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Interaction of heavy metals with dehydrated carbon

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Abstract. Dehydrated carbon material was prepared from date palm leaflets via sulphuric acid treatment. The acid causes dehydration via the removal of water. In addition it causes oxidation to the dehydrated carbon surface. The carbon was tested for the removal of Pb^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Ag^{+}, Pd^{2+} and Hg^{2+} from aqueous solution in terms of different pH, time and concentrations and temperature. Optimum pH was found to be in the range of 3-5 for the metals under investigation. Sorption of Pb^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+} was found fast, reaching equilibrium within ~ 2 hr while the sorption of Ag^{+}, Pd^{2+} and Hg^{2+} (nitrate and chloride media) was slow and required ~80 hr to reach equilibrium. Activation energy, E_a, for the sorption of Pb^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+} was < 17 kJ/mol indicating a diffusion controlled ion exchange process, however, for Ag^{+}, Pd^{2+} and Hg^{2+} sorption, E_a was > 40 kJ/mol indicating a chemically controlled process. Equilibrium sorption capacity was much higher for Ag^{+}, Pd^{2+} and Hg^{2+} than for Pb^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+} with increased uptake, for both metals, by rising the temperature (25-45 ^{o}C). Scanning electron microscopy, X-ray diffraction and energy dispersive spectroscopy showed that Ag^{+} and Pd^{2+} were reduced to their respective elemental states. For Hg^{2+}, reduction took place to elemental mercury from nitrate media and to Hg_2Cl_2 from the chloride media. However, no reduction processes were involved in the sorption of Pb^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}.

Key words: heavy metals, sorption, reduction, dehydrated carbon

Introduction

During the past few years, there has been an increasing interest in the determination of concentrations, sources and fluxes of heavy metals in the environment. There is a widespread concern with the effects of technological advances on the chemical composition of the total environment including streams, lakes, oceans, atmosphere and soil systems. Existing physical and chemical technologies for the removal of heavy metals from wastewater including electro-coagulation, chemical precipitation, membrane filtration and reverse osmosis are either too expensive or not appropriate for the treatment of dilute solutions. Adsorption technologies provide a cheaper and effective option. In this paper, dehydrated carbon via sulfuric acid treatment was prepared from date palm leaflets, an abundant agricultural waste in Oman and the Gulf States and was investigated for the removal of Pb^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Ag^{+}, Pd^{2+} and Hg^{2+}. Dehydrated carbon showed different interaction behaviour for Ag^{+}, Pd^{2+} and Hg^{2+} compared with Pb^{2+}, Zn^{2+}, Cu^{2+} and Co^{2+}.

Materials and Methods

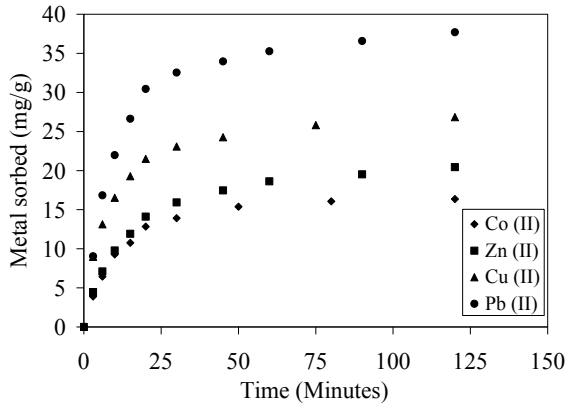
Clean date palm leaflets were chemically-carbonized as by mixing clean air-dried palm leaflets (20 g) with 80 ml sulfuric acid (13 M). The mixture was heated to 170 ± 2 ^{o}C in 20 min. with occasional stirring and the temperature was kept in that range of temperature for 25 minutes. After filtration and washing till free from the acid, the carbon was left at 120^{o}C in the oven till dryness. The carbon was characterized in terms of surface area, pHzpc, Boehm titration, FTIR, SEM and x-ray diffraction. Solutions of Pb^{2+}, Ag^{+} were prepared from their respective nitrate form, however Zn^{2+}, Cu^{2+}, Co^{2+}, Pd^{2+} were prepared from their respective chloride form. Hg^{2+} solutions were prepared in both nitrate and chloride forms.

Metals were analyzed using AA for Pb^{2+}, Zn^{2+}, Cu^{2+}, Co^{2+}, Ag^{+}, Pd^{2+} was analysed using spectrophoptometric iodide method (Bruzzoniti *et al*., 2003). Hg^{2+} was analysed using AA with hydride generation.

Results and Discussion

Sulfuric acid acts as a strong dehydrating and oxidizing agent, carbonizing cellulose and hemicelluloses by the removal of water. Under the carried out conditions of the sorbent preparation, carbonization (via dehydration) with partial oxidation took place to the carbohydrate part (cellulose and hemicelluloses) in addition to partial oxidation and fragmentation to the lignin components (Cox *et al.* 1999). FTIR showed that the dehydrated carbon possesses –COOH, -OH, C=C and other carbon oxygen species on the surface. Boehm titration showed that 1.28, 0.48 and 0.5 meq/g correpnoding to carboxyl, lactone and hydroxyl groups on the surface. pHzpc was 2.75. Surface area was measured using nitrogen sorption at 77 K was 44 m^2/g. such low surface area might be because of the abundant polar functional groups on the surface.

a)



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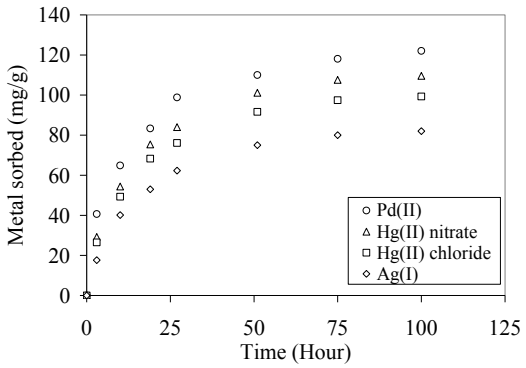

Fig. 1. Sorption kinetics of (A) Pb^{2+}, Cu^{2+}, Zn^{2+}, Co^{2+} and (b) Ag^{+}, Pb^{2+} and Hg^{2+} on dehydrated carbon at 25 ^{o}C.

Kinetic studies showed a peculiar behavior for those metals. Sorption of Pb^{2+}, Zn^{2+}, Cu^{2+} and Co^{2+} shows a much fast kinetics reaching equilibrium within ~2 hours, however, with less metal uptake. On the other hand, Ag^{+}, Pd^{2+} and Hg^{2+} shows a slow kinetics as equilibrium requires ~ 50 hours to be reached, with higher metal uptake than that for Pb^{2+}, Zn^{2+}, Cu^{2+} and Co^{2+} as presented in figure 1. Rising the temperature has shown increased sorption with data fitting pseudo second order model more than pseudo first order model. Ea was found to be in the less than 15 kJ/mol for the sorption of Pb^{2+}, Zn^{2+}, Cu^{2+} and Co^{2+}, however, Ea was > 40 kj/mol for the sorption of Ag^{+}, Pd^{2+} and Hg^{2+}.

Equilibrium studies showed that sorption of these metals at their respective optimum pH values showed a good fitting for the Langmuir model than the Freundlich model with much higher sorption capacities for the removal of , Ag^{+}, Pd^{2+} and Hg^{2+} than Pb^{2+}, Zn^{2+}, Cu^{2+} and Co^{2+}. Equilibrium pH was found to be less than initial pH indicating protons release in solution reflecting ion exchange processes. Scanning electron microscope analysis of metal loaded dehydrated carbon showed the presence pf metallic precipitates of Ag, Pd and Hg (from nitrate media) Hg_2Cl_2 crystals (from chloride media) from their respective solutions, Figure 2(a-d). X-ray diffraction confirmed the presence of metallic Ag, Pd and Hg_2Cl_2 crystals. Energy dispersive spectroscopy confirmed the presence of the metallic state of Hg from nitrate media. On the other hand, there was no change observed on metal loaded carbons by Pb^{2+}, Zn^{2+}, Cu^{2+} and Co^{2+} in SEM analysis or X-ray diffraction.

The presence of reduced forms (metallic such as Ag, Pd and Hg or Hg_2Cl_2 crystals) on dehydrated carbon surface reflects their reduction. At the same time, dehydrated carbon could not reduce Pb^{2+}, Zn^{2+}, Cu^{2+} and Co^{2+} to lower oxidation state and ion exchange was the dominating mechanism. This reduction property reflects also the slow kinetics, higher sorption capacity and higher activation energy for the sorption of Ag^{+}, Pd^{2+} and Hg^{2+}. Sorbent reuse studies showed that by acid stripping, the carbon can be reused for the sorption of b^{2+}, Zn^{2+}, Cu^{2+} and Co^{2+} efficiently, however for the other reducible metals, separation of the precipitated reduced forms of the metal cations is required.

Conclusion

Dehydrated carbon is capable of reducing Ag^{+}, Pb^{2+} and Hg^{2+} but not Pb^{2+}, Cu^{2+}, $Zn^{2+}$and Co^{2+} and this is reflect on the difference in their sorption behavior towards dehydrated carbon. The carbon seems promising in field work applications.

References

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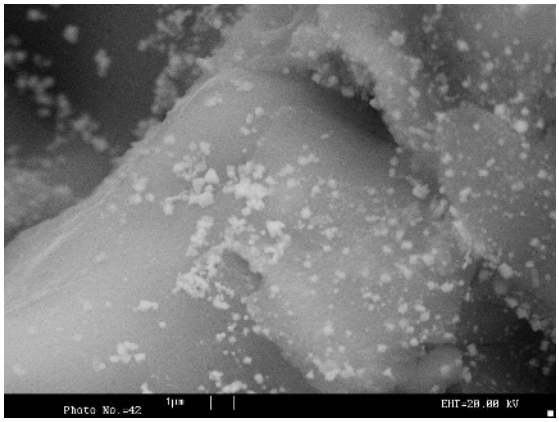
(a)



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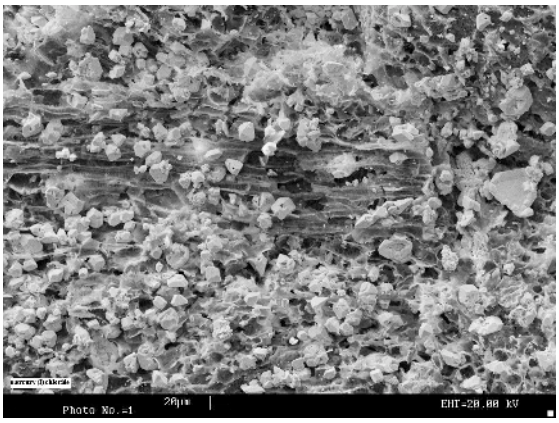

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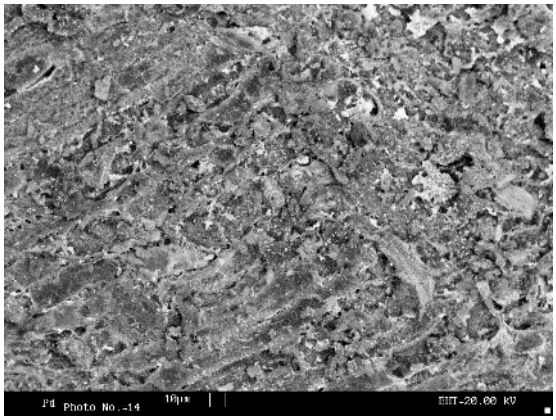

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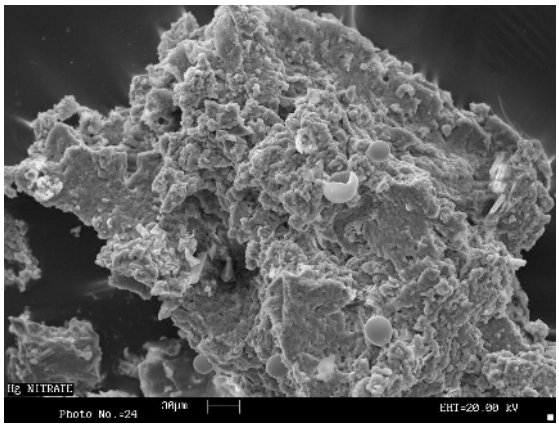

Fig. 2. SEM photographs of metal loaded dehydrated carbon: (a) Ag, (b) Pd, (c) Hg_2Cl_2 crystals and (d) mercury microdroplets