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Removal of Cr(VI) from Aqueous Solution by Adsorption onto Activated Carbon derived from Giant Reed

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Abstract

Chromium (Cr) is one of the most hazardous heavy metal with a high carcinogenic and recalcitrant nature. In present study, activated carbon (AC) prepared from Giant Reed (Arundo donax) was utilized as an adsorbent for the removal of hexavalent chromium [Cr(VI)] from aqueous solution. Activated carbon was prepared from Giant Reed by chemical activation using zinc chloride and phosphoric acid at 500°C in ratio 1:1 by weight for 3 hrs. The activated carbon thus obtained was characterized by iodine number (I_N), methylene blue number (MB_N) and SEM image. Iodine number, methylene blue number and surface area was found to be 892 mg/gm, 430 mg/gm and 991 m^2/gm for zinc chloride AC and 784 mg/gm, 555 mg/gm and 970 m^2/gm for phosphoric acid AC respectively. SEM micrographs showed that the prepared activated carbon had a well-developed porous structure. Adsorption of chromium (VI) onto the activated carbon was studied using batch-adsorption techniques. The percentage removal of Cr(VI) was found to be higher in H_3PO_4 activated carbon compared to $ZnCl_2$ activated carbon and is comparable to commercial AC. Present study revealed highest potential of Giant Reed for producing AC as a low cost adsorbent for the removal of Cr(VI) from contaminated water.

Keywords: *Activated Carbon; Adsorption; Hexavalent Chromium; Giant Reed.*

1. Introduction

Chromium is one of the major inorganic environmental pollutants, which is added to natural water from a variety of industrial wastes. The major sources are from dyeing, electroplating, leather tanning, metal processing, paint and pigments, and the textile and steel fabrication industries and exists mainly in two forms: Cr(III) and Cr(VI). Cr(III) is considered as an essential trace nutrient for human, while Cr(VI) is highly toxic due to its high

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solubility and mobility. Owing to the adverse health caused by Cr (VI), it is necessary to remove it from contaminated water. Various methods have been reported, mainly adsorption, chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction for the removal of chromium ions from aqueous solutions [1-3]. The major drawbacks related with these methods are high cost, toxic sludge generation or incomplete metal removal.

Adsorption by activated carbon (AC) is one of the effective techniques for Cr (VI) ion removal from water and wastewater. Activated carbon is an extremely environmental-friendly carbon porous material with increasing number of applications in different domains. ACs present various desirable characteristics such as tunable porosity, light weight, electrical conductivity, chemical and physical stability and a possibility to present different morphologies. According to the International Union of Pure and Applied Chemistry (IUPAC), pores are classified based on the average pore size: micropores (dimension < 2 nm), mesopores (2 nm < dimension < 50 nm) and macropores (dimension > 50 nm). Each group of pores corresponds to a specific function, that is, the macropores are transport pores, the mesopores are transitional pores used both in the adsorption of larger molecules and in the rapid transport of smaller molecules, and micropores are where adsorption occurs. Many reports have appeared on the development of low-cost activated carbon from renewable resources such as agricultural and industrial waste for chromium removal. It includes apricot stone [4], coconut shell [5], groundnut hull [6], pecan nut shell [7], Terminalia arjuna nuts [8] etc. Giant reed (Arundo donax L.), is a tall perennial grass, found in wetlands and riparian natural surroundings and is believed to be local to eastern Asia. In Nepal there are lots of wetlands, where this invasive plant grows. It contains high amount of lignin and cellulose which displays many attractive characteristics for the production of highly porous carbon. The aim of this study is to prepare and characterize activated carbons from Giant Reed by chemical activation to remove chromium (VI) ion from water.

2. Experimental

2.1. Materials

Giant Reed used in this study was obtained from wet lands of Kathmandu, Nepal. All reagents used were A.R. grade, purchased from Qualigen, India. Distilled water was used for preparation of various solutions. The stock solution of chromium sample was prepared by dissolving calculated amount of potassium dichromate ($K_2Cr_2O_7$) in distilled water.

2.2. Preparation of Carbons

The Giant Reed was washed with distilled water for several times, oven-dried for 24 h at 110°C to reduce the moisture content, crushed, and sieved to a particle size of 250µm. H_3PO_4 was impregnated into reed powder and zinc chloride was dissolved in water and then impregnated into the reed powder. The impregnation ratio of precursor to activating agent was 1:1 by weight. The mixture was kept at 110˚C for 24 h to incorporate all the chemicals in the interior of the particles, and then carbonized for 3 h in a horizontal furnance at 400˚C in inert condition of N_2 gas. After that, the prepared H_3PO_4 activated carbon was washed with 0.1N NaOH followed with warm distilled water to make it free of acid. For $ZnCl_2$ activated carbons, it was thoroughly washed with 0.1 M hydrochloric acid and distilled water to remove the residual $ZnCl_2$. The sample was then dried at 110˚C and sieved to a particle size of 100µm to obtain a powder for subsequent analyses and uses.

2.3 Characterization of Activated Carbon

Iodine number of Activated carbon (AC) was determined according to ASTM D4607-94 method [9]. Methylene blue number of AC was determined by single point adsorption isotherm studies according to Standard Method [10]. Surface area of AC was estimated by iodine and methylene blue numbers using multiple regressions [11]. Surface morphology of the AC was studied by scanning electron microscope (SEM) Hitachi S-4800.

2.4 Adsorption Experiment

As The adsorption experiments were performed by batch adsorption method. 0.025 gm of AC was added to 25 mL of Cr (VI) solution taken in 250 mL conical flasks. The suspensions were agitated in an electric shaker at constant speed of 120 rpm. Concentration of hexavalent chromium in solution was determined by UV/Vis spectrophotometer at 540 nm by 1, 5-diphenylcarbazide method [12, 13]. The adsorption experiment was carried out at room temperature.

3. Results and Discussions

3.1 Iodine Number (I_N), Methylene Blue Number (MB_N) and Surface Area

The iodine number is defined as the milligrams of iodine adsorbed by one gram of carbon when the iodine residual concentration of the filtrate is 0.02N [11]. Methylene blue number (MBN) is defined as the maximum amount of dye adsorbed by 1 g of adsorbent [14]. Iodine has a small molecular size and can readily penetrate deep micropores of the AC. So iodine number gives approximate measure of the micropore content of the carbon. Likewise, methylene blue number indicates the mesopore distribution in the carbon and indicates the ability of AC to adsorb medium size molecules. I_N, MB_N and surface area of plain carbon, commercial AC and prepared ACs prepared using different activating agents are presented in Figure 1.

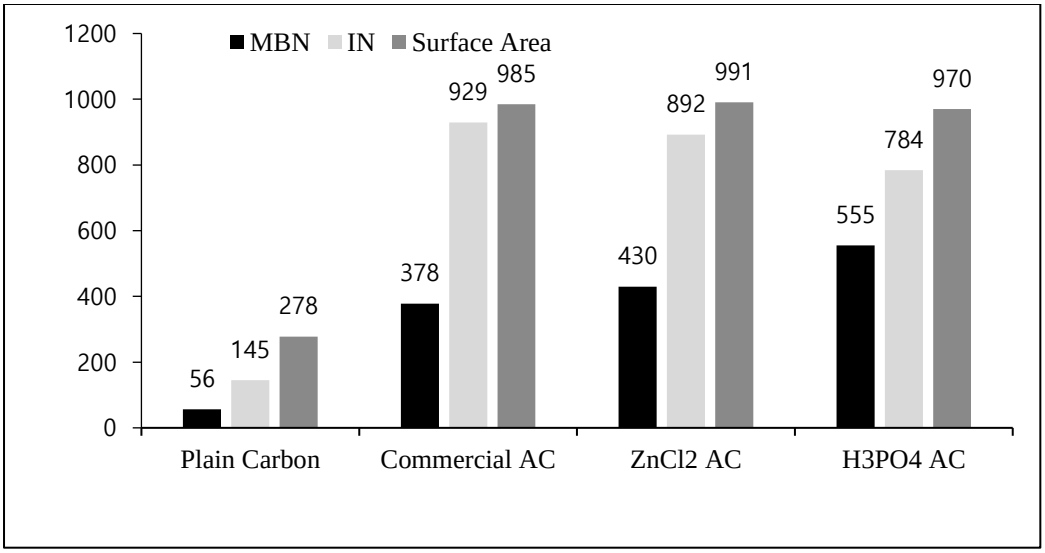


Figure 1. I_N, MB_N and surface area of plain carbon, commercial AC and ACs prepared using different activating agents

As shown in

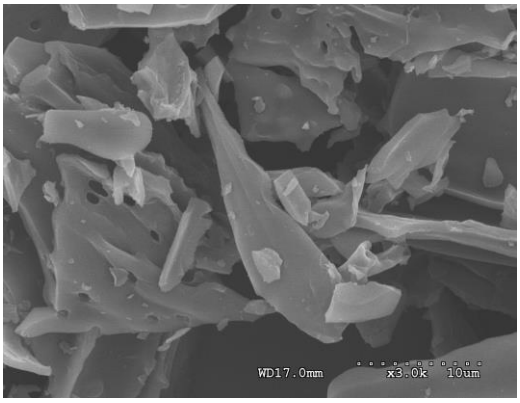
Figure1, I_N, MB_N and surface area of the plain carbon are much lower in comparison to the H_3PO_4 and $ZnCl_2$ activated carbons. This may be because the char (plain carbon) prepared from giant reed has not been activated. Hence, activation using suitable chemical agents highly increased the porosity of carbon. Among the activated carbons, $ZnCl_2$ AC showed higher Iodine number of 892 mg/g and surface area of 991 m^2/g whereas H_3PO_4 activated carbon showed high methylene blue number of 555 mg/g. It suggested that, $ZnCl_2$ activated carbon shows

high microporosity than that of H_3PO_4 activated Carbon. On the other hand, mesoporosity was higher in the H_3PO_4 activated carbon. These values are comparable to that of commercial AC indicating that both ACs are highly microporous and mesoporous.

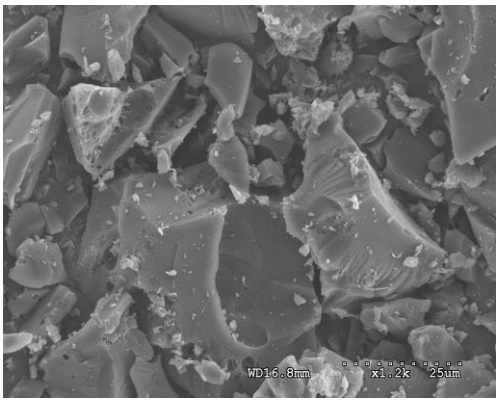
These differences in the development of porosity have been linked to the different activation mechanism for each activating agent. $ZnCl_2$ is a catalyst dehydration agent of the lignocellulosic structures, thus acting as template for the creation of microporosity. It means, the volume of micropores developed is similar to the volume of $ZnCl_2$ introduced into the particle which creates a uniform microporosity. For activation of H_3PO_4, the mechanisms of porosity development are different. In this case, the acid promotes dehydration, depolymerization, condensation and cross-linking reactions in the lignocellulosic precursor, forming phosphate ester linkage structures. The addition or insertion of the phosphate groups produces a dilation that, after removal of the acid, leaves the matrix in an expanded state with an accessible pore structure [15-16]. Therefore, $ZnCl_2$ develops both wide micropores and small mesopores and H_3PO_4 develops essentially microporosity with some larger mesopores and even macropores.

3.2 Scanning Electron Microscopy

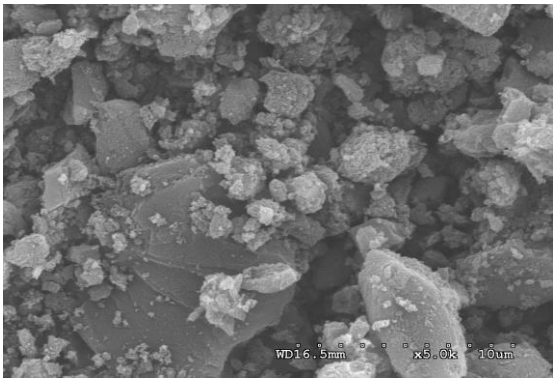
SEM is a very useful tool to examine the morphological characteristic of activated carbon. SEM micrographs of plain AC and ACs prepared by using different activating agents are presented in Figure 2.



(a) H_3PO_4 AC



(b) $ZnCl_2$ AC



(c) Plain carbon

Figure 2. SEM micrographs of plain AC and ACs prepared by using different activating agents

As shown in Figure 2, the surface of plain carbon was smooth with no pores. The surface of $ZnCl_2$ and H_3PO_4 activated carbon has some pores.

3.3 Comparison of Removal of Cr(VI) by Adsorption onto various ACs

Comparison on percentage removal of Cr(VI) ions by various ACs is presented in the Figure 3. The percentage removal was found to be higher in H3PO4 activated carbon compared to ZnCl2 activated carbon as well as commercial AC. High adsorption capacity of H3PO4 activated carbon for Cr (VI) ion may be attributed to its mesoporous structure.

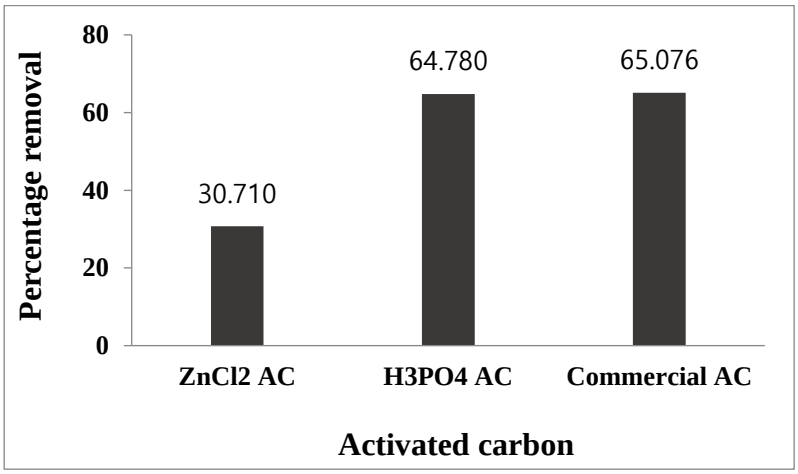


Figure 3. Comparison on percentage removal of Cr (VI) ions by various ACs

4. Conclusion

In this study, the Giant Reed AC has been prepared and utilized for the adsorption of Cr(VI) from aqueous solution. Iodine no. and methyelene blue no. indicates that, the $ZnCl_2$ activated carbon is micro-porous whereas H_3PO_4 activated carbon is meso-porous material in structure. SEM micrograph indicates that the both ACs show well developed pore structure on its external surface. The Cr(VI) adsorption capacity of the H_3PO_4 AC was comparable with commercial AC. Therefore, it is concluded that giant reed AC could be inexpensive and efficient adsorbent for Cr(VI) removal from water.

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