



Investigating the potential of synthetic humic-like acid to remove metal ions from contaminated water

Ting Yang*, Mark E. Hodson

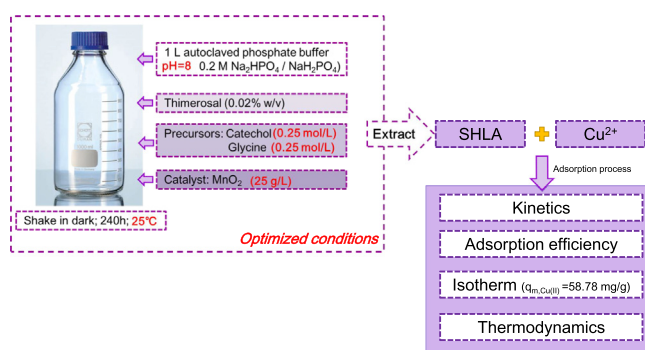
Environment Department, University of York, Heslington, Wentworth Way, York YO10 5NG, United Kingdom



HIGHLIGHTS

- A synthetic humic-like acid (SHLA) with a high COOH content was synthesized.
- All experimental data were fitted with four kinetics and three isotherm models.
- The maximum adsorption capacity of the SHLA was 58.8 mg/g at 313 K.
- SHLA shows great potential as an adsorbent to remove metals from water/wastewater.

GRAPHICAL ABSTRACT



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ABSTRACT

Humic acid can effectively bind metals and is a promising adsorbent for remediation technologies. Our studies initially focussed on Cu²⁺ as a common aqueous contaminant. Previous studies indicate that carboxylic groups dominate Cu²⁺ binding to humic acid. We prepared a synthetic humic-like acid (SHLA) with a high COOH content using catechol (0.25 M) and glycine (0.25 M) with a MnO₂ catalyst (2.5% w/v) at pH = 8 and 25 °C and investigated the adsorption behaviour of Cu²⁺ onto it. The SHLA exhibited a range of adsorption efficiencies (27%–99%) for Cu²⁺ depending on reaction conditions. A pseudo-second-order kinetic model provided the best fit to the experimental data ($R^2 = 0.9995\text{--}0.9999$, $p \leq 0.0001$), indicating that chemisorption was most likely the rate-limiting step for adsorption. The equilibrium adsorption data showed good fits to both the Langmuir ($R^2 = 0.9928\text{--}0.9982$, $p \leq 0.0001$) and Freundlich ($R^2 = 0.9497\text{--}0.9667$, $p \leq 0.0001$) models. The maximum adsorption capacity (q_m) of SHLA increased from 46.44 mg/g to 58.78 mg/g with increasing temperature from 25 °C to 45 °C. Thermodynamic parameters ($\Delta G^0 = 2.50\text{--}3.69$ kJ/mol; $\Delta S^0 = 0.06$ kJ/(mol·K); $\Delta H^0 = 15.23$ kJ/mol) and values of R_L (0.0142–0.3711) and n (3.264–3.527) show that the adsorption of Cu²⁺ onto SHLA was favourable, spontaneous and endothermic in nature. Over six adsorption/desorption cycles using 0.5 M HCl for the desorption phase, there was a 10% decrease of the adsorption capacity. A final experiment using a multi-metal solution indicated adsorption efficiencies of up to 84.3–98.3% for Cu, 86.6–98.8% for Pb, 30.4–82.9% for Cr, 13.8–77.4% for Ni, 9.2–62.3% for Cd, 8.6–51.9% for Zn and 4.6–42.1% for Co. Overall, SHLA shows great potential as an adsorbent to remove metals from water and wastewater.

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* Corresponding author.

E-mail address: ty672@york.ac.uk (T. Yang).

1. Introduction

Water contamination caused by metals (e.g., copper, cadmium, lead, zinc, chromium, and nickel) is a serious environmental and health issue worldwide (Gupta et al., 2016; Kavcar et al., 2009; Machado et al., 2017; Saha et al., 2017; Zhang et al., 2017a). Metals can be of great concern because at elevated concentrations they can be extremely toxic, non-biodegradable and tend to accumulate in living organisms (Rezania et al., 2016; Zou et al., 2016). Thus, it is essential to remove excessive concentrations of metals from water and wastewater for human health and ecological stability. Significant industrial sources of copper release into the environment include metal cleaning, electroplating, smelting, mining, the paper industry, batteries and pesticides (Al-Qodah and Al-Shannag, 2017; Awual et al., 2013; Gupta, 1998). Excessive intake of copper can cause serious toxicological concerns, such as gastrointestinal problems, cystic fibrosis, kidney damage, neurotoxicity, cramps, hair loss, anaemia, hypoglycemia, and even death (Al-Qodah and Al-Shannag, 2017; Fu and Wang, 2011; Ihsanullah et al., 2016). The maximum permissible concentrations of Cu in drinking water as defined by the EPA, WHO and EEA are 1.3 mg/L, 1.5 mg/L and 2 mg/L, respectively (EPA, 2009; EU, 1998; WHO, 2004).

Various methods to remove metals from water have been investigated in the past decades, including chemical precipitation, adsorption, ion exchange, membrane filtration, phytoremediation, electrodialysis, photocatalysis and flotation (Mahmud et al., 2016; Rezania et al., 2016). Of these, adsorption is regarded as one of the most simple, cost-effective and efficient (Gupta et al., 2016; Gupta and Saleh, 2013). As the adsorbent is the key to adsorption techniques, many organic and inorganic adsorbents have been studied, such as active carbon, nanosized metal oxides, carbon nanotubes, clay minerals, biochar and polymers (e.g. chitin/chitosan based materials and humic acid based materials) (Adebisi et al., 2017; Ahmaruzzaman and Gupta, 2011; Anastopoulos et al., 2017; Ca et al., 2017; Gupta and Nayak, 2012; Ihsanullah et al., 2016; Inyang et al., 2016; Li et al., 2010; Mahdavi, 2016; Saleh and Gupta, 2012; Tang et al., 2014; Uddin, 2017; Zhang et al., 2016).

Humic acid (HA) is a natural biopolymer and major component of humic substances (Stevenson, 1994). Due to the abundant oxygen-containing functional groups present in HA (e.g., including carboxyl, phenol, hydroxyl, amine, and enol), humic acid can effectively bind several metals (Perminova and Hatfield, 2005). Recently, humic acid and humic acid-based materials have been considered as a promising adsorbent and have attracted increasing attention (Arslan et al., 2007; Jin et al., 2016; Lin et al., 2011; Yang et al., 2015). The majority of humic acids used in these studies are natural humic acids extracted from soil, lignite or sediment (Arslan et al., 2007; He et al., 2016; Unuabonah et al., 2016; Yang et al., 2015). However, humic acid can also be synthesized by abiotic humification processes, that is the transformation of humic precursors (e.g., amino acids, sugars, and quinones) to humic substances catalyzed by materials containing metallic oxide (e.g., MnO₂, Fe₂O₃, and Al₂O₃). Humic acid synthesized by abiotic humification is called synthetic humic-like acid (SHLA) (Fukushima et al., 2009; Hardie et al., 2009; Qi et al. (2012a, 2012b); Zhang et al., 2017b; Zhang et al., 2015). Compared with natural humic acid, the advantage of synthetic humic-like acid is that the structural characteristics of SHLA can be manipulated by changing the reaction conditions of the abiotic humification process, such as the species of catalyst and the ratio of precursors (Fukuchi et al., 2012; Jokic et al., 2004; Zhang et al., 2015). Therefore, abiotic humification processes can provide a potential and promising way to synthesize humic acids with better metal sorption ability than their naturally occurring counterparts and the novelty of our study lies in its investigation of a SHLA that has been synthesized to optimize its adsorption capacity.

The aims of the experiments reported here were to determine the adsorption efficiency and adsorption kinetics, together with isotherm fits and thermodynamics for adsorption of Cu²⁺ by an optimized SHLA

under a range of conditions, to determine how re-usable the material was via a series of adsorption/desorption cycles and to investigate whether a SHLA optimized for Cu²⁺ would also efficiently remove metals from solutions containing a mixture of metals.

2. Materials and methods

2.1. Materials

Catechol (C₆H₆O₂, >99% purity), glycine (C₂H₅NO₂, >99% purity), glucose (C₆H₁₂O₆, >99% purity), thimerosal (C₉H₉HgNaO₂S, >97% purity), manganese oxide (MnO₂, >99% purity), and copper nitrate trihydrate (Cu(NO₃)₂·3H₂O, >99% purity) were purchased from Sigma-Aldrich. Sodium phosphate dibasic dihydrate (Na₂HPO₄·2H₂O, >99% purity), sodium phosphate monobasic dihydrate (NaH₂PO₄·H₂O, >99% purity) and sodium nitrate (NaNO₃, >99% purity) were purchased from ACROS Organics. Calcium chloride (CaCl₂, >99% purity) was purchased from Fisher Chemical. Multi-element standard solution IV (1000 mg/L) was purchased from MERCK. Ultra-pure water was prepared using a PURELAB Classic ultra-pure system (ELGA, UK) from deionized water.

2.2. Preparation of optimal synthetic humic-like acid

Previous studies indicate that carboxylic groups dominate Cu²⁺ binding to humic acid (Gondar et al., 2006; Xu et al., 2016; Yang et al., 2015). In preliminary work for this study, SHLAs were synthesized at different temperatures (25 °C–45 °C), pH (6–8), and with varying precursor species (glycine, catechol and glucose), initial precursor concentrations (0.25 M:0.25 M–1 M:1 M) and mass of MnO₂ catalyst (1.3%–2.5%) (Table S1). Based on these initial experiments we synthesized a SHLA (SHLA 12 in Table S1) with an optimized high COOH content from a pH 8, 0.25 M glycine: 0.25 M catechol mixture at 25 °C with 2.5 wt% MnO₂ as a catalyst.

To ensure that the humification was abiotic, sterile conditions were maintained throughout the experiments. All glassware and pure water were autoclaved (121 °C for 27 min, 0.12 MPa) prior to use. An 1000-mL aliquot of autoclaved phosphate buffer (pH 8, 0.2 M Na₂HPO₄/NaH₂PO₄ autoclaved at 121 °C for 27 min, 0.12 MPa) containing 0.02% (w/v) thimerosal (to ensure sterility) was placed in a 3 L beaker, to which 25.00 g of MnO₂ was added. 27.53 g of powdered catechol and 18.77 g of glycine to give 0.25 M concentrations of each were added to the suspensions. The mixture was shaken in the dark at 25 °C for 240 h. After incubation, SHLA was extracted and purified using the standard method recommended by the International Humic Substances Society (IHSS) (Swift, 1996). Details of the extraction and purification process are given in the Supplementary materials. When synthesizing materials for environmental deployment, the toxicity of the reagents and products should be considered. The extraction process used to isolate the SHLA results in the isolation of pure SHLA; an attraction of the use of SHLAs in environmental applications is that humic acids and SHLAs occur naturally in the environment and therefore represent less of a risk to the environment than some other materials such as nanoparticles. The reagents used to synthesize the SHLA have low toxicities (see Material safety data sheets such as: (Sigma-Aldrich, 2014; Sigma-Aldrich, 2015; Sigma-Aldrich (2017a, 2017b))). Whilst thimerosal is highly toxic in concentrated form (Sigma-Aldrich, 2013), the dose used in this study was just 0.02% (w/v), concentrations higher than this (0.001–0.1%) are routinely used in human medical applications (National, 2001; Veen and Joost, 1994). Thimerosal was used in this study to maintain sterile conditions as we wished to be certain that our SHLA was produced by abiotic processes. However, to reduce environmental risks we would anticipate that in the commercial production of SHLA for use as a remedial agent, thimerosal would not be used; sterility would be established by autoclaving.

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