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Adsorption of Cd(II) and Pb(II) ions from aqueous solutions using mesoporous activated carbon adsorbent: Equilibrium, kinetics and characterisation studies

Edidiong Asuquo*, Alastair Martin[1], Petrus Nzerem[2], Flor Siperstein, Xiaolei Fan

School of Chemical Engineering and Analytical Science, The Mill, Sackville Street, University of Manchester, Manchester, M13 9PL, United Kingdom

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ABSTRACT

In this study, cadmium and lead ions removal from aqueous solutions using a commercial activated carbon adsorbent (CGAC) were investigated under batch conditions. The adsorbent was observed to have a coarse surface with crevices, high resistance to attrition, high surface area and pore volume with bimodal pore size distribution which indicates that the material was mesoporous. Sorption kinetics for Cd(II) and Pb(II) ions proceeded through a two-stage kinetic profile-initial quick uptake occurring within 30 min followed by a gradual removal of the two metal ions until 180 min with optimum uptake ($q_{e,exp}$) of 17.23 mg g^{-1} and 16.84 mg g^{-1} for Cd(II) and Pb(II) ions respectively. Modelling of sorption kinetics indicates that the pseudo first order (PFO) model described the sorption of Pb(II) ion better than Cd(II), while the reverse was observed with respect to the pseudo second order (PSO) model. Intraparticle diffusion modelling showed that intraparticle diffusion may not be the only mechanism that influenced the rate of ions uptake. Isotherm modelling was carried out and the results indicated that the Langmuir and Freundlich models described the uptake of Pb(II) ion better than Cd(II) ion. A comparison of the two models indicated that the Langmuir isotherm is the better isotherm for the description of Cd(II) and Pb(II) ions sorption by the adsorbent. The maximum loading capacity (q_{max}) obtained from the Langmuir isotherm was 27.3 mg g^{-1} and 20.3 mg g^{-1} for Cd(II) and Pb(II) ions respectively.

1. Introduction

The advent of industrialization and the increasing rate of consumption in our society has brought with it increased levels of industrial pollution resulting in a significant level of ecosystem destruction with high pollutant concentrations such as heavy metals and organic compounds in water resources raising global concern on the threat posed by industrial activities on the environment [1]. A large proportion of water pollutants that affect our environment results from industrial activities and their ever increasing nature have led to the present state of our global environment. This is because of the huge chemical input associated with these processes and the inefficient resource utilisation of the input components leads to huge generation of waste streams that require disposal into the environment. The low efficiency of the treatment processes used in these industrial sites for the treatment of industrial effluents further increases the pollutant load in treated discharged effluents. Thus, wastewater from these industrial activities is mostly contaminated with organic and inorganic pollutants amongst which are heavy metal ions, phosphates, sulphates, organic and hydrocarbon compounds. Some of these compounds are known as priority pollutants in many waste streams such as those originating from industrial activities relating to petroleum production, refining and petrochemicals, pulp and paper manufacture, battery manufacture, tanneries, paint and pigment industries, fertilizer, herbicide and pesticide industries as well as mining and metallurgical plants [2–4].

Amongst the list of pollutants that affect our environment, heavy metals are becoming more prominent due to the diverse routes of its exposure, its toxic implications across time scales and the level of industrial development in recent decades. The main source of input of heavy metals into the environment has been from industrial activities which lead to challenges in their reduction and remediation. Since these heavy metals possess

* Corresponding author.
E-mail address: edidiong.asuquo@postgrad.manchester.ac.uk (E. Asuquo).
[1] Present address: Department of Engineering, Lancaster University, Bailrigg, Lancaster LA1 4YR.United Kingdom.
[2] Present address: Department of Chemistry, Nigerian Turkish Nile University, Research Institution Area, Abuja, Nigeria.

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diverse toxicity and are not biodegradable, their toxic impact may develop over a long period of time as is the case in closed mines or mining sites that have fallen into disrepair and abandoned. This may lead to a variety of chemical speciation of these heavy metals in the soil, air and water environments and with different routes of exposure their toxic implications are magnified over a long time due to their long half-lives [5].

Lead and cadmium are two common toxic heavy metals that man is increasingly being exposed to due to their properties and wide applications in materials and technologies that define human survival. For example lead metal is used in the construction and building industry as a component of metal alloys and in the nuclear industry as a radiation shield. Lead is also relevant in the electroplating industry, textile industry, metal processing and finishing, as solders with tin (Sn), fusible alloys, storage batteries (lead-acid car battery), explosive materials, photographic materials and fuel additives [6–8]. Lead pigments are used in a variety of applications like chromate for road markings and oxides for glass and chemicals. Cadmium is used for the manufacture of the following materials; batteries; pigments; coatings and platings; stabilizers for plastics; nonferrous alloys and photovoltaic devices [9]. Cadmium is released into the environment in a variety of ways such as tobacco smoking, mining, smelting and refining of non-ferrous metals; fossil fuel combustion, incineration of municipal waste (especially cadmium-containing batteries and plastics), metal plating industries, manufacture of phosphate fertilizers, recycling of cadmium-plated steel scrap as well as electric and electronic waste [10–12].

Due to their widespread use, these two metals can have toxic effects on humans as well as flora and fauna. Human exposure to lead ions can be from lead dust which originates from the degradation of lead paints and other routes including drinking contaminated water from lead pipes. Due to accumulation of lead in the environment from anthropogenic sources, human exposure to lead ions has become a problem in the society in both developing and developed countries. Lead speciation also affects the rate of absorption as the human body is known to absorb organic lead faster than inorganic lead. Lead is a heavy metal poison that affects the functioning of the blood, liver, kidney and brain of the human being [6]. It is known as a large cation especially prone to react with sulfhydryl (-SH) groups in proteins in a manner similar to cadmium ions. It acts by complexing with oxo-groups in enzymes affecting virtually all steps in the process of heme-synthesis and porphyrin metabolism [13,14]. At high concentrations lead is known to cause encephalopathy, cognitive impairment, kidney and liver damage, anaemia and toxicity to the reproductive system [15–17]. The USEPA discharge limit for lead in effluents is 0.005 $mg\,L^{-1}$, while the limit for discharged effluents into aquatic water by the World Health Organisation (WHO) is 0.01 $mg\,L^{-1}$[18,19,8].

Cadmium is an element with no known positive biological function on humans and is one of the most serious environmental pollutants especially in the vicinity of smelters. It has a high affinity for sulfhydryl (-SH) groups of proteins for which it competes with Zn(II) in biological systems and is known as a human carcinogen [10]. Due to its low-concentration-long-term effect in drinking water, cadmium belongs to the chemicals list of endocrine disruptors and priority control pollutants issued by USEPA [20,21]. The toxic implications of cadmium in the environment has made the US Environmental protection Agency (USEPA) to set the level of cadmium in drinking water to 0.002 $mg\,L^{-1}$ and the World Health Organisation (WHO) maximum permissible limit for cadmium in drinking water is 0.003 $mg\,L^{-1}$ [12,10,22,11,23].

Due to the toxic implications of these two metals, approaches that promote their removal from aqueous effluents have been classified as priority in the last two decades and a number of technologies have been explored [24]. The use of adsorption has become one of the techniques explored in recent years. A number of materials have been synthesised and used for the adsorption of Cd(II) and Pb(II) ions such as amino propyl-modified mesoporous carbon [25]; chemically modified polyacrylonitrile-based fiber [26] and spherical mesoporous silica [27,28]. In spite of these advances in material synthesis for adsorption of pollutants such as heavy metals, the material at the forefront of adsorption technology is still activated carbon. Activated carbon has gained widespread use for the treatment of heavy metal ions and other pollutants because of its inherent physical properties such as large surface area, porous structure, high adsorption capacity and large reactive surface [29–31]. It is widely used due to its exceptional high surface area (ranges from 500 to 5000 $m^2\,g^{-1}$), well developed microporosity and wide spectrum of surface functional groups. These properties of activated carbon are generally controlled by the manufacturing process which depends on the nature of raw materials, activating agents and conditions of activation [32,33,29].

Commercial activated carbon is often the preferred adsorbent for the removal of pollutants due to its versatile nature for a wide variety of compounds; however its widespread use is often restricted due to high associated cost. This has driven research into the use of inexpensive alternative activated carbon precusors such as waste materials from agriculture, wood and fisheries industry [34]. This drive in research on low cost precusors for the synthesis of activated carbon has led to an exponential increase in studies reporting the use of these activated carbon adsorbents obtained from waste materials for the removal of both organic and inorganic pollutants. This research platform also requires that studies on the use of the commercial activated carbon for the removal of the target pollutants that are of interest in the environment should also be undertaken to serve as a standard for comparing the low cost based activated carbon adsorbents obtained from waste precursors. This will provide information that is significant for the commercial exploitation of the synthesis of activated carbon adsorbents from low cost precusors. In this regard, more studies have been reported in literature with focus on the removal of organic pollutants such as dyes, phenols, volatile organic compounds than heavy metal ions using commercial activated carbon [34–37]. The increasing environmental and health challenges posed by toxic heavy metal pollution as the advancement in industrialisation reaches the shores of the developing economies requires that more investigations should be carried out with respect to the use of commercial activated carbon adsorbents for those heavy metal ions that are prevalent in these countries.

Hence, this study is designed to provide information on the use of a commercial activated carbon adsorbent for the removal of two prominent heavy metals that are toxic and are prevalent in developing economies as a result of their drive towards industrialisation. A commercially manufactured activated carbon (Chemviron Carbon) was used as adsorbent for this study. Characterisation of both physical and chemical properties of the commercial activated carbon (CGAC) will be investigated to give insight on the material and this will be used to correlate with the ions uptake in aqueous phase. In addition, Cd(II) and Pb(II) ions kinetic and equilibrium sorption as well as the modelling of the transport of the two ions onto the surface of the commercial activated carbon will be investigated.

2. Materials and methods

2.1. Chemicals and adsorbent

Standard stock solutions of 1000 $mg\,L^{-1}$ of the two metal ions were prepared by dissolving appropriate amounts of analytical grade reagent [cadmium nitrate tetrahydrate-Cd $(NO_3)_2{\cdot}4H_2O$