

Preparation and Modification of Activated Carbon from Oil-Palm Shell and its Adsorption Capacity through Speciation of Chromium

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Abstract

A preparation and modification of activated carbon from oil-palm shell has been investigated in this paper. A pretreatment method has been established to avoid partial fusion and swelling in the carbonization stage. Carbonization has been studied at different temperatures and the structure of the microporous chars has been characterized. Activated carbon has been prepared from steam gasification of chars obtained at 800 °C. This activation increases both total and narrow microporosity and develops a substantial mesoporosity. Activated carbon with different pore size distribution is impregnated with zirconium chloride and iron chloride salts to give impregnated carbon with different metals loading. The presence of active metal on an impregnated activated carbon surface greatly affects the adsorption affinity since some inorganic compounds will then be adsorbed preferentially.

Keywords: Oil-palm shell, carbonization, steam-activation, porosity.

Introduction

Pollution of heavy and toxic metals in the environment is now recognized as great concern. Among these metals, particular concern has been focused on arsenic (As), chromium (Cr), lead (Pb), mercury (Hg) and selenium (Se) which pose a particular hazard in public health and the environment and their accurate separation is now of increasing importance. In water analysis relying on the adsorption method, much effort has gone into determining transition and heavy metals present as cationic complexes where as anionic elements have received relatively little attention. Many researchers have tried to apply adsorption as a simple and cost effective method for concentrating trace levels metals in water. By contrast, relatively few information is available on the adsorption of specific inorganic compounds onto activated charcoal. Among the compounds of As, Cr, Hg, Pb and Se, the adsorption of mercury (II) compounds onto activated charcoal has been studied most. There are only few publications¹⁻³ dealing with the adsorption of arsenic, chromium, selenium and mercury species onto activated charcoal.

The presence of active metal such as zirconium (Zr) and iron (Fe) on an impregnated activated carbon

surface has greatly affected the adsorption affinity since some inorganic compounds will then be adsorbed preferentially. The present work reports modification and investigations of the adsorption of As, Cr, Pb, Hg and Se onto zirconium loaded activated carbon and describes the optimal conditions required for their preconcentration.

Material and Methods

Preparation of activated carbon: In the first step, palm shells were cleaned of loose fibers and traces of kernel and then ground, washed and dried at 100° C before sieving. As received, oil palm stones were crushed and sieved. Materials of grain size 1.4-2.0 mm were selected for use. These materials (agricultural solid wastage) appeared to be suitable materials for dense and high-grade activated carbons because of their inherent high solid density and high fixed carbon content but low ash content. The preparation of high grade activated carbon pyrolysis of the pretreated oil palm kernel was performed in a quartz tube horizontal reactor which was placed in a tube furnace (Thermolyne 21100).

The furnace has programmable temperature controls such as heating rate, pyrolysis temperature and retention time. About 100 g of raw materials was placed into the middle of the quartz tube which was seated at the center of the tube furnace. 100% water vapor with flow rate of 100 ml min⁻¹ was used as the inert gas flushing through the reactor right from the beginning of the pyrolysis process. The experiments were carried out from room temperature to 400°, 600° and 800°C for retention times of 1 and 2 h at each pyrolysis temperature and a heating rate of 40° C min⁻¹ was used.

Preparation of Zr-activated carbon: A fixed weight (in grams) of activated charcoal was put into zirconyl nitrate solution and the suspension was stirred with a magnetic stirrer at room temperature for a certain time. The resulting material (Zr-AC) was filtered off, washed with water until free of nitrate and air-dried.

The pH of the sample solution was adjusted to 9±0.2 with NH₃-NH₄Cl buffer solution and 1.0 ml of 0.1M FeCl₃ solution (about 5.6 mg Fe) was added. The precipitate that formed was allowed to coagulate for at least 20 min, after which 0.100 g of activated charcoal powder was added. The mixture was shaken and left to stand for a while before filtration. After filtration, the loaded filters were air-dried at room temperature overnight.

The filtrate was poured into a second polyethylene-leaching bottle and the pH of the sample solution was adjusted to 3.9 ± 0.2 with NaOH and HNO₃ solutions. Zr-AC (0.100g) was added to the sample and after stirring, the mixture was left to stand for a while before filtration. Loaded filters were air-dried at room temperature overnight. (Steps 1 and 2 were also performed in reverse order).

Results and Discussion

Quantitative separation of Cr (VI) and Cr (III) was possible in the pH range 3.5 to 9.0, where Cr (IV) was adsorbed onto Zr-AC almost quantitatively (>97.5 %) and the adsorption of Cr (III) was insignificant (less than 1.0 %) ³⁻⁶.

The adsorption of Cr (VI), on Zr-Ac in the present study: The adsorption behavior of dichromate ion, Cr₂O₇²⁻ was studied as a function of the pH of the sample solution and found to be similar to that of chromate ion. The adsorption of Cr (VI) onto Zr-AC occurred almost immediately. Increasing the sample volume from 100 mL to 500 mL had no effect on the amount of Cr (VI) adsorbed. When 0.100 g Zr-AC was used as adsorbent, the adsorption of Cr (VI) increased linearly up to $98.22 \mu\text{g L}^{-1}$ chromium concentration. ⁴

The slowdown in the adsorption at higher pH value (9.0 ± 0.2) meant that the adsorption capacity of Zr-AC had been reduced. One can see the adsorption capacity of Zr-AC was excellent in between pH range 3.8 ± 0.2 - 7.0 ± 0.2 as shown in figure 1. The adsorption was good (allowable) until the pH value was 8.0 but when the pH value was 9.0 ± 0.2 , the adsorption became slow and the capacity was $37.66 \mu\text{g L}^{-1}$. The amount of Zr-AC can be increased up to 0.3 g without any sample excitation problems in the EDXRF measurements due to the increasing thickness of sample on the filter and heavier matrix, but amounts greater than 0.2 g was difficult to handle for placing into cuff.

Co-precipitation of Cr (III) with Fe (OH)₃: Cr (III) was quantitatively collected on Fe(OH)₃ precipitate at pH 9.0 and the colloidal precipitate was bound to (AC) activated carbon (0.100g), both to facilitate the filtration of the precipitate and to achieve a sufficient and uniform sample for EDXRF determination. When the Fe (OH)₃ precipitate was allowed to coagulate for at least 20 min. before the addition of activated charcoal, the filtration rate was considerably enhanced.

The amount of coprecipitated Cr (III) increased linearly up to $100 \mu\text{g L}^{-1}$ chromium concentration, after which sample pH value increased slightly until 9.0 ± 0.2 . When the pH value was 3.0 ± 0.2 , the adsorption capacity was almost zero with the pH value at 9.0 ± 0.2 and the adsorption capacity was $98.32 \mu\text{g L}^{-1}$ as shown in figure 1 for Cr (one example). Under the conditions employed, Cr

(VI) was not collected by the Fe (OH)₃ precipitate. The adsorption capacity of Cr (VI) onto Zr-AC and Cr (III) onto activated carbon (AC) is shown in table 1.

Conclusion

In the preparation of high grade activated carbon, the pyrolysis results showed that it was feasible to prepare carbon with relatively high BET surface areas from oil palm stones with solid density and high fixed carbon contents which are favorable from the point of view of cost and environmental pollution control. The optimum conditions for pyrolysis were heating to a final temperature of 800 °C and holding at this temperature for 2 h, producing activated carbon with a maximum BET surface area of $762.365 \text{ m}^2 \text{ g}^{-1}$.

A procedure was developed for pre concentration, pH of 3-8 and 7-9 were found to be optimum for the selective sorption of Cr (VI) and Cr (III) on Zr-AC carbon and precipitate of Fe (OH)₃ on normal activated carbon respectively. Zr-AC carbon was found best adsorbent for higher oxidation state of above elements at broad pH range. The method developed is well suited for the separation of Cr (VI) and Cr (III) from each other and for the determinations using EDXRF. Its intrinsic solute adsorbing properties made this method as excellent adsorbent in the drinking water treatment plants. This activated carbon can also be used for the pre-concentration of chromium species in drinking water with 100 mL sample volume with a concentration factor of 10. In addition, Zr-AC is a potentially useful material for the removal of Cr (VI) from waste water solutions.

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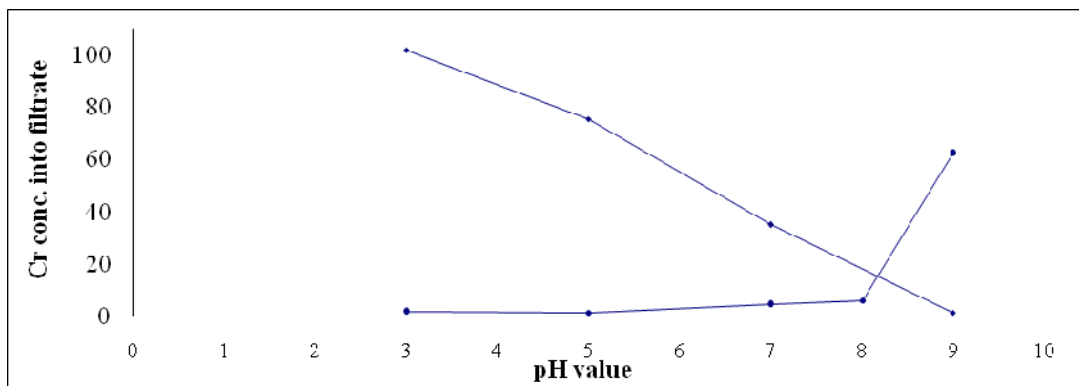


Figure 1: Adsorption -♦- Cr (III) and -●-Cr (VI) on AC and Zr-AC

Table 1
Adsorption Capacities of Activated Carbon (AC) and Modified Activated Carbon (Zr - AC) at different pH values

pH Value		3.0	5.0	7.0	8.0	9.0
Cr(III)	Conc. into filtrate (µg L ⁻¹)	101.75	75.34	35.01	17.98	1.68
	Adsorption onto AC %	0	24.66	64.99	82.02	98.32
Cr(VI)	Conc. into filtrate (µg L ⁻¹)	1.78	1.41	4.48	5.18	62.34
	Adsorption onto Zr-AC %	98.22	98.59	95.52	94.82	37.66

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