GERMANIUM RECOVERY FROM FLY ASHES BY ACTIVATED CARBONS

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1. Introduction

The combustion by-products of certain coals can provide a potential source of valuable elements that can be recovered. In most of the cases, the concentration level of the element makes its recovery non-viable, except for those cases in which the element has a high value and its recovery becomes economically attractive. The recovery method depends on several parameters, among them, the compounds formed by the element in the ashes, mineralogy of the by-product, etc.

Among the elements present in the combustion residues, Germanium is of special interest. In the last decades Germanium (Ge) has been considered as a valuable element. This element has many applications, principally in fibre optics communication networks, infrared vision systems and polymerisation catalysts. These end uses represented 85% of worldwide germanium consumption for 2000 [1]. In addition, certain Ge compounds have a low mammalian toxicity, but they have a marked activity against certain bacteria, which makes them of interest as chemotherapeutic agents, as well as, their health promotion functions. Therefore, they are often used in medicines and nutriments [2]. Consequently, Ge has now established important uses in a wide number of specialist fields.

Applying specific leaching conditions, Ge can be extracted from the fly ashes to aqueous media. Thus, this work focuses in the recovery of Ge from aqueous solutions. Concentration and separation of germanium from aqueous solutions are of technological significance. Many methods for the removal of inorganic ions from aqueous solutions have been reported, i.e. ion exchange, chemical precipitation, solvent extraction, electrochemical methods and adsorption [3]. It has been shown that adsorption on activated carbons can be an effective and versatile method for inorganic elements removal under specific conditions due to their excellent properties, but they are not effective for concentrating them.

In general, adsorption by activated carbon is not so effective to remove metals and inorganic pollutants as for removal of organic compounds, due to its hydrophobic behaviour. Consequently, the use of an organic compound as a ligand in order to form a Ge chelate [5-8], which could be more easily adsorbed on activated carbon, has been studied. Therefore, knowledge of Ge chemistry and complex formation is a valuable information for the development of a separation method.

The ligand chosen in this study was catechol since it is widely known that Ge can form complexes with oxygen-containing organic ligands, in particular with carboxylic acids and hydroxy acids [9,10]. Figure 1 presents the catechol structure and a schematic representation of the Ge-catechol complex. Catechol was selected as a ligand for several reasons: (i) selectivity for Ge to form a chelate, (ii) high molecular weight of the formed chelate, what can improve the adsorption process, and (iii) catechol is a common and cheap reagent. The reaction between Ge and catechol for the formation of the complex is:

$$Ge(OH)_4^0 + 3H_2Cat^0 \leftrightarrow Ge(Cat)_3^{2-} + 2H^+ + 4H_2O \quad [11]$$
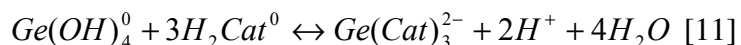
Figure 1. Structures of the catechol and Ge-catechol

The main focus of this study is to evaluate the use of activated carbon for Ge recovery from diluted aqueous solution combing complex formation of Ge (by a specific ligand) and its adsorption on the activated carbon. The influence of experimental conditions in the adsorption process, such as contact time, carbon dosage and the effect of ionic strength have been studied. Also, desorption process has been analyzed using HCl to elute the adsorbed metal, based on the destruction of the Ge complex in acid media.
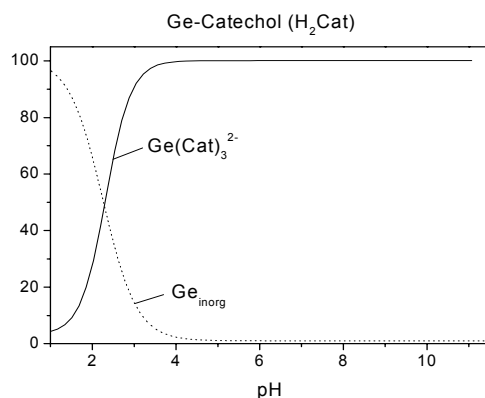

2. Experimental

2.1. Adsorbent characterization

Two powdered commercially available activated carbons (AC) were used in this research (SA-30 from Westvaco Co. and a carbon black T-10153). The nomenclature used is SA for sample SA-30 and T for T-10153. The porous texture characterization was assessed by nitrogen (77 K) and CO_2 (273 K) adsorption, in an Autosorb-6 apparatus (by Quantachrome Corp.). Specific surface area and micropore volume were calculated by fitting nitrogen adsorption data to BET and Dubinin-Radushkievich equation, respectively. Narrow micropore volume was determinated by fitting Dubinin-Radushkievich equation to CO_2 isotherm data. The characterization was completed by temperature programmed desorption experiments in order to get information on the surface chemistry of the carbon materials. A complete characterization is essential to be able to define the properties of the selected materials and to predict their performance in the removal of Ge in solution.

2.2. Reagents

Figure 2 shows the speciation diagram of the germanium complex as a function of pH at 25 °C [11].

Working solution of Ge-catechol (50 mg/L) was prepared by dissolving the appropriate weight of high-purity GeO_2 (>99.99%, Fluka) in ultra-pure water and also the appropriate weight of catechol in NaOH media. The pH of the solution was measured and adjusted with HCl until pH=10.

Figure 2. Speciation diagram curve of Ge-catechol as a function of pH at 25°C [11].

2.3. Method

The Ge-complex adsorption experiments were obtained from closed batch measurements. Each Ge complex solution (25 ml) with an initial concentration of 50 mg/l were placed in a glass flask and a known amount of activated carbon was added to each flask. The flasks were covered to avoid evaporation and placed on a shaker at constant shaking speed. All the experiments were carried out at a constant temperature (23ºC). After the equilibrium period, the AC was filtered and the Ge concentration in the residual solution was determined by ICP technique. The initial pH of the solution during adsorption process was 10, a pH value where the complex is stable (see Figure 2). The final pH was always over 4.

The desorption process is based on the destruction of the complex formed between germanium and the organic ligand at pH values lower than 4 (see Figure 1, speciation diagram of Ge-catechol as a function of pH at 25ºC). The activated carbon used after the adsorption process was dried overnight and put into contact with 25 ml of HCl 1M (pH < 1) in covered flasks to avoid evaporation. The solution was shaken at constant speed for 1 hour at room temperature. After this period, the carbon was filtered and the concentration of Ge was measured by ICP.

3. Results and Discussion

3.1. Characterization of textural properties and surface chemistry of the AC.

Figure 3 shows the N_2 adsorption isotherms for the selected materials. It can be observed that the N_2 isotherms exhibit an important adsorption at low relative pressures (i.e., below 0.1) and a wide knee and an important slope at higher relative pressures. The knee of the isotherms is specially wide in these activated carbons which, together with the slope at relative pressures higher than 0.2, indicate the presence of mesoporosity. Therefore, these samples show a wide pore size distribution (i.e., both micro and mesoporosity), which is an important issue for adsorption in solution. Table 1 compares the results of the characterization of the activated carbons.

Table 1. Porous texture characterization results of commercial activated carbons.

Sample	S_{BET} (m^2/g)	$V_{DR}(N_2)$ (cc/g)	$V_{DR}(CO_2)$ (cc/g)
SA	1645	0.74	0.44
T	1649	0.63	0.41

The characterisation of the surface chemistry of the commercial activated carbons was done through temperature programmed desorption experiments (TPD), The experiments were done with a simultaneous TG-DSC equipment coupled to a mass spectrometer (TA Instruments), what permits to follow, simultaneously, changes in weight and gas evolution.

Table 2. Quantification of TPD for activated carbons.

| Sample	$\mu molCO_2$/g	$\mu molCO$/g	$\mu molH_2O$/g
SA	532	1560	2660
T	351	450	849
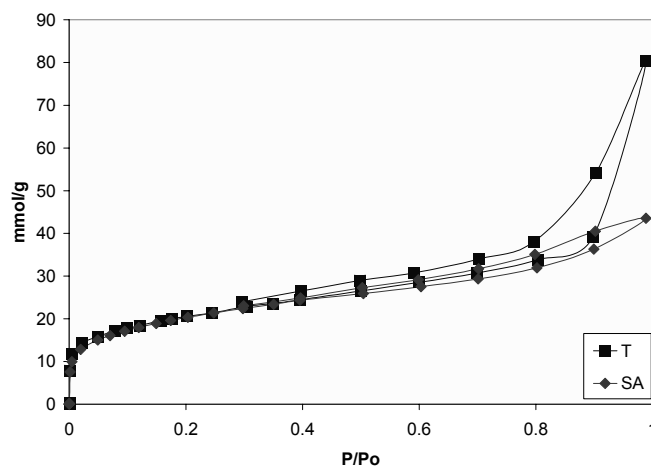
Figure 3. N_2 adsorption isotherms of the different commercial activated carbons

3.2. Effect of contact time on Ge adsorption.

The effect of contact time was evaluated for the commercial activated carbons (SA and T). Figure 4 presents this effect on the adsorption of Ge-catechol in order to analyse the adsorption percentage of Ge. In these experiments, a known volume of Ge-complex solution (25 ml) with a carbon dosage of 0.1g was kept in a shaker for a period of time from 0 to 420 minutes.

As it can be observed in Figure 4, the amount of Ge adsorbed increases with time and reaches the equilibrium quickly. However, we found important differences, in the kinetics of adsorption and the amount adsorbed at equilibrium for both commercial activated carbons. The adsorption capacity of T sample is about two fold larger than SA sample. Thus, the amount adsorbed in activated carbon T was 35 mg(Ge)/l after 1 hour (70% adsorption), whereas for SA activated carbon it was 19 mg(Ge)/l after the same period of time (almost 40% adsorption). It must be remarked that although both carbon materials present similar specific surface area, their adsorption capacities are quite different, indicating that the surface chemistry plays an important role since the complex is charged. SA activated carbon contains more oxygen surface groups and this could be responsible for its lower adsorption (see Table 2). Therefore, from the obtained results it can be concluded that: (i) the proposed idea of complexing Ge to adsorb it on an activated carbon is effective, and (ii) the adsorption percentage depends on the properties of carbon material used in the adsorption process, i.e., porosity, particle size, and surface chemistry.

More work is in progress in order to evaluate the importance of porosity (in terms of surface area and pore size distribution) and surface chemistry, in terms of nature of surface functional groups, on the adsorption capacity and the kinetics of adsorption.
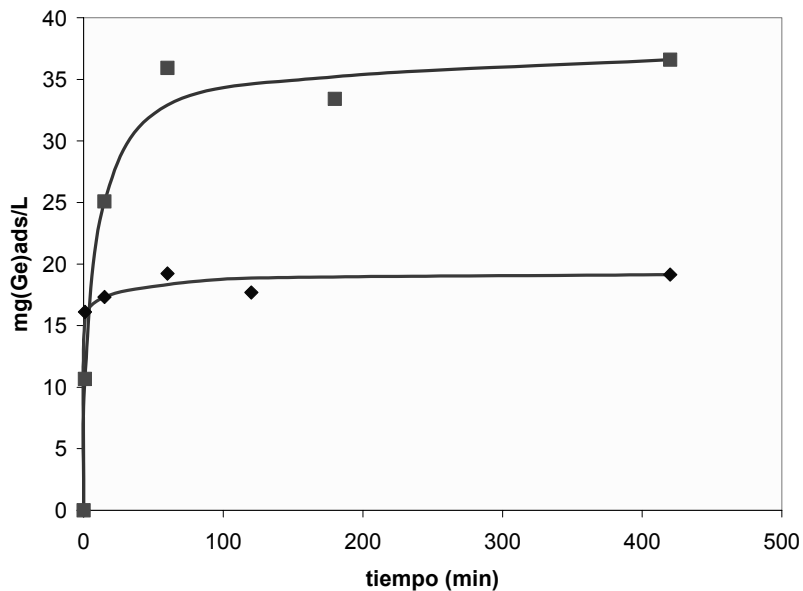

Figure 4. Effect of contact time on the adsorption process of Ge-catechol.

3.3. Effect of carbon dosage.

Another important parameter that must be evaluated in the adsorption process of Ge from diluted aqueous solution is the AC dosage. Figure 5 shows the removal of the Ge complex as a function of AC dosage by T and SA samples. The amount of AC was varied from 0.025 to 0.2 g. The same experimental conditions as those explained above were used. The contact time was fixed to 2 hours.

The amount of Ge adsorbed increases with the weight of carbon in both cases, and the optimum quantity of AC was fixed at 0.1 g for T activated carbon and at 0.2 g for SA activated carbon, as it can be observed in Figure 5. In both cases, they adsorb similar amount of Ge at high carbon dosages. This result indicates that the porosity is not being used with the same efficiency by the two AC, probably, due to their different surface chemistry
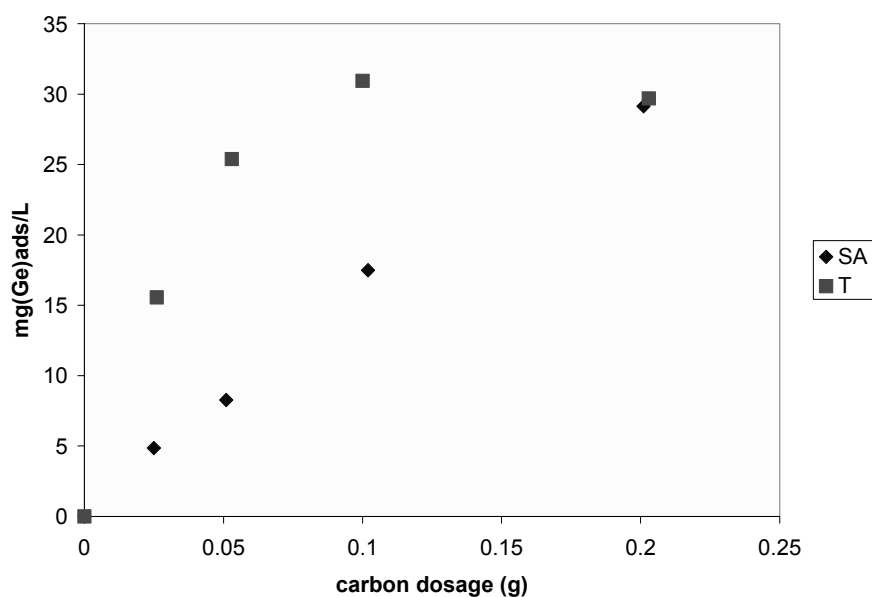

Figure 5. Effect of carbon dosage on the adsorption capacity of Ge-catechol.

3.4. Effect of ionic strength on the adsorption process

Adsorption process of metal ions from aqueous solutions by activated carbons is governed by electrostatic and non-electrostatic interactions [12]. Among the factors that can control both interactions, the ionic strength has been studied modifying it on both activated carbons. Figure 6 shows the variation of the adsorption of Ge-complex on both activated carbons as a function of ionic strength at pH 10. The results indicate that the initial electrostatic interactions between the Ge-complex $[Ge(Cat)_3]^{2-}$ and the carbon surface are repulsive and a gradual increase in the ionic strength provokes a progressive increase in the Ge adsorption. In both cases, when the ionic strength is zero the Ge adsorbed is the lowest due to the repulsive interactions. The addition of

NaCl reduces the repulsion effect between the complex and the surface of the activated carbon by a screening effect [12]. This effect is more pronounced for SA sample. This is a consequence of the higher acidic character of AC SA compared to sample T. A more acidic character introduces a higher repulsive interactions at the initial pH used in the adsorption conditions.
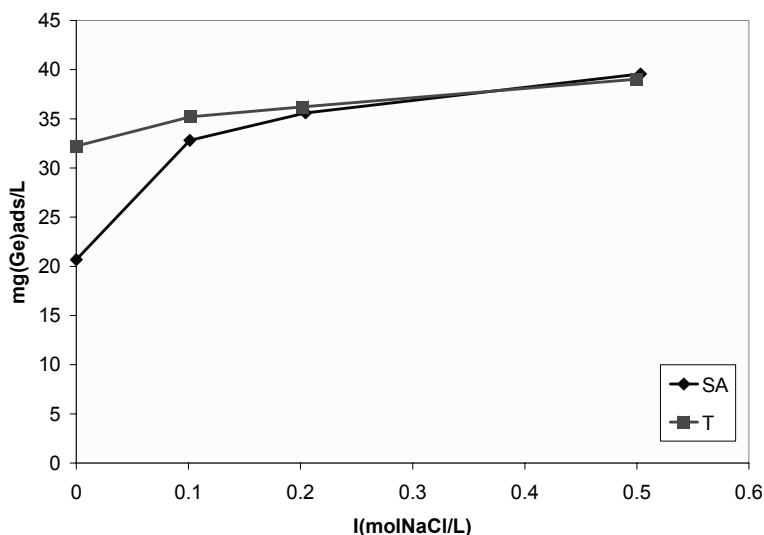
Figure 6. Effect of ionic strength on the adsorption process of Ge complex.

3.5. Evaluation of desorption process

In order to prove the efficiency of the desorption process, the spent AC T was dried and put into contact with 25 ml of HCl 1M (pH < 1). Table 3 shows the concentration (mg/l) of Ge adsorbed and Ge in solution after the desorption process.

Table 3. Ge concentration after the adsorption process at different times and after the desorption process with 25 ml of HCl 1M.

	Ge adsorbed (mg/l)	Ge desorbed (mg/l)
1min	11	12
15 min	25	22
60 min	36	33
180 min	33	30
420 min	37	34

These results show the efficiency of the proposed desorption process using the variation of pH in order to elute the Ge-complex. Almost 100% of the adsorbed Ge is desorbed. These results show the possibility of applying the proposed method in order to concentrate Ge from a diluted solution, reducing the volume of HCl in the desorption process. Preliminary studies have shown that it is possible to obtain 700 mg(Ge)/L from 50 mg(Ge)/L solutions.

4. Conclusions

The main conclusions obtained to the moment can be summarised as follows: (i) the use of AC for the adsorption of germanium complex from a diluted aqueous solutions is a simple, rapid and efficient method, (ii) by the appropriate selection of the experimental variables, activated carbons can adsorb up to a 70% of the initial Ge, (iii) the ionic strength has an important effect on the adsorption process; the addition of NaCl reduces the repulsive interaction between Ge-chelate and the surface of the activated carbon, (iv) surface area seems to control the retention of the Ge-complex, whenever the influence of the surface chemistry is compensated, and (v) the obtained results for the desorption process also show that the proposed method is highly efficient method (100% desorption), that allows to concentrate Ge from the initial solution.

5. Acknowledgements

6. References

[1] Editor in Chief R. Bruce King. Enclyclopedia of Inorganic Chemistry. Volume 3 1283-1319.

[2] Gao HW, Liu WG. Spectrophotometric Investigation of Germanium Complex Solution with o-Chlorophenylfluorone and Determination of Trace Amounts of Germanium. Bull. Korean Chem. Soc. 2000; (21) 11:1090-1094

[3] Demirbas E, Kobya M, Öncel S, Sencan S. Removal of Ni(II) from aqueous solution by adsorption onto hazelnut shell activated carbon: equilibrium studies. Bioresource Technology 2002; 84:291-293.

[5] Murakami K, Olamoto Y, Kumamara T. J. Flow Inject. Anal. 1992; 9: 195.

[6] de Pena Y P, Gallego M, Valcarcel M. J. Anal. Atom. Spectrom. 1994;41:817.

[7] Santelli R E, Gallego M, Valcarcel M. Talanta 1994;41:817.

[8] Xingguang S, Meijia W, Yihua Z, Jiahua Z, Hanqi Z, Qinhan J. Semi-online preconcentration of Cd, Mn and Pb on activated carbon for GFASS. Talanta 2003; 59:989-997.

[9] Matis K.A, Stalidis G.A, Zoumboulis A.I. Flotation of Germanium from Dilute Solutions. Separation Science and Technology 1988; 23:347-362.

[10] Pokrovski G.S, Martin F, Hazemann J.L, Schott J. An X-ray absorption fine structure spectroscopy study of germnium-organic ligand complexes in aqueous solution. Chemical Geology 2000; 163:151-165.

[11] Pokrovski G.S, Schott J. Experimental study of the complexation of silicon and germanium with aqueous organic species: Implications for germanium and silicon transport and Ge/Si ratio in natural waters. Geochimica at Cosmochimica Acta 1998; 62:3413-3428.

[12] López-Ramón V, Moreno-Castilla C, Rivera-Utrilla J, Radovic L.R. Ionic strength effects in aqueous phase adsorption of metal ions on activated carbons. Carbon 2002 41:2009-2025.