

Effect of oxygen functional groups on mercury retention in activated carbons

Sotiropoulou R.E.P.^{1,*}, Serafidou M.², Skodras G.¹

¹University of Western Macedonia, Bakola & Sialvera, 50132 Kozani, Greece

²Aristotle University of Thessaloniki, Administration Building, University Campus, 541 24 Thessaloniki, Greece

*corresponding author: e-mail: rsotiropoulou@uowm.gr

Abstract

Two commercial activated carbons (F400 and RWE) were tested for their Hg⁰ retention capacity, in order to elucidate shortcomings that still exist, with respect to the oxygen functional groups. The number and the nature of oxygen containing functional groups were altered by heating under H₂ at 1100°C or treatment with HNO₃. The activated carbons tested were found suitable for mercury retention and the observed differences are attributed to their diversified characteristics (surface chemistry and pore structure). Acidic activated carbons promptly adsorb Hg⁰, since it behaves as a Lewis basis. When oxygen groups were almost completely removed, by H₂ thermal treatment, the Hg⁰ retention ability became practically zero. Acid treatment increased both the number and the acidic oxygen groups; resulting in increased Hg⁰ retention. The Langmuir isotherm equation was used to describe the adsorption (physisorption and chemisorption) of Hg⁰, occurring in activated carbons. The fitting curve of the Langmuir equation and the correlation coefficient R² indicate quite fair linear approximation (R² = 0.9773). Reflecting the spontaneous nature of the adsorption reaction, the Gibbs free energy change calculated is negative (-23.5 kJ/mol and -30.9 kJ/mol, for the RWE and F400 respectively).

Keywords: mercury, oxygen groups, active surface area, Langmuir equation

1. Introduction

Mercury, given its highly-volatile character, toxicity, bioaccumulation and persistence to oxidation, has been acknowledged as a pollutant of global interest, listed among the 10 most harmful chemicals for public health by the World Health Organization has listed mercury among the 10 most harmful chemicals for public health (WHO, 2010). The global concerns about it are clearly depicted by the “Minamata convention on mercury”, which is aimed at limiting the release of Hg into the environment (EU, 2017). The poor performance of conventional ‘end-of-pipe’ devices (e.g. wet scrubbers, bag-filters and electrostatic precipitators) necessitated the development of advanced adsorbents, which are particularly well suited for the removal of harmful pollutants from the flue gas.

Activated carbons (AC) promptly mitigate mercury and other trace elements emissions, due to its large surface

area and various active functional groups located on the edges of the graphene layers. The surface of such carbons is heterogeneous, it consists of the faces of graphene sheets and of edges of such layers. The edge sites are much more reactive than the atoms in the interior of the graphene sheets. The chemisorbed foreign elements (O, S, N, Cl etc.), and in particular oxygen, are predominantly located on the edges. Chemical and morphological heterogeneities of carbon sorbents play important roles in gas-phase adsorption. The specific chemical complexes and topological structures of carbon that favor or impede elemental mercury uptake are not fully understood.

In this work, the impact of oxygen functional groups on elemental mercury binding on AC surface sites was investigated. Towards that, two well-known, commercial activated carbons (raw or treated) were tested for their Hg retention ability.

2. Methodology

Two commercial activated carbons (F400 and RWE) were tested for their Hg⁰ retention capacity, in order to elucidate shortcomings that still exist, with respect to the oxygen functional groups. The number and the nature of oxygen containing functional groups were altered by employing thermal (non-isothermal (10°C/min) heating up to 1100°C, under H₂ flow (55 cm³/min)) and acid mild treatment (treatment with 1 N HNO₃, for 3 hrs, and subsequent washing with distillate water and drying) methods that leave the pore structure of the activated carbons unchanged. Basic-acid titrations based on Boehm method (Boehm H.P., 2002) were performed, in order to determine the number and nature of oxygen groups presented in carbon matrix, of both raw and modified activated carbons. The pH of the surface of both raw and modified activated carbons was also measured (Boehm, 2002; Skodras, et al., 2007).

Mercury adsorption tests were performed in a bench-scale adsorption unit comprising a fixed-bed activated carbon reactor and a mercury permeation device (VICI Metronics Inc, Santa Clara, CA) as a source of elemental mercury Hg⁰. Tests were performed at 50°C under 200 cm³/min nitrogen flow, while, mercury inlet concentration varied to account for the adsorption isotherms. The Langmuir isotherm equation was used to describe both physisorption and chemisorption of Hg⁰, occurring in activated carbons.

3. Results and Discussion

Both activated carbons tested were found suitable for Hg retention (Figure 1). The F400 was proven much more efficient due to its acidic nature (Table 1).

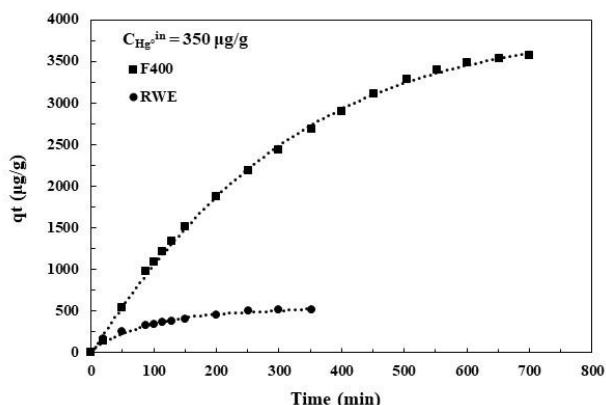


Figure 1. Cumulative Hg⁰ in F400 and RWE activated carbons, at 50°C

A clear decrease of the mercury retention ability was observed at higher pH values (Figure 2), since Hg⁰ behaves as a Lewis basis, promptly reacting with acidic active sites such as oxygen functional groups.

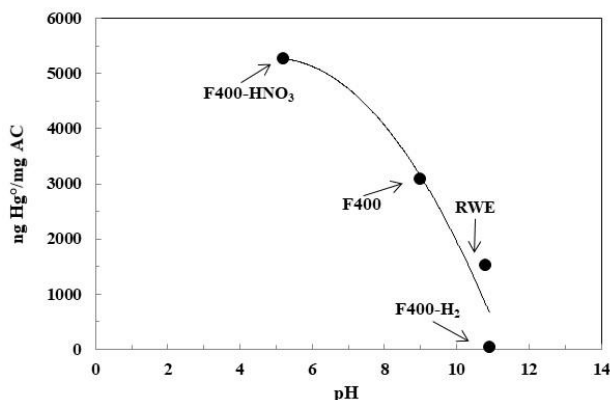


Figure 2. Variation total mercury hold up with pH values of the activated carbon

It should be noted that although F400-H₂ and RWE activated carbons present similar pH values, Table 1, RWE presents much higher Hg adsorption capacity due to the presence of oxygen functional groups that have been completely removed by the H₂-treatment of the activated carbon (Table 1).

Table 1. Surface acidic and basic groups of the activated carbons tested

Functional group (mmol/100 g)	Activated carbon			
	RWE	F400	F400-H ₂	F400-HNO ₃
Carboxyls	1.70	0.50	0.15	36.30
Lactones	0.05	1.85	0.85	9.40
Phenols	0.45	0.10	0.80	0.80
Carbonyls	9.15	9.15	2.50	85.00
Total acidic	11.35	11.60	4.30	131.50
Total basic	12.30	11.70	25.50	30.50
All groups	23.70	23.30	29.80	162.00

The Langmuir isotherm equation effectively described both physisorption and chemisorption of Hg⁰, occurring

in RWE and F400, Figure 3. The Gibbs free energy change (ΔG) of adsorption reaction was calculated -23,5 kJ/mol and -30,9 kJ/mol, for the RWE and F400 respectively, indicating that mercury adsorption is mainly physical enhanced by chemisorption. The ΔG values are negative, revealing the spontaneous nature of the adsorption reaction.

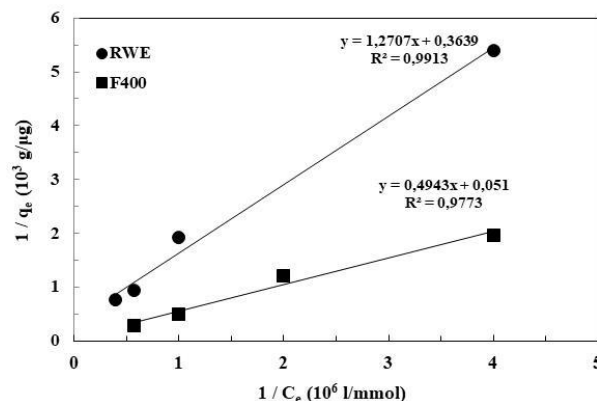


Figure 3. Fitting of Langmuir isotherm equation

4. Conclusions

Oxygen functional groups have been investigated for their promotion of effective elemental mercury binding on AC surface sites. Lactone and carbonyl functional groups yield the highest mercury binding energies and Hg hold up is improved via chemisorptions, since it is oxidized to Hg²⁺, while, phenols and carbonyls facilitate physisorption. When oxygen groups were almost completely removed, by H₂ thermal treatment, the Hg retention ability became practically zero, despite that the pore structure of the activated carbon remained unaltered. Therefore, it is the presence of oxygen functional groups that controls Hg adsorption and the pore structure actually affects only intraparticle mass transfer. The Langmuir isotherm equation effectively described both physisorption and chemisorption of Hg⁰, occurring in RWE and F400 activated carbons. The Gibbs free energy change calculated was negative to -23.5 kJ/mol ($R^2 = 0.9913$) and -30.9 kJ/mol ($R^2 = 0.9773$), for the RWE and F400 respectively.

References

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