REMOVAL OF HEXAVALENT CHROMIUM USING NOVEL TWO-STEP ACTIVATED BIOCARBON

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ABSTRACT

The removal of heavy metals from wastewater is needed as they have high toxicity that can affect human health. Activated biocarbon produced from various raw materials offers huge potential in hexavalent chromium removal from aqueous solution. In present study, the resulting biocarbon has been activated by two-step approach. Batch mode experiment was conducted at room temperature to investigate the effect of various parameters to the metal removal efficiency. The optimum contact time for hexavalent chromium removal was found to be 1 hr. The optimum biocarbon dosage was 0.125 g. The optimum initial concentration of hexavalent chromium was 100 mg/L. The optimum pH was 2. In addition, equilibrium adsorption isotherms was characterized to analyze the obtained experimental data. Results showed that Langmuir isotherm type 1 was the best fit linearized isotherm (R^2 = 0.9938). In conclusion, a novel and effective activated biocarbon was prepared and it has potential hexavalent chromium removal from various industrial wastewaters.

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LIST OF ABBREVIATIONS

°C	degrees Celsius
ANOVA	Analysis of Variance
Cr(III)	trivalent chromium
Cr(VI)	hexavalent chromium
DPC	1,5-Diphenylcarbazide
EPA	Environmental Protection Agency
g	gram
hr	hour
LSD	Least Significance Difference
MCL	maximum contaminant level
mg/g	milligram per gram
mg/L	milligram per litre
mL	millilitre
R^2	correlation coefficient
rpm	revolutions per minute

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Chromium is one of the natural heavy metals used in manufacturing and chemical industries. Two oxidation states are available in the aquatic environment which are trivalent chromium (Cr(III)) and hexavalent chromium (Cr(VI)) (Khedr, Shouman, Fathy, & Attia, 2014). Trivalent chromium acts as essential nutrient for human and can be found naturally in rocks, soil, plants, animals, and volcanic emissions (Focus, 2000). Meanwhile, hexavalent chromium is a toxic form that mostly created from human industrial activities such as metal plating, welding, chemical, building material, fertilizer, leather tanning, pigment application, painting, and surface coating (Owlad, Aroua, Daud, & Baroutian, 2008; Gupta & Mote, 2014; Khedr et al., 2014). It is produced by heating process of Cr(III) in the presence of mineral bases and oxygen (Focus, 2000). United States EPA (Environmental Protection Agency) has set standard maximum contaminant level (MCL) in water at 0.10 ppm (0.10 mg/L) (US EPA, 2013) while California EPA is more stringent of MCL at 0.02 ppm (0.02 mg/L) (Office of Environmental Health Hazard Assessment (OEHHA), 2011). However, they are still released into environment by leakage, poor storage and improper waste industrial disposal. Cr(VI) has been assessed to have potential health risks to human (US EPA, 2013). It is proposed that if people consume drinking water containing Cr(VI) over a lifetime, it can develop skin irritation, stomach ulcer, liver and kidney damage, nerve tissue damage, various cancers and even death (Owlad et al., 2008).

Due to the mutagenic and carcinogenic characteristics of hexavalent chromium, a number of wastewater treatment methods for Cr(VI) removal have been stated, generally chemical precipitation, reverse osmosis, ion exchange, electrodialysis, photo-catalysis, membrane filtration, adsorption and biosorption. Although some methods are considered effective, there are limitations such as high operating cost, high energy requirement, technical complication and sludge generation (Owlad et al., 2008; Khedr et al., 2014). Joshi, Raut, Kulkarni and Dhokpande (2014) summarized that adsorption method as one of the effective methods in hexavalent chromium removal due to the low cost, practical, and environmental friendly. However, this method has low adsorption capacity and less intensity of biosorption compared to other methods.

Activated biocarbon carries a great opportunity to be in large-scale production because it uses cost-effective renewable resources such as biomass (Owlad et al., 2008). Besides, it possesses high adsorption capacity due to its surface area and pore characteristics (Gottipati, 2012). Current researches have put a lot of focus in improving its adsorption capacity. The activated biocarbon can be modified physically by high thermal exposure, chemically by either acid or base activation agents, and biologically by using various microorganisms (Bhatnagar, Hogland, Marques, & Sillanpaa, 2013). Some of potential low cost raw materials that have been researched are rice husk, sugarcane bagasse, orange peel, saw dust (Gupta & Mote, 2014), palm tree branches (Khedr et al., 2014), palm shell (Nomanbhay & Palanisamy, 2005), palm kernel (Kundu, Redzwan, Sahu, Mukherjee, Gupta, & Hashim, 2014), pruning mulberry shoot (Wang, Wu, Wang, Qiu, Liang, Fang, & Jiang, 2010), tree bark (Kumar & Tamilarasan, 2013; Hunge, Rahangdale, & Lanjewar, 2014), leaves, coconut shell (Gottipati & Mishra, 2010), peach kernel (Modrogan, Costache, & Orbulet, 2007), nut shell (Modrogan et al., 2007), and tamarind pod shell (Desai, Charyulu, & Suggala, 2014). Acidic modification performed a great result in oxidizing the porous surface of the activated carbon hence it improves the affinity between the activated carbon and hexavalent chromium (Bhatnagar et al., 2013). For examples, HNO_3, H_2SO_4, H_2S, HCl and H_3PO_4 can displace hydroxide groups with oxygen-containing functional groups (Bhatnagar et al., 2013). Phosphoric acid (H_3PO_4) is widely used as activation agents as many papers showed it has given high surface areas and more microspore structure (Khedr et al., 2014; Kundu et al., 2014; Makeswari & Santhi, 2013; Wang et al., 2010).

There is no research on potential activated biocarbon using two-step approach. In present research, the two-step activated biocarbon is a novel work (Appendix 1). It has been modified using two-step activation such as physical and acidic modification using H_3PO_4. The correlation of adsorption capacity to the various parameters and its adsorption isotherm were investigated.

1.2 OBJECTIVES

1. To prepare novel and effective activated biocarbon through two-step activation

2. To investigate the effect of contact time on hexavalent chromium removal

3. To analyse the effect of biocarbon dosage on hexavalent chromium removal

4. To analyse the effect of initial concentration of Cr(VI) solution on hexavalent chromium removal

5. To investigate the effect of pH on hexavalent chromium removal

6. To ascertain the best Cr(VI) removal characteristic using Langmuir and Freundlich isotherm models

CHAPTER 2

LITERATURE REVIEW

2.1. CONVENTIONAL TREATMENTS FOR HEXAVALENT CHROMIUM REMOVAL

Owlad et al. (2008) has reviewed about hexavalent chromium removal methods. Membrane filtration is one of the conventional methods that uses either by inorganic, polymeric, or liquid membrane to remove heavy metal such as Cr(VI). However, this method requires high operational cost. Ion exchange technique is a very effective method that uses ion exchange resins to uptake hexavalent chromium from wastewater but it requires pre-treatment system to remove secondary effluent. Furthermore, it is not designed for all types of heavy metal due to its specificity hence it is an expensive heavy metal removal technique. Electrochemical treatment is another technique which requires costly physical and physicochemical pre-treatment systems.

2.2. ADSORPTION METHOD

Adsorption method is a process of molecules attachment on the surface of the adsorbent. The method uses low cost and is readily available, profitable, practical, environmental-friendly and effective compared to other conventional methods (Owlad et al., 2008). The most common adsorbent used is activated carbon from different raw materials. It has large surface areas and well-developed micropores and even functional groups such as carboxylic group (Gottipati, 2012; Bhatnagar et al., 2013). Commercial activated carbon has been available to remove Cr(VI) from wastewater. However, the sorbent is expensive because it can only adsorb few milligrams of Cr(VI) per gram of activated carbon (Owlad et al., 2008). In other hand, biosorbent has given a promising method to remove contaminants from wastewater because its materials come from free agricultural wastes like hazelnut shell, wool, sawdust, etc. The advantages include cost-effective, efficient, reduction of sludge regeneration, and possible metal recovery (Joshi et al., 2014). However, the adsorption efficacy is still lower than the conventional methods.

2.3. ENHANCEMENT OF BIOCARBON ADSORPTION CAPACITY

Various agricultural wastes have been utilized for potential biocarbon like coconut shell, saw dust, rice husk, sugarcane bagasse, peanut hull carbon, etc. Raw material such as tendu leaf (*Diospyros melanoxylon*) refuse has been studied by Mane, Bhosle, Deshmukh, & Jangam, 2010. The leaf was immersed into sulfuric acid and it showed a better biosorbent compared to commercial activated carbon. It was suggested that pH played an important role in adsorption activity with the optimum pH obtained at pH 2.0. This was because at low pH condition, high concentration of Cr(VI) was reduced into Cr(III) leaving lower concentration of Cr(VI) which could be rapidly adsorbed.

Khedr et al. (2014) has conducted a study on physical and chemical effect on hexavalent chromium removal using palm tree branches as potential biocarbon. The materials were mixed with 20% and 50% phosphoric acid respectively and left overnight in room temperature and put in oven of 100°C to evaporate the excess water. After that, it was dried again in oven at 110°C for 1 hr. Thermal activation was taken place in furnace at 500°C for 2 hr. It was shown that the highest adsorption efficiency occurred in activated carbon treated with 50% H_3PO_4. It was also suggested that Cr(VI) adsorption was best conducted at low pH.

Owlad et al. (2008) also stated that chemical modification showed increased adsorption capacity of adsorbents. It was suggested that it gave improved number of active binding sites resulted in better ion exchange activity. Corresponding to Bhatnagar et al. (2013), acidification is stated to be more suitable for adsorption of metal ions while basification is more towards anions. Gottipati & Mishra (2010) also stated that pH acts as a crucial parameter in the Cr(VI) removal. The presence of microspore is essential to give large surface area and pore volume hence maximum adsorption capacity can be achieved.