 h as described by Keränen et al. (2013). The sawdust was then ground using a Retsch SK100 cross beater mill with a 0.5 mm sieve. The sawdust and peat were subsequently sieved to obtain a particle size fraction of 90–250 μm. This particular size fraction (90–250 μm) was chosen in order to maintain a uniform particle size range throughout the experiments. The inclusion of smaller particles (e.g. <90 μm) would have resulted in poorer settling properties and the inclusion of larger sized particles (>250 μm) would have affected the biosorbents' modification processes.

Mineral sorbents *AQM PalPower T5M5 magnetite* (T5M5) (powdered) and *AQM PalPower M10* (M10) (particle size 0–63 μm, batch experiments; particle size 1–4 mm and 5–15 mm, column experiments) were provided by Aquaminerals Finland Oy (Paltamo, Finland). M10 is composed of oxides of magnesium, iron, silicon, calcium and aluminium and is reported to possess high metal sorption capacity (Aquaminerals Finland Oy Ltd, 2015). No information regarding the composition of the mineral product T5M5 was provided by the supplier.

2.2. Biomass modification

2.2.1. Citric acid modification of sawdust

The modification method used was a modified version of the method reported by Yang et al. (2010). Pine sawdust (30 g) was poured into a 250-mL three-necked round-bottom flask connected to a reflux condenser. 250 mL of Milli-Q water was added to the flask and the mixture was stirred at 60 °C for 30 min by means of a magnetic stirrer in the reflux condenser, with the side necks closed with rubber septa. In sequence, 50 mL of reagent solution containing 12 g of citric acid and 2.4 g of sodium hypophosphite was poured into the sawdust mixture through one of the side necks and stirring was continued at 60 °C for 60 min. After this, the slurry-like mixture of citric acid modified sawdust (Citric acid-SD) was transferred to a flat glass bowl with an even spread and heated in an oven pre-set at 105 °C for 22 h, and then for 3 h at 120 °C. Next, the Citric acid-SD product was washed several times with Milli-Q water (about 5 L used in total) until the pH reached 4 and allowed to dry overnight in an oven at 60 °C. The resulting yield of Citric acid-SD was 57.4%.

2.2.2. HCl modification of peat

Natural peat (15 g) was weighed in a glass beaker and 250 mL of 0.2 M HCl was added. The mixture was stirred in a magnetic stirrer plate at 25 °C for 2 h. The mixture was then transferred to