

Sorption of cadmium in columns of sand-supported hydrothermally carbonized particles

J. M. V. Minani, J. W. Foppen and P. N. L. Lens

ABSTRACT

Sanitation in urban slums, especially in countries in Sub-Saharan Africa, is a challenge. One of the solutions to sanitation is to valorize waste, and to convert bio-waste present in the slum in a cheap and affordable way into lignite via hydrothermal carbonization (HTC). HTC is simple, cheap, converts all carbon (100%), eliminates pathogens completely, and requires wet starting products/biomass, thereby avoiding complicated drying schemes. In this research, we investigated the effectiveness of removing a divalent metal-ion, cadmium, using equilibrium batch experiments and columns of sand-supported hydrothermally carbonized colloidal lignite (HTCCL) derived from sugar, maize, and grass. Our results indicated that equilibrium sorption could be best described by a Langmuir isotherm. The uptake capacity varied from 0.11 to 0.21 mg Cd/g HTC, dependent on the type of HTC used. These values were relatively low compared to other carbonaceous sorbents. However, removal efficiencies in column experiments were remarkably high: 70–100% during 20–24 pore volumes or bed volumes of flushing. We concluded that HTCCL is a promising sorbent that can be used to treat heavily polluted water and/or wastewater.

Key words | biowaste, cadmium, carbon particles, HTC, removal, sorption

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INTRODUCTION

Urban population growth rates in Africa are among the highest in the world, and this is particularly true for growth rates in so-called informal settlements. In fact, data show that in large African cities informal settlements harbor the majority of the urban population: 70% in Dar-es-Salaam, (Chaggu 2004), 77% in Blantyre, and 80% in Luanda (Palamuleni 2002), to name a few examples. Conditions in informal settlements or slums are characterized by high population densities, poor urban infrastructure, lack of space, lack of secure tenure, and poor water supply and sanitary conditions. This leads to the uncontrolled discharge of domestic wastewater, faecal sludge, and solid waste, causing spreading of pathogenic microorganisms, toxic heavy metals, and nutrients within the slum and into downstream areas in the catchment. Most of the solid waste in slums is biodegradable. For instance, Kulabako *et al.* (2004) estimate that in Bwaise III slum in Kampala, Uganda, more than 90% of the solid waste produced is biodegradable and includes peelings of bananas, cassava and potatoes, generated from homes and commercial eating places, and wastes generated from local markets that sell fresh foods. In the Kenyan case,

Henry *et al.* (2006) estimate that more than 80% of solid waste produced by low income groups in major Kenyan cities is biodegradable.

Adsorption to various carbon-like products is a widely used technology in water and wastewater treatment (Kirk *et al.* 2003; Dianati-Tilaki *et al.* 2004; Hanzlik *et al.* 2004; Mohan & Chandler 2006; Mohan & Pittman 2007; Rao *et al.* 2007; Shin *et al.* 2011; Inyang *et al.* 2011). A relatively novel process is hydrothermal carbonization (HTC) of organic waste materials (Titirici *et al.* 2007). HTC occurs under wet conditions and relatively low temperatures (around 200 °C), and is used to transform plant biomass and bio-waste into colloidal lignite particles. HTC is a very simple technology (Titirici *et al.* 2007), which converts all carbon (100%) into lignite. When applied to the slum, additional advantages of HTC are that the process of HTC at these relatively low temperatures will eliminate pathogens completely, and HTC requires wet starting products/biomass, thereby avoiding complicated faecal sludge drying schemes. The justification for this study was the idea that HTC might be a promising technology to convert waste

produced in the slum into colloidal lignite (HTCCL), which could be used to treat water and/or wastewater. To our knowledge the removal potential of sand filters to which HTC is added has not yet been described in the literature. In this research our objective was to determine the removal capacity of HTC for cadmium, a divalent metal ion, toxic at low concentrations, known to be used in many production applications polluting the environment, and used in many studies similar to ours, focusing on the removal potential of sorbents. Using batch and column experiments, we first wanted to establish a proof of concept of the capacity of HTC to remove pollutants from water.

MATERIALS AND METHODS

Hydrothermally carbonized colloidal lignite

We used three types of HTCCL slurries produced from maize, grass, and sugar (Carbon Solutions, Berlin, Germany). Sugar was included as a benchmark substrate, since it produces the purest form of carbon without formation of functional groups containing nitrogen, sulfur, or phosphorus. The bottles containing the HTC slurries were stored in a refrigerator. Prior to use, the slurries were equilibrated up to room temperature.

Artificial wastewater

Artificial wastewater (AW) was prepared by dissolving 587.8 mg $\text{CaCl}_2 \cdot \text{H}_2\text{O}$, 87.7 mg NaCl, 7.5 mg KCl, 167.8 mg NaHCO_3 , and 85 mg NaNO_3 in 1 L milli-Q water. To this, and dependent on the experiment, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ was added in various quantities. The pH of the solutions was kept constant at pH 7.5 using Tris buffer. The ionic strength of the solutions was 0.02 M.

Characterization of HTCCL slurries

The zeta potential and the pH point of zero charge (pH_{PZC}) of the HTCCL particles were determined at 25 °C using a Zetasizer Nano ZS (Malvern, Worcestershire, UK). The pH_{PZC} was determined from 50–250 times diluted HTCCL slurries, dependent on the particle mass in the three slurries. Then, samples were filtered by a 0.45 μm cellulose-acetate filter, and a 10 mL filtered sample of each HTCCL type was inserted in the MPT-2 unit of the Zetasizer Nano ZS for auto-titration.

To obtain a qualitative understanding of the size distribution, the nanometer particle size range was determined using the Zetasizer Nano ZS. Micrometre sized particles were observed using a camera mounted on top of a light microscope (Olympus EHT), determining the dimensions of 50 particles per photo, while the millimetre size range was determined from 50 particles using a ruler.

Batch sorption experiments

Kinetic and equilibrium sorption batch experiments with HTCCL were carried out in duplicate using various cadmium concentrations in AW. In the kinetic experiments, different retention times, ranging from 1 min to 4 days, were applied. Duplicate equilibrium experiments using batch reactors of 200 mL were carried out for cadmium concentrations varying from 5 to 750 $\mu\text{g/L}$ for a fixed dose of 1 g (dry weight) HTCCL per litre. All sorption experiments were carried out at room temperature (21 ± 0.5 °C). The pH of the solutions was adjusted to 7.5 using NaOH solution. All batch reactors were rotated at 100 rpm. After the experiment, each batch was centrifuged for 1 min at 3,500 rpm, and filtered through a 0.2 μm cellulose acetate filter. Then, Cd concentrations in the filtrate were measured using a graphite furnace atomic absorption spectrophotometer (Thermo Elemental Solaar MQZe GF95). The mass of sorbed Cd^{2+} was determined as the difference of input mass and recovered mass. Measured isotherm data were fitted with two-parameter isotherms (Langmuir and Freundlich), and three-parameter isotherms (Sips and Redlich–Peterson), using non-linear least squares curve fitting in Microsoft Excel (Solver).

Column experiments

Column experiments were carried out using borosilicate columns (Omnifit, Cambridge, UK) of 2.5 cm inner diameter and length of 15 or 25 cm. Quartz-sand (Kristall quartz-sand, Dorsilit, Germany) was used as porous medium. Of this sand, 32.2 weight-% was in the size range of 0.43–0.56 mm, 41.0% in the range of 0.56–1.1 mm, and 26.4% was in the range of 1.1–1.6 mm. From this, the average particle size was 0.86 mm. Prior to packing to the column, the quartz-sand was washed with concentrated HCl (20%) to remove chemical impurities and then rinsed with demineralized water until the electrical conductivity (EC) of the effluent was close to zero. For the sand-HTCCL prepared from sugar, separately in a beaker 75 g of sand was mixed with 822.4 mL of HTC slurry, which corresponded to 25 g of HTC particles or 25 weight-% (weight

HTCCL/weight (sand + HTC)). For the sand-HTCCL from maize, 75 g of sand was mixed with 140.5 mL of HTC maize slurry, and for the sand-HTCCL from grass, 75 g of sand was mixed with 295.2 mL of HTCCL grass, both corresponding to 20 weight-%. The sand-HTCCL slurry mixtures were gently poured under saturated conditions into the columns to a total bed height of 10–10.2 cm.

Columns of sand without HTCCL were prepared, to serve as control columns. To avoid air entrapment while filling the column, the columns were occasionally tapped and agitated. The column was connected to a pump (MasterFlex model 77201-60, USA) to flush solution into the columns. The pump discharge was adjusted in order to have a constant pore water flow velocity of 1 m/hour (discharge of approx. 3.4 mL/min). Prior to an experiment, the sand-supported HTCCL media in the column was equilibrated by flushing the column with ultra-pure water (EC = 0.8 μ S/cm; MilliQ water; Millipore Corporation; Billerica, MA, USA). All column experiments were carried out in duplicate and at room temperature.

Prior to the Cd removal experiments, tracer experiments were carried out using a 0.02 M NaCl solution. Cl^- concentrations of the influent solution (C_o) and effluent (C_t) were measured on an ion chromatograph (ICS-1000 Dionex) to determine chloride breakthrough curves.

To determine Cd removal efficiencies in the columns, AW without Cd was flushed through a column until the EC of the effluent equalled the EC of the influent. Then, 5–7 pore volumes of AW with Cd followed by 6–8 pore volumes of AW without Cd was flushed through the column. Samples were collected every 4 min. The initial Cd^{2+} concentration (C_o) flushed into the column varied from 0.40 to 0.65 mg/L. For all columns, a flow rate of 3.4 mL/min was maintained, except for the case of columns filled with HTCCL prepared from grass, where clogging was observed. For this type of column, the pump discharge was lowered to 1.2 mL/min. After each run, the column was excavated to determine the HTCCL concentration (g HTC/g sand) as a function of column bed depth. For this, samples were dried at 70 °C, weighed, combusted at 600 °C for 2 hours in a muffle oven to combust the HTCCL particles, and weighed again.

RESULTS

HTCCL particle characterization

The HTCCL slurry from maize had the highest solids concentration (177.9 mg/L; see Table 1), followed by HTCCL

Table 1 | Overview of HTC characteristics

Parameter	Sugar	Maize	Grass
pH slurry	2.9	4	4.8
EC slurry (μ S/cm)	3,600	7,670	12,880
Solid content (g/L)	30.4 \pm 2.0	177.9 \pm 9.4	84.7 \pm 4.9
Zeta potential (mV)	-12.8 \pm 3.6	-4.74 \pm 0.3	-14.5 \pm 0.8
pH _{PZC}	< 1.1	3.7	1.7
Particle size	Tri-modal	Bi-modal	Bi-modal
Small (nm)	50–150	200–600	20–40
Medium (μ m)	4–18	2–18	2–5
Large (mm)	1–2	–	–
<i>Langmuir</i>			
q_{max}	0.21	0.17	0.11
b	60	3	63

prepared from grass (84.7 mg/L) and from sugar (30.4 mg/L). In general, the particle size of all HTCCL slurries was bi-modally or tri-modally distributed with most particles in the nanometre and micrometre size range (Table 1). The slurry from sugar also contained larger particles of 1–2 mm, which were visible by eye. The zeta potential varied between -4.7 and -14.5 mV, indicating favourable conditions for sorption of the positively charged cadmium ions. The pH_{PZC} value of each HTCCL particle type was below 3.7, indicating that at the pH at which we did our experiments (pH 7.5) the particles were negatively charged.

Equilibrium batch experiments

Data obtained from batch sorption experiments as a function of time (kinetic batch sorption exp) indicated that steady state conditions were reached after 24 hour for all three HTCCL types (data not shown). Equilibrium batch experiments indicated that sorption as a function of equilibrium cadmium concentration could be characterized by a typical 'hook-shape' (Figure 1). Sugar-derived HTCCL had the highest capacity to sorb cadmium (Figure 1), while maize-derived HTCCL had the lowest capacity. All isotherm descriptions fitted the data relatively well (data not shown), but the two-parameter Langmuir isotherm fitted the data best (Figure 1). Using

$$q_e = \frac{q_{\text{max}} b C_e}{(1 + b C_e)} \quad (1)$$

to describe the Langmuir sorption isotherm, where q_e is amount of cadmium retained by the adsorbent (mg/g),

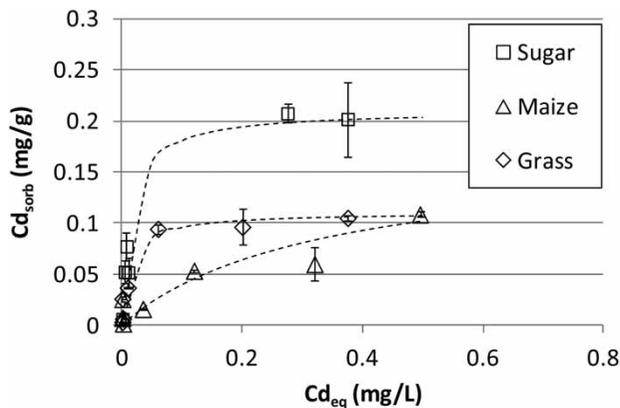


Figure 1 | Sorption isotherms of cadmium onto HTC particles. Dashed lines depict Langmuir isotherms with values corresponding to q_{\max} and b given in Table 1.

q_{\max} is maximum uptake (mg/g) at saturation, C_e is equilibrium concentration of cadmium in solution (mol/L), and b is the Langmuir adsorption constant (L/mg), the maximum uptake, q_{\max} , ranged from 0.11 to 0.21 mg/g, while values for the Langmuir adsorption constant, b , ranged from 3 to 63 L/mg (Table 1).

Column experiments

The weight-% of HTCCL particles was 1.2% for HTCCL prepared from grass, 5.6% for HTCCL prepared from maize, and 21.7% for HTCCL prepared from sugar. The reason for these differences was the particle size: HTCCL particles prepared from sugar were much larger (up to mm size) than HTCCL particles from maize and grass, with the latter one having the smallest particles (Table 1). As a result, most HTCCL particles from maize and grass remained in suspension, and were flushed out during packing of the column, while only the largest particle fraction remained in the sand.

Breakthrough of the conservative chloride tracer in the column prepared from sand only (without HTCCL particles) was rapid (Figure 2): the relative concentration was 0.5 after 1 pore volume (~5 min), and close to 1 within 2 pore volumes (10 min). After the application of the NaCl tracer, relative breakthrough rapidly decreased, and was close to zero after 4–5 pore volumes. The breakthrough curve was symmetrically shaped, and from this we concluded that the set-up of our column system was good. In addition, from the steepness of the rising and falling limbs, we inferred that dispersion in our column set-up was low. Compared to chloride, cadmium breakthrough in sand without HTCCL was retarded, but increased to 1 after 20 min or 4 pore volumes. Although the flow regime and cadmium application were identical to the

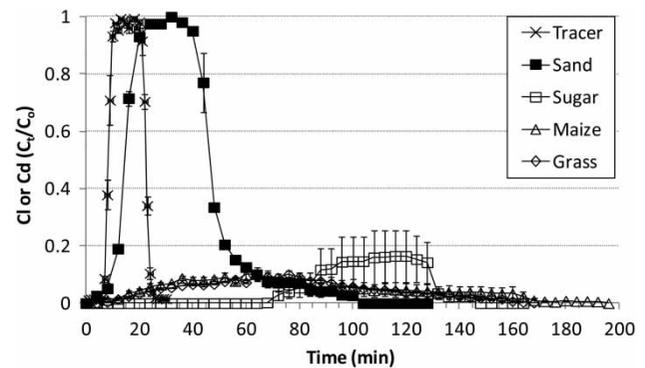


Figure 2 | Tracer (NaCl) breakthrough and cadmium breakthrough in columns of sand and sand-supported HTCCL columns.

sand-only column, breakthrough of cadmium in the column of sand-supported HTCCL prepared from sugar was absent until 70 min (14 pore volumes), and then relative concentrations slowly increased to maximum values of 0.16–0.18 after 100–120 min (20–24 pore volumes). Breakthrough of cadmium in the columns of HTCCL prepared from maize or grass started to slowly rise after 10 min (2 pore volumes) to reach maximum relative concentration values of 0.1 after 60–80 min (12–14 pore volumes).

DISCUSSION

In our research, the two most important parameters characterizing the HTCCL particles were size and zeta potential. With regard to the size, the HTCCL slurries we used had a wide particle size distribution ranging from nanometre to millimetre. Also, the HTCCL particles prepared from sugar were much larger than the particles prepared from maize and grass. The smaller the particles produced from the hydrothermal carbonization process, the larger the surface area available for metal ions like Cd^{2+} to sorb to, thus increasing the removal capacity of the HTCCL particles. Titirici et al. (2007) reported particle sizes ranging from 20 to 200 nm for the HTCCL materials produced from crude plant material, sugar beet chips, pine cones, pines needles, oak leaves, and orange peels. Furthermore, Inagaki et al. (2010) reported particle sizes of 0.25 and 5 μm for HTCCL of saccharide solutions with two different concentrations of 0.15 mol/L, and 1.5 to 3.0 mol/L for a hydrothermal carbonization process carried out at 190 °C for 5 hours. These authors concluded that the size of carbon particles depended on carbonization conditions, the precursor

biomass, its concentration, the temperature, and the reaction time.

The batch experiments showed that HTCCL prepared from sugar had a higher removal capacity than HTCCL prepared from grass, while HTCCL prepared from maize had the lowest removal capacity (Figure 1). This seemed to correspond with the zeta potential and the pH_{PZC} , which was 3.7, 1.7, and less than 1.1 for HTCCL prepared from maize, grass and sugar, respectively. The removal of Cd^{2+} by HTCCL can be explained by two mechanisms: (1) sorption and/or cation exchange, whereby physical forces, such as electrostatic attraction and repulsion, and van der Waal's attraction play a dominant role; and (2) diffusion of Cd^{2+} to particular binding sites present on HTCCL particles. Titirici *et al.* (2007) demonstrated the presence of functional groups such as $-\text{OH}$, COOH , $\text{C}=\text{O}$ by infrared spectroscopic analysis of HTCCL materials fabricated from pine needles, pine cones, oak leaves, and orange peels, which can act as binding sites for heavy metals. We assumed that our HTCCLs had similar functional groups. Of these, the carboxylic groups are weak acids, therefore partly deprotonated at pH 7.5 (our experiments), and were possibly responsible for the capturing of Cd^{2+} . The Langmuir isotherm fitted the data best. From this, we inferred that Cd^{2+} sorption was according to a monolayer on the HTCCL particle, and that, apparently, HTCCL had a finite number of sites available for sorption. Furthermore, there appeared to be no interaction between sorbed species or transmigration of sorbate into the surface, resulting in an infinite number of binding sites. The uptake capacity represented by the parameter q_{max} varied from 0.21 mg Cd/g HTCCL prepared from sugar, to 0.17 mg Cd/g HTCCL (maize), and 0.11 mg/g HTCCL (grass), whereas q_{max} for Cd^{2+} of other sorbents prepared from carbon ranges from 0.17 to 20.1 mg/g (e.g. Marinkovski *et al.* 2006; Yadana-parthi *et al.* 2009; Lo *et al.* 2011). Compared to these values, we concluded that the Cd^{2+} uptake capacity of HTCCL was on the low side. It should be noted, however, that we used plain HTCCL, and that its q_{max} might still be increased by optimizing the HTC production process.

In the columns of sand-supported HTCCL material, the contact time of Cd^{2+} to HTCCL particles was low, and probably insufficient for reaching equilibrium conditions. In fact, the slow rise to breakthrough plateau phases with maximum C/C_0 values of 0.1–0.2, the asymmetrical shape of all breakthrough curves, and the tailing during the final stages of the experiment pointed towards kinetic sorption. The kinetic sorption process for both grass and maize occurred in exactly the same way, giving rise to identical C/C_0 values

as a function of time, while for HTC prepared from sugar, the shape of the Cd^{2+} breakthrough curve differed. This might have been due to the HTCCL particles: most of the HTCCL prepared from sugar was present in the form of millimetre sized particles, visible by eye, and giving rise to a concentration of 21.7 weight-%, while most of the HTCCL particles prepared from grass and maize were present as micrometre or nanometre sized particles, giving rise to a concentration of only 1–5 weight-%. These particle size differences may have resulted in differences in HTCCL particle distribution within the columns, resulting in different accessibilities of Cd^{2+} ions to HTCCL particles, which in their turn give rise to differences in breakthrough behaviour. It is equally interesting to note that, despite these differences in weight-%, the removal capacity was between 90 and 100% for HTCCL prepared from both maize and grass, and between 70 and 100% for HTCCL-sugar. From this we concluded that most of the removal of Cd^{2+} was apparently due to the presence of nanometre–micrometre sized particles, and not due to the larger millimetre sized ones, which were typical for HTCCL prepared from sugar. The HTCCL columns removed 70–100% Cd^{2+} , while breakthrough started to occur after 10–25 pore volumes. In the literature, removal percentages vary from 21% (Lo *et al.* 2011) to 72% (Jusoh *et al.* 2007) to over 90% (e.g. Yadana-parthi *et al.* 2009) for columns consisting of various carbonaceous materials at different dosages. Our results indicated that the HTCCL particles used in this study had similar Cd^{2+} removal capacities.

Overall, HTC is a promising technology to convert waste produced in the slum into colloidal lignite, which could be used to remove heavy metals from water and/or wastewater. A proof of concept of the removal capacity of HTCCL was delivered in this paper. Based on our work, we think there is potential to continue our research, and to assess the removal capacity of HTCCL for other compounds, like nutrients, organic chemicals, and also pathogenic microorganisms.

CONCLUSIONS

- The maximum Cd^{2+} uptake capacity in batch experiments was 0.1 mg/g for HTCCL prepared from maize and grass and 0.2 mg/g for HTCCL prepared from sugar.
- In columns, removal of cadmium was 70–100% for at least 20–24 column pore volumes of flushing Cd^{2+} polluted synthetic wastewater, depending on the type of HTCCL used.

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