

Títol del treball:

Adsorption of heavy metals with new graphene-based materials

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Abstract

This study evaluates the performance of four different graphene-based materials as adsorbents for the removal of heavy metals (Cu^{2+} , Cd^{2+} and CrO_4^{2-}) from aqueous solutions. The adsorbents were firstly characterized by scanning electron microscopy, thermogravimetric analysis and porosimetry. The effect on the adsorption of different parameters, such as contact time, pH of the aqueous solution, adsorbent concentration and initial metal concentration, is studied here. The maximum removal percentage for Cu^{2+} and Cd^{2+} are 98.92% and 94.88% respectively, when an initial concentration of 5 mg/L at pH=6 and 2 g/L of adsorbent were used. In the case of CrO_4^{2-} an adsorbed percentage of 67.93% was obtained with 10 g/L of adsorbent, an initial concentration of was 5 mg/L and pH=2. Competitive experiments for Cu^{2+} and Cd^{2+} were performed, the results showed no significant decrease in the adsorption of the metals compared to the single metal experiments.

The adsorption processes were characterized by applying different adsorption isotherm models (Langmuir, Freundlich and Temkin) to the experimental data. The Langmuir isotherm model fitted well with the experimental data obtained for Cu^{2+} , Cd^{2+} and CrO_4^{2-} for most of the four adsorbents, resulting in maximum adsorption values (q_{max}) of between 2.6 to 5.4 mg/g for Cu^{2+} and Cd^{2+} . This q_{max} was a lower (~0.5 mg/g) for CrO_4^{2-} .

The results showed that these graphene-based adsorbents can be used to effectively remove Cu^{2+} , Cd^{2+} and CrO_4^{2-} from aqueous solutions, having single metal or multi-metal composition as there is not competition for the adsorbent in the experimental conditions tested.

Key words: adsorption, Cu^{2+} , Cd^{2+} , CrO_4^{2-} , graphene oxide, adsorption isotherms

Resum

Aquest estudi avalua el funcionament de quatre grafens com a adsorbents per a l'eliminació de metalls pesants (Cu^{2+} , Cd^{2+} i CrO_4^{2-}) de solucions aquoses. Primerament, els adsorbents van ser caracteritzats amb microscòpia electrònica de rastreig, anàlisi termogravimètrica i porosimetria. L'efecte en l'adsorció de diferents paràmetres, com el temps de contacte, el pH de les solucions aquoses, la concentració d'adsorbent o la concentració inicial de metall, han estat estudiats. Els percentatges màxims d'adsorció per Cu^{2+} i Cd^{2+} són 98,92% i 94,88% respectivament, quan es van utilitzar una concentració inicial de 5 mg/L, pH=6 i 2 g/L d'adsorbent. En el cas del CrO_4^{2-} es va obtenir un percentatge d'adsorció d'un 67,93% amb 10 g/L d'adsorbent, una concentració inicial de metall de 5 mg/L i pH=2. Es van dur a terme experiments competitius per Cu^{2+} i Cd^{2+} , els resultats van mostrar que no hi havia una disminució significativa de l'adsorció en comparació amb l'obtinguda amb els experiments amb un sol metall.

Els processos d'adsorció es van caracteritzar aplicant diferents models d'isotermes d'adsorció (Langmuir, Freundlich i Temkin) a les dades experimentals. Les dades experimentals obtingudes per Cu^{2+} , Cd^{2+} i CrO_4^{2-} s'ajustaven bé al model de Langmuir per la majoria dels quatre adsorbents, donant valors màxims d'adsorció (q_{max}) d'entre 2,6 a 5,4 mg/g per Cu^{2+} i Cd^{2+} . En el cas del CrO_4^{2-} , el valor q_{max} era més baix (~0,5 mg/g).

Els resultats mostren que els grafens estudiats poden ser utilitzats de forma efectiva en l'eliminació de Cu^{2+} , Cd^{2+} i CrO_4^{2-} de solucions aquoses. Atès que no hi ha competència entre els metalls es poden aplicar a solucions multi-metall o d'un sol metall en les condicions assajades.

Paraules clau: adsorció, Cu^{2+} , Cd^{2+} , CrO_4^{2-} , òxid de grafè, isotermes d'adsorció

Resumen

Este estudio evalúa el funcionamiento de cuatro grafenos en su uso como adsorbentes para la eliminación de metales pesados (Cu^{2+} , Cd^{2+} y CrO_4^{2-}) de soluciones acuosas. En primer lugar, se caracterizaron los adsorbentes por microscopia electrónica de rastreo, análisis termogravimétrico i porosimetría. En segundo lugar, se ha estudiado el efecto de diferentes parámetros, como el tiempo de contacto, el pH de las soluciones acuosas, la concentración de adsorbente o la concentración de metal inicial, en la adsorción. Los porcentajes máximos de adsorción para Cu^{2+} y Cd^{2+} son 98,92% y 94,88% respectivamente, cuando se usa una concentración inicial de 5 mg/L a pH=6 y 2 g/L de adsorbente. En el caso del CrO_4^{2-} se obtuvo un porcentaje de adsorción de un 67,93% con 10 g/L de adsorbente, una concentración inicial de 5 mg/L y pH=2. Se realizaron experimentos con soluciones de Cu^{2+} y Cd^{2+} para estudiar su competitividad hacia el adsorbente, los resultados mostraron que no había una disminución significativa de la adsorción en comparación con los experimentos con un solo metal.

Los procesos de adsorción se caracterizaron aplicando diferentes modelos de isotermas de adsorción (Langmuir, Freundlich y Temkin) a los datos experimentales. Los datos experimentales obtenidos para Cu^{2+} , Cd^{2+} y CrO_4^{2-} se ajustaban bien al modelo de isoterma de Langmuir para la mayoría de los cuatro adsorbentes, obteniéndose valores máximos de adsorción (q_{max}) de entre 2,6 y 5,4 mg/g para Cu^{2+} i Cd^{2+} . Este valor q_{max} era inferior ($\sim 0,5$ mg/g) para CrO_4^{2-} .

Los resultados muestran que estos adsorbentes pueden ser utilizados de forma efectiva en la eliminación de Cu^{2+} , Cd^{2+} y CrO_4^{2-} de soluciones acuosas. Pudiéndose utilizar tanto con soluciones que contengan un único metal como multimetálico ya que no compiten por el adsorbente en las condiciones experimentales utilizadas.

Palabras clave: adsorción, Cu^{2+} , Cd^{2+} , CrO_4^{2-} , óxido de grafeno, isoterma de adsorción

Introduction

Heavy metals

The presence of heavy metals in water courses due to the discharge of industrial wastewater constitutes one of the most serious pollution problems. Given that these metals are non-degradable and most of them are toxic, they can affect the quality of water supply and cause many problems on aquatic life. Even at low concentrations, these elements can be accumulated through the food chain and affect animals, plant life, and therefore human health (Benzaoui, Selatnia, & Djabali, 2018). Among these hazardous wastes, there is particular concern in treatment of water containing zinc, copper, nickel, mercury, cadmium, lead and chromium (Cao & Li, 2014). This is the case of wastewaters from electroplating operations that contain relatively high concentrations of zinc, copper, nickel and chromium. Chromium exists in two stable oxidation states Cr^{3+} and Cr^{6+} , which is known to be more toxic than Cr^{3+} . Because of the high metal concentrations in electroplating effluents, biological wastewater treatments cannot be applied and alternative treatments are required (Martín-Lara, Blázquez, Trujillo, Pérez, & Calero, 2014). The discharge of Cr^{6+} to surface water is regulated to 0.05 mg/L, for copper is 3 mg/L and for cadmium 0.5 mg/L, according to the DECRET 130/2003 of the Catalonia Government, whereas total chromium is regulated to be discharged at 3 mg/L (Generalitat de Catalunya, 2003).

Although being essential for human health, copper can be very harmful above specified concentrations limits, causing anemia, kidney damage, stomach intestinal distress, coma, and eventual death (Kandah, Al-Rub, & Al-Dabaybeh, 2004). Long-term exposure to cadmium can cause damage to the kidneys, liver, bone, and blood (Hasan et al., 2006). Chromium (VI) compounds are highly toxic because of their remarkable carcinogenic, teratogenic and mutagenic effects to human and other living organisms (Cohen, Kargacin, Klein, & Costa, 1993).

Metal removing by adsorption

In order to achieve the metal concentration limits established by the legislation, a large number of methods, including reverse osmosis, solvent extraction, reduction and precipitation, ion exchange and adsorption have been used for the removal of heavy metals from water effluents. Among these methods, adsorption method is one of the most effective choices (Leng, Guo, Su, Yi, & Xing, 2012).

There are two types of adsorption: physical, in which the increase in the adsorbate concentration at the interface is due to non-specific van der Waals forces; and chemical caused by chemical reactions between the adsorbate and the adsorbent which create covalent or ionic bonds (Gupta et al., 2015). The adsorption process depends on many factors such as temperature, pH of the solution, metal concentrations, contact time, particle size, temperature, nature of the adsorbate and adsorbent, etc.

Nowadays, adsorption is considered as an efficient and low-cost technique for removing noxious heavy metal ions from wastewater effluents. This process is flexible in design and operation and allows for producing high-quality treated effluents. Among the different sorbent materials, activated carbons are the most widely used for the adsorption of heavy metal due to their large surface area, high adsorption capacity, porous structure and high internal surface area. The main drawbacks are their high initial and regeneration costs. The search for alternatives to activated carbon is of concern in heavy metals remediation and it has been focused in two possible alternatives: the use of low cost sorbents such as agricultural wastes, industrial by products and wastes and natural substances, and the development of carbon-based sorbents such as carbon nanotubes and graphene-based sorbents (Fu & Wang, 2011).

Graphene oxides

Graphene, a single atomic layer of sp^2 carbon atoms, has attracted tremendous scientific attentions on account of its exceptional properties, such as extraordinary electronic and mechanical properties. It has enormous applications in sensors, batteries, nanoelectronics, hydrogen storage and nanocomposites (Leng et al., 2012).

The hexagonal arrays of carbon atoms in graphene sheets are ideal for strong interactions with other molecules. However, graphene is insoluble and hard to disperse in all solvents due to strong van der Waals interactions that can hamper sorption of organic compounds or metal ions. Therefore, the functionalization of graphene sheets can be important for their future applications (Georgakilas et al., 2012). The large theoretical surface area provided the excellent adsorption capacity of graphene. Due to this property, many investigations have been carried on utilizing graphene as an adsorbent to remove contaminants from aqueous solution (Zhao, Li, & Wang, 2011). Several studies have been conducted, for example, under acidic conditions, the adsorption of Cu^{2+} onto three carbonaceous materials (graphene oxide, multi-walled carbon nano-tubes and activated carbon) was estimated, and graphene oxide showed higher adsorption efficiency than the other two carbonaceous materials (Ren, Li, Tan, & Wang, 2013).

Moreover, the large-scale production of functionalized graphene at low cost should result in good adsorbents for water purification. The graphene oxides studied in this project were synthesized by Prof. Pavel Pazdera from the Masaryk University of Brno (Czech Republic). These materials were synthesized under conditions that were not revealed by the fabricant due to IPR protection. Four different graphenes were received and taken into study. Their references were 227A, 97D, GO-I and GO-II.

Methodology

Reagents and instruments

A stock solution of 100 mg/L of each metal (Cu^{2+} , Cd^{2+} and CrO_4^{2-}) was prepared by adding the appropriate amounts of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ and K_2CrO_4 (Panreac, Barcelona, Spain) in ultra-pure water. All the solid substances and adsorbents were weighted with an analytical balance (COBOS precision, Spain). Experimental solutions of the desired initial concentration were prepared by dilution of the stock one. Calibration solutions of the different metals were obtained by dilution of a 1000 mg/L standard solution (SPEX CertiPrep, United Kingdom) of each metal. The pH of the solution was adjusted to the desired value by adding different amounts of HNO_3 0.1M (Panreac, Barcelona, Spain). The metal concentration in solution was determined using an inductively-coupled plasma emission spectrometer (VARIAN, Liberty series ICP-AES).

Characterization of the adsorbents

- **Scanning electron microscopy (SEM) and surface microanalysis**

The morphology of the adsorbents was observed by a scanning electron microscope (Model ZEISS DSM 960A). Samples were examined at a magnification range of 200x to 3000x. The SEM was equipped with an energy-dispersive X-ray (EDX) spectrometer Burker Nano XFlash Detector 5010 to determine the composition of the surface of the adsorbents.

- **Thermogravimetric analysis (TGA)**

Thermogravimetric analysis was performed to determine the stability and the processes that happen when the adsorbents are submitted to high temperatures by using a METTLER TOLEDO TGA/DSC 1.

- **BET Surface area and porosimetry**

The BET surface area and porosimetry was only performed for GO-I due to the lack of sufficient quantities of 97D and 227A. The sample was analysed by Dr. Rafel Prohens from the Polymorphism and Calorimetry Unit (Scientific and Technological Centers, University of Barcelona).

Batch experiments

- **Effect of contact time**

The equilibrium time was determined by adding 0.04 g of adsorbent per 20 mL of the experimental solution for Cu^{2+} and Cd^{2+} . In the case of CrO_4^{2-} , the amount of adsorbent was 0.2 g for 20 mL of solution. In all the cases the initial concentration of metal was 5 mg/L.

- **Effect of the pH of the aqueous solution**

To determine the optimum pH of metal solution, experiments were carried out in solutions of different pH (2, 4 and 6). In the case of Cu^{2+} , the graphene used was 97D while for CrO_4^{2-} the adsorbent used was GO-I. These adsorbents were chosen due to their high affinity for the respective metals.

- **Effect of the adsorbent concentration**

Different amounts of adsorbent were studied by adding the quantity to be tested to 20 mL of a metal solution containing 5 mg/L of Cu^{2+} at pH=6, and the same concentration of CrO_4^{2-} at pH=2, and shaking them until equilibrium was attained. In the case of Cu^{2+} , the graphene used was 97D while for CrO_4^{2-} the adsorbent used was GO-I.

- **Effect of the initial metal concentration**

Separate tests at different initial metal concentrations (5, 7.5 and 10 mg/L) were performed by adding 0.04 g of graphene to 20 mL of single-metal solutions of Cu^{2+} and Cd^{2+} , and 0.2 g of graphene to the solutions of CrO_4^{2-} .

- **Competitive adsorption of Cu^{2+} and Cd^{2+}**

Competition experiments were only performed for ions Cu^{2+} and Cd^{2+} using 0.04 g of one of the adsorbents (97D) and 20 mL of metal solution containing 5 mg/L of each metal at pH=6.

Results and discussion

Characterization of the adsorbents

The characterization of the adsorbents can provide important information to understand its behaviour in the adsorption process.

- **Scanning electron microscopy (SEM) and surface microanalysis**

Fig. 1, 2, 3 and 4 show SEM images and surface composition, determined by EDX, of each adsorbent. It can be seen that the composition of all the adsorbents is relatively similar, being basically composed of carbon, with percentages higher than 90%, and oxygen, with percentages between 4-8%. These results are logic as the adsorbents are graphene oxides. The only exception is the adsorbent GO-I (Fig. 3), where a remarkable percentage of tungsten (4.34%) was determined, this element may be a residue from the synthesis process. This fact explains the metallic appearance of this adsorbent in comparison to the other three adsorbents, which look more carbonaceous.

The SEM images also enable to determine the particle size for each adsorbent. The images show irregularly shaped particles of the different graphenes. For 227A an average diameter of 60.12 μm is calculated. Adsorbent 97D presents an average diameter of 15.38 μm . In the case of GO-I, it has an average diameter of 70.86 μm . Finally, GO-II particles present an average diameter of 4.54 μm .

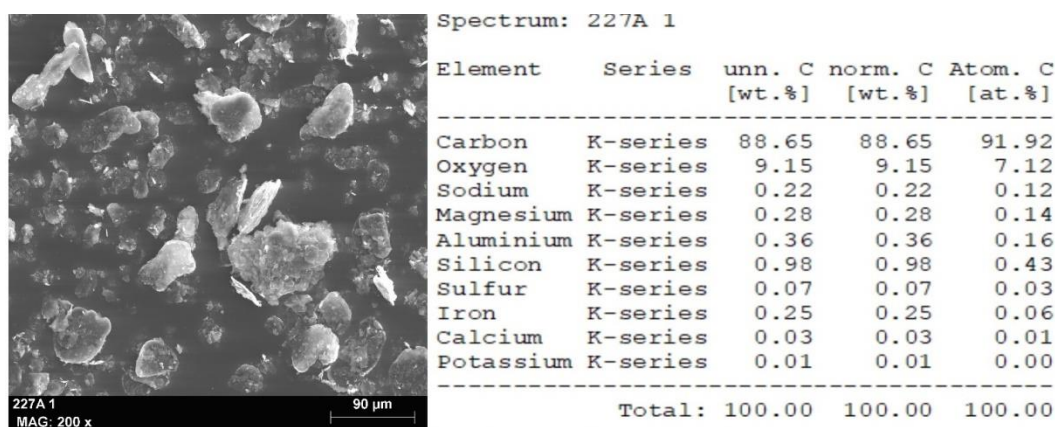


Fig. 1 SEM image and component microanalysis of 227A.

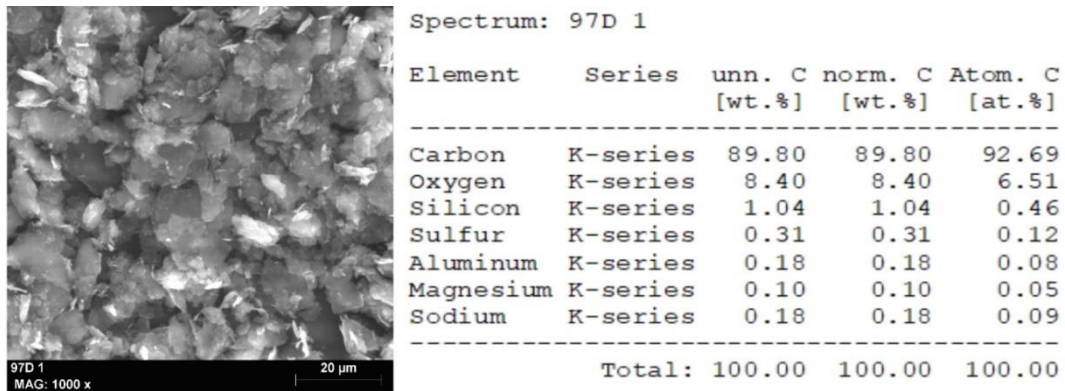


Fig. 2 SEM image and component microanalysis of 97D.

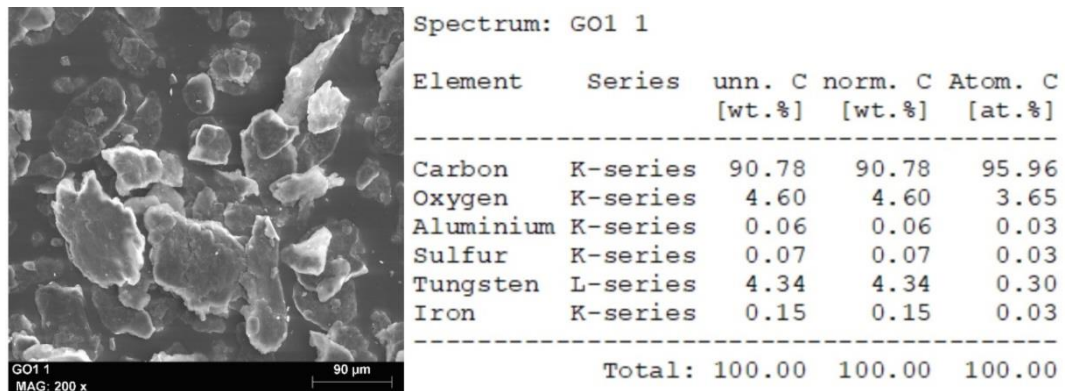


Fig. 3 SEM image and component microanalysis of GO-I.

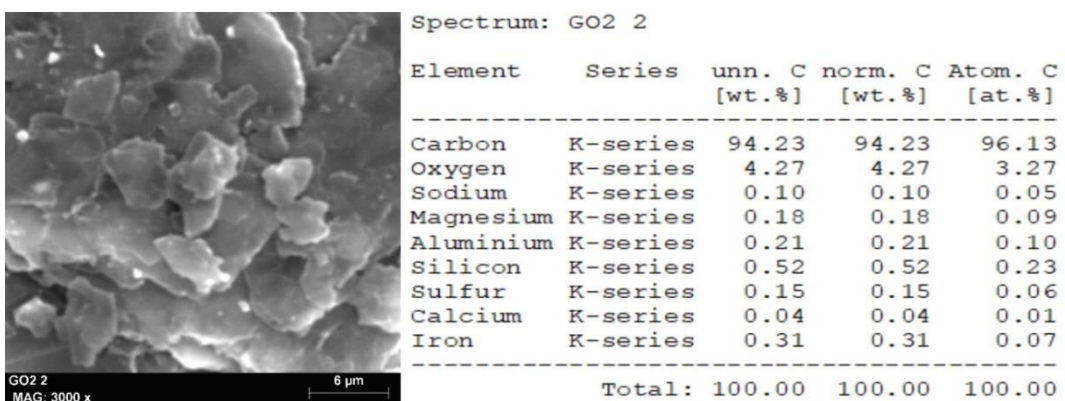


Fig. 4 SEM image and component microanalysis of GO-II.

- **Thermogravimetric analysis (TGA)**

Fig. 5 and **6** show the thermogravimetric analysis of two of the adsorbents, GO-I and 97D. The first one (**Fig. 5**) was chosen as a general representation of the other two graphenes studied here (227A and GO-II) and the second one (**Fig. 6**) was chosen because it presents a differential characteristic. In general, a loss of weight at low or moderate temperatures (up to 150°C) corresponds to the loss of volatile components in the system such as water, organic solvents of low molecular weight or absorbed gases. At temperatures between 150-250°C can be detected the loss of components of low molecular weight as additives, water of crystallization or even first decomposition products at low temperatures. At temperatures above 225-250°C normally begins thermal degradation and at temperatures above 500°C, the carbonization of hydrocarbon compounds is produced. It can be seen that 97D is stable and does not suffer decomposition until temperatures of approximately 600°C. However, in the case of GO-I, and the rest of the graphenes (results are not presented here), it suffers a decomposition process starting at a temperature of approximately 200°C. This fact may be due to the decomposition of a functional group that taking into account the results obtained in the EDX analysis is composed of C and O. It has been reported that the exothermic peak at 200-250°C (presented on the DTA curve for the GO-I sample) was related to decomposition of epoxy and carboxyl groups (Georgakilas et al., 2012).

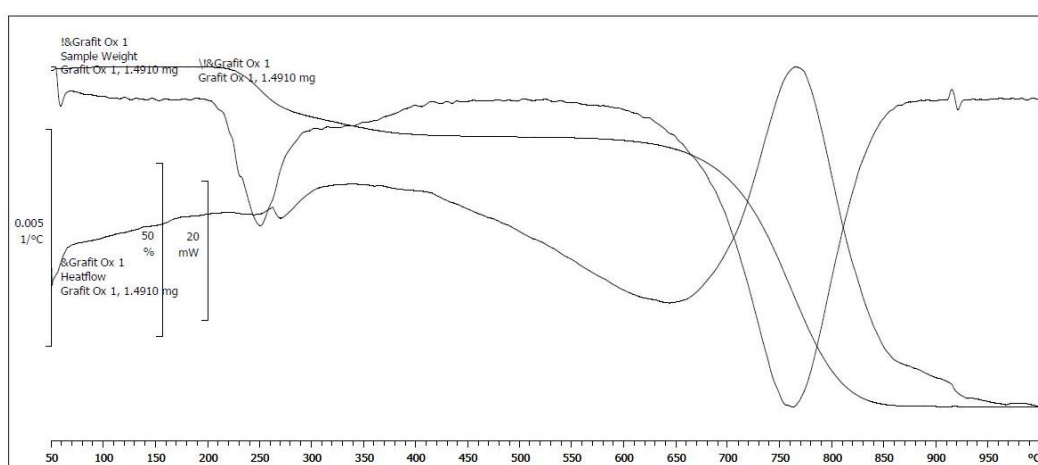


Fig. 5 Thermogravimetric analysis of GO-I.

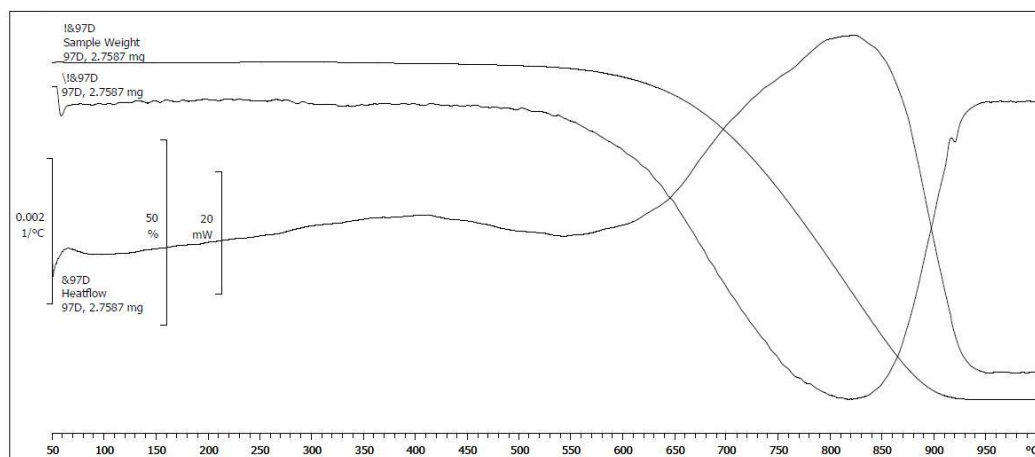


Fig. 6 Thermogravimetric analysis of 97D.

- **BET Surface area and porosimetry**

Surface area and porosity are two properties of an adsorbent that can impact their performance. In this case these parameters have been studied for GO-I. The results show a BET surface area of $14.23 \text{ m}^2/\text{g}$ and an average pore width of 196.71 \AA . The surface area is lower than those reported for different graphene oxides; however the values depend on the synthesis method used. Although the theoretical specific surface area of graphene is $2630 \text{ m}^2/\text{g}$, the typical experimental values of the specific surface area ranges from ~ 100 to $\sim 1000 \text{ m}^2/\text{g}$ (Dai, Wang, Ma, & Wu, 2015). Moreover, the pore size of the adsorbent also strongly depends on the synthesis method and especially of the length of time spent in the oxidizing of the solution.

Batch experiments

- **Effect of contact time**

Adsorption equilibrium is established when an adsorbate containing phase has been contacted with the adsorbent for sufficient time. The percentage of adsorbed metal is calculated as follows:

$$\%adsorbed = \frac{C_0 - C_e}{C_0} \cdot 100 \quad \text{Eq. 1}$$

Where:

C_0 : initial concentration (mg/L)

C_e : equilibrium concentration (mg/L)

The time needed for each metal and adsorbent to achieve equilibrium depends on the metal and adsorbent concentrations as well as of their chemical properties.

In the case of Cu^{2+} and Cd^{2+} , it can be seen in **Fig. 7** and **8** that with an amount of sorbent of 2 g/L and an initial concentration of 5 mg/L, the equilibrium is reached in 1 hour for three out of the four adsorbents. Only when the adsorbent 97D was used, a time of 3 hours was needed to attain the equilibrium at the same conditions. In the case of CrO_4^{2-} adsorption (**Fig. 9**), an equilibrium time of 3 hours was required when an adsorbent concentration of 10 g/L at pH=2 was used.

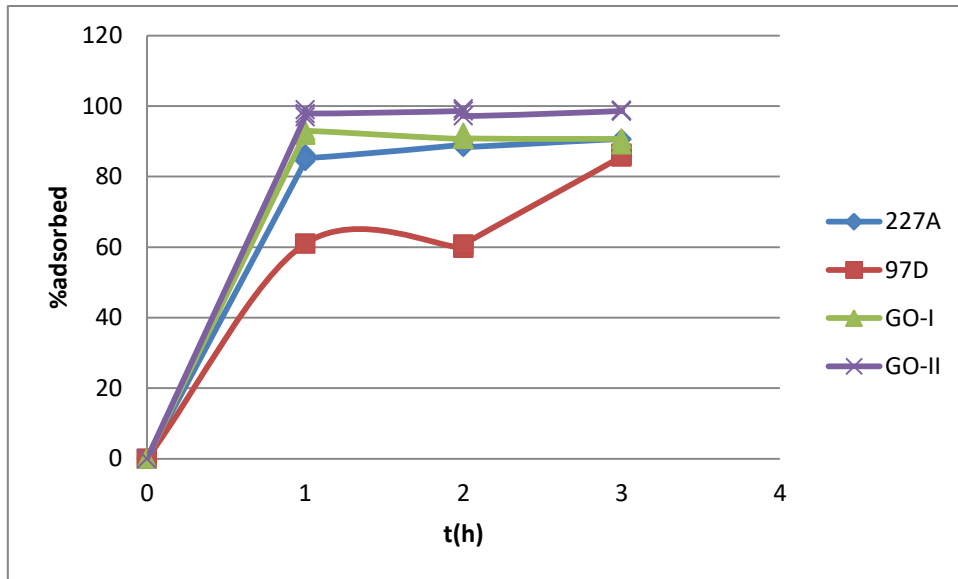


Fig. 7 Effect of contact time on the adsorption of Cu^{2+} for each graphene. Adsorbent concentration= 2 g/L, initial Cu^{2+} concentration= 5 mg/L at pH=6. (n=3).

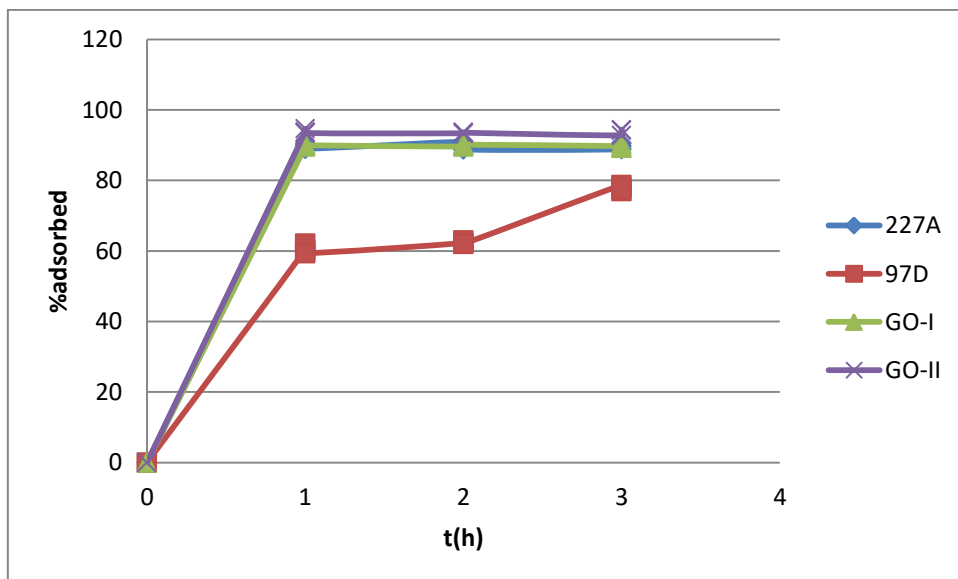


Fig. 8 Effect of contact time on the adsorption of Cd^{2+} for each graphene. Adsorbent concentration= 2 g/L, initial Cd^{2+} concentration= 5 mg/L at pH=6. (n=3).

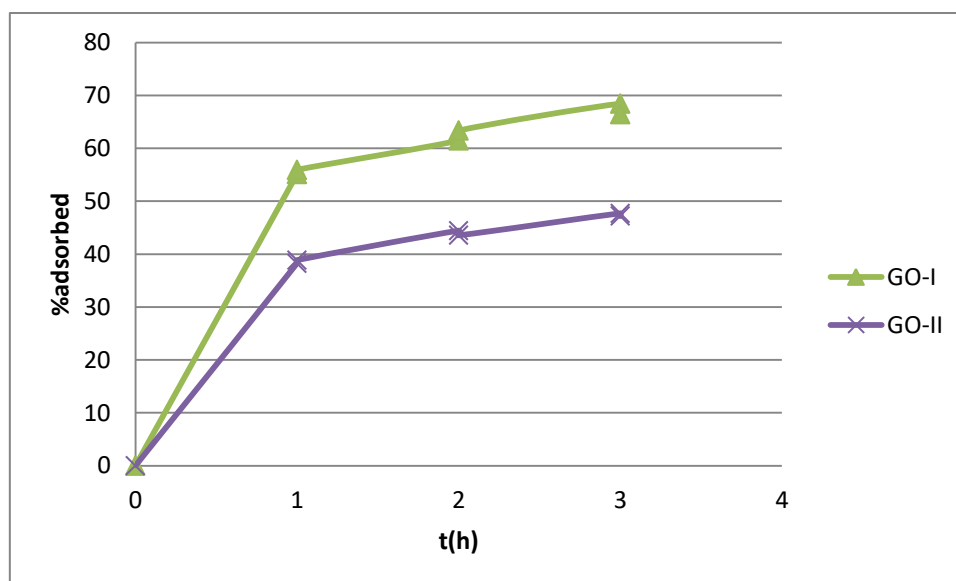


Fig. 9 Effect of contact time on the adsorption of CrO_4^{2-} for each graphene tested. Adsorbent concentration= 10 g/L, initial CrO_4^{2-} concentration= 5 mg/L at pH=2. (n=3).

- **Effect of the pH of the aqueous solution**

The pH of metal ion solution can have an important effect on the adsorption efficiency as the functional groups of the adsorbent can be protonated at low pH. Moreover, the metal ion can be hydrolysed at pHs>5-6 depending on the metal ion.

As can be seen in **Fig. 11**, the percentage of adsorbed metal for Cu^{2+} increases when the pH increases. The adsorption of Cu^{2+} is pH dependent, and the removal efficiency increases when the pH increases. These results are explained by the competition between Cu^{2+} and H_3O^+ for adsorption sites on the adsorbent. At low pH levels, an excess H_3O^+ competes with Cu^{2+} , resulting in a low level of adsorbed Cu^{2+} . When the pH increases, these functional groups are deprotonated and are hence available for Cu^{2+} (Mi et al., 2012). In the case of Cd^{2+} , the same trend was expected to be observed, assuming that both divalent ions have the same behaviour.

On the contrary, in the case of CrO_4^{2-} , the adsorption percentage decreased as the pH is increased from 2 to 6 (**Fig. 11**). At pH=2, the predominant form of Cr^{6+} is its protonated form, HCrO_4^- (**Fig. 10**) (Anatoly, 2011). This species can electrostatically

interact with the protonated groups of the sorbent that are positively charged at low pHs leading to a bigger adsorption at low pHs.

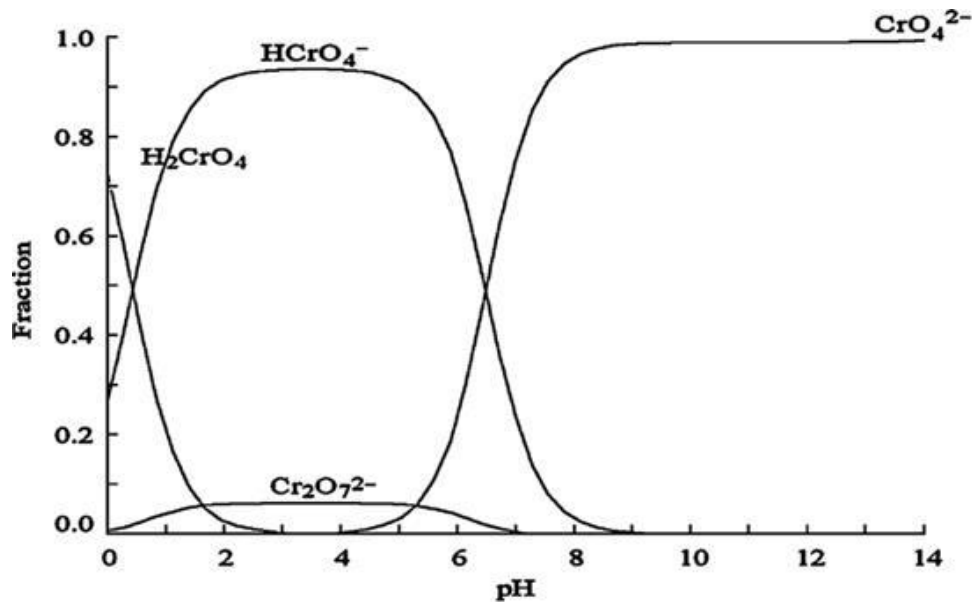


Fig. 10 Speciation diagram of Cr⁶⁺.

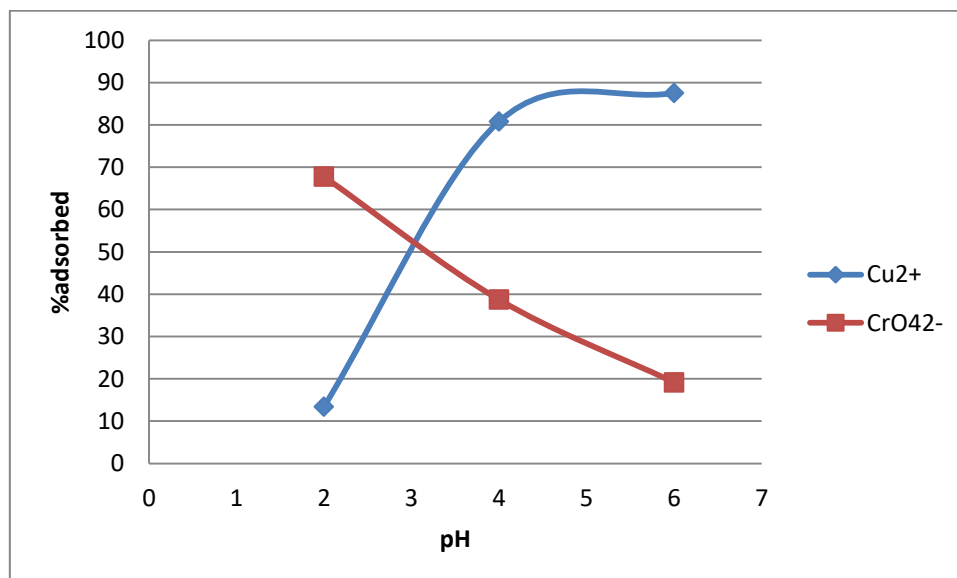


Fig. 11 Effect of pH of the aqueous solution on the adsorption of Cu²⁺ and CrO₄²⁻. For Cu²⁺, the graphene 97D was used (2 g/L), 5 mg/L of Cu²⁺ at pH=6. For CrO₄²⁻, sorbent GO-I was used (10 g/L), 5 mg/L of CrO₄²⁻ at pH=2. Equilibrium time: 3h. (n=3).

- **Effect of the adsorbent concentration**

The amount of sorbent used in the batch experiments has an effect on the efficiency of the metal adsorption process.

As can be seen in **Fig. 12**, the adsorption percentage of Cu^{2+} increased when the adsorbent concentration increased from 1 to 2 g/L. However, it showed a decrease when the amount was increased to 3 g/L. This fact can be caused by an aggregation of the sorbent which avoided the interaction of the functional groups of the adsorbent surface with the metal ions. For Cd^{2+} , the results were assumed to be the same as for Cu^{2+} as they both are divalent ions.

In the case of CrO_4^{2-} , the amount of adsorbent had to be risen to 10 g/L of adsorbent due to a poor adsorption when working with low amounts.

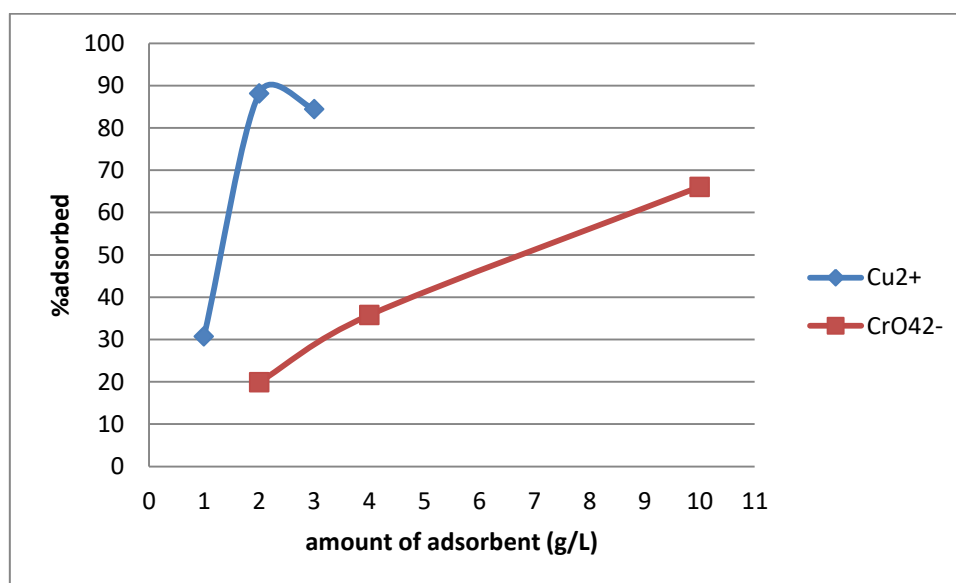


Fig. 12 Effect of the adsorbent concentration on the adsorption of Cu^{2+} and CrO_4^{2-} . For Cu^{2+} , the graphene 97D was used, 5 mg/L of Cu^{2+} at pH=6. For CrO_4^{2-} , sorbent GO-I was used, 5 mg/L of CrO_4^{2-} at pH=2. Equilibrium time: 3h. (n=3).

- **Effect of the initial metal concentration**

For each metal and each adsorbent, it was studied how the initial concentration of the solutions affected the adsorption processes.

The results presented in **Fig. 13**, **14** and **15** show that the percentage of adsorption decreases when the initial metal concentration increased. These results can be explained by the lack of free sites on the surface of the graphene when more metal ions were present in the solutions. As can be seen, the highest removal percentages were obtained at the lowest initial concentration (5 mg/L) tested for all the metals and adsorbents. Moreover, no significant differences were observed between the graphenes 227A, GO-I and GO-II. However, in the case of 97D, the results are lower in all the experiments although a higher length of time ($t=3$) was required to achieve the equilibrium. These results can be explained, by the differences observed in the thermogravimetric analysis between 97D and the rest of adsorbents (**Fig. 5** and **6**), showing that epoxy or carbonyl group are presented in all the adsorbents except in 97D.

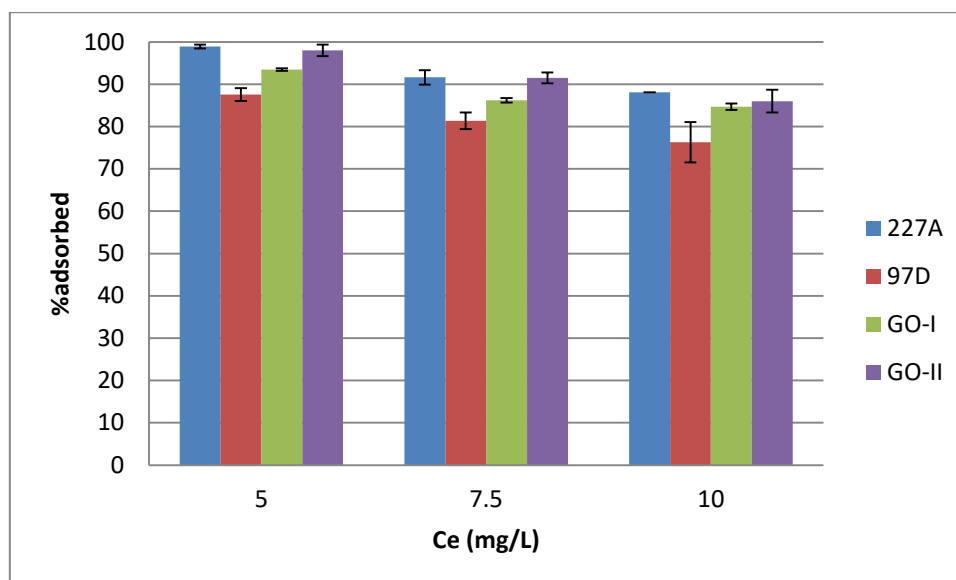


Fig. 13 Effect of the Cu^{2+} initial concentration on its adsorption for each graphene. Adsorbent concentration= 2 g/L at pH=6, $t=1\text{h}$, except for 97D $t=3\text{h}$. ($n=3$).

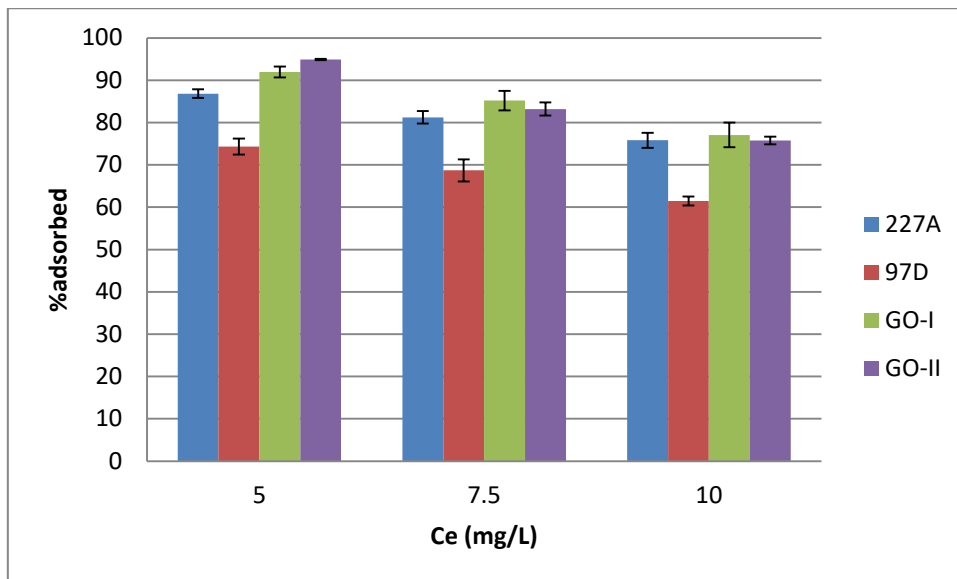


Fig. 14 Effect of Cd²⁺ initial concentration on its adsorption for each adsorbent. Adsorbent concentration= 2 g/L at pH=6, t=1h, except for 97D t=3h. (n=3).

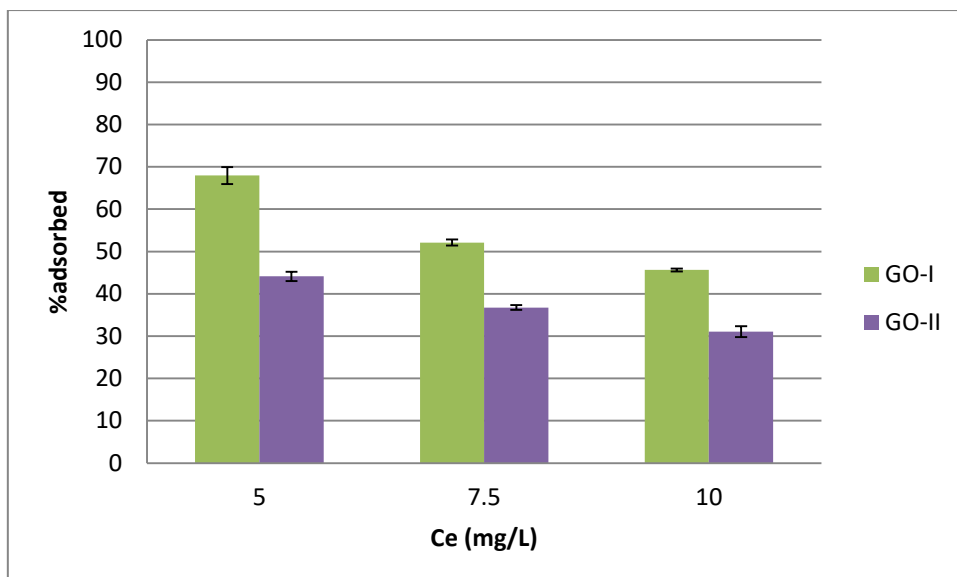


Fig. 15 Effect of CrO₄²⁻ initial concentration on its adsorption for each adsorbent tested. Adsorbent concentration= 10 g/L at pH=2, t=3h. (n=3).

- **Competitive adsorption of Cu^{2+} and Cd^{2+}**

The adsorption of a metal by the graphene can be affected by the presence of another metal in the initial solution which can compete with it for the sorption sites at the adsorbent surface. As, in general, wastewater effluents have a multi-metal composition, some experiments with an aqueous solution containing the same initial concentrations (5 mg/L) of Cu^{2+} and Cd^{2+} were performed

The results obtained are shown in **Fig. 16** and were compared with those obtained using a single metal solution at the same conditions. As can be seen in this figure no significant differences in the adsorbed percentage were observed showing that in the experimental conditions used there is no competition of Cu^{2+} and Cd^{2+} for the sorption sites of the graphene 97D surface.

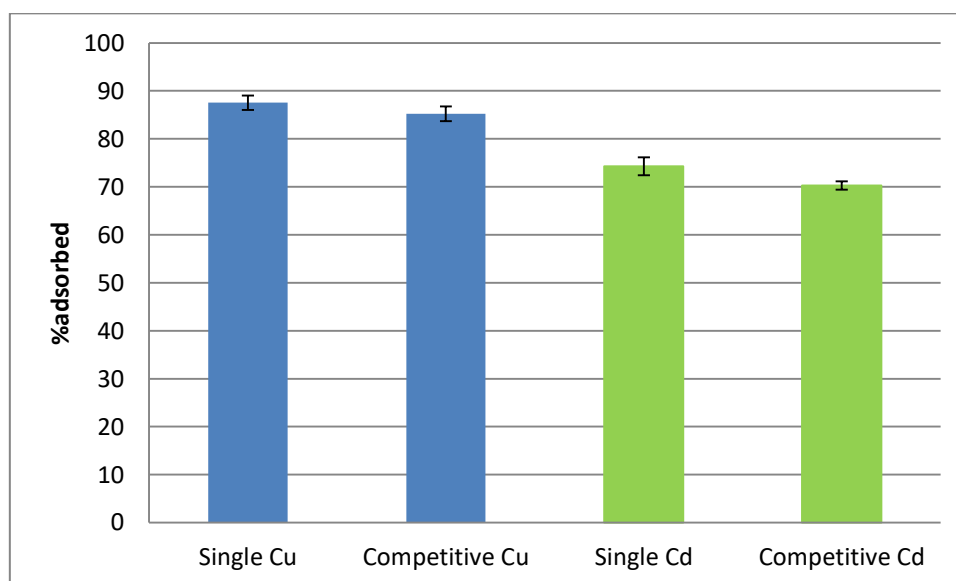


Fig. 16 Comparison of the adsorption of Cu^{2+} and Cd^{2+} by 97D. Adsorbent concentration= 2 g/L, initial concentrations= 5 mg/L at pH=6. Equilibrium time: 3h. (n=3).

Adsorption isotherm models

In general, an adsorption isotherm is an invaluable curve describing the phenomenon of adsorption of a substance from the aqueous media to a solid-phase at a constant temperature and pH. Here, three isotherm models (Langmuir, Freundlich, and Temkin) were applied to analyse the equilibrium experimental data of the sorption of Cu^{2+} , Cd^{2+} and CrO_4^{2-} on different graphene-based sorbents.

The amount of metal ions adsorbed at equilibrium per unit mass of adsorbent is determined by the following formula:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad \text{Eq. 2}$$

Where:

C_0 : initial concentration (mg/L)

C_e : equilibrium concentration (mg/L)

V : volume of solution (L)

m : mass of adsorbent (g)

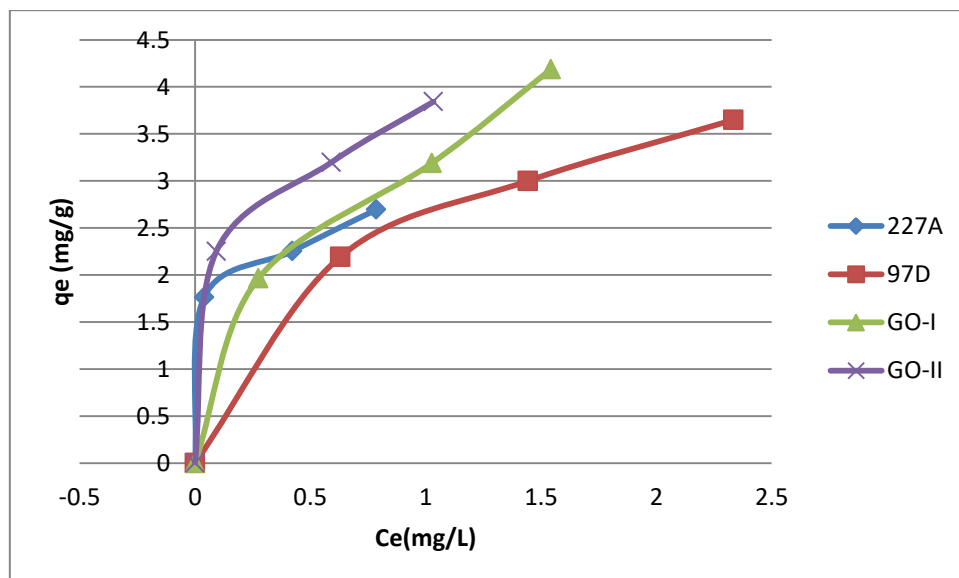


Fig. 17 Adsorption isotherms of Cu^{2+} for each adsorbent. Adsorbent concentration= 2 g/L at pH=6, t=1h, except for 97D t=3h. (n=3).

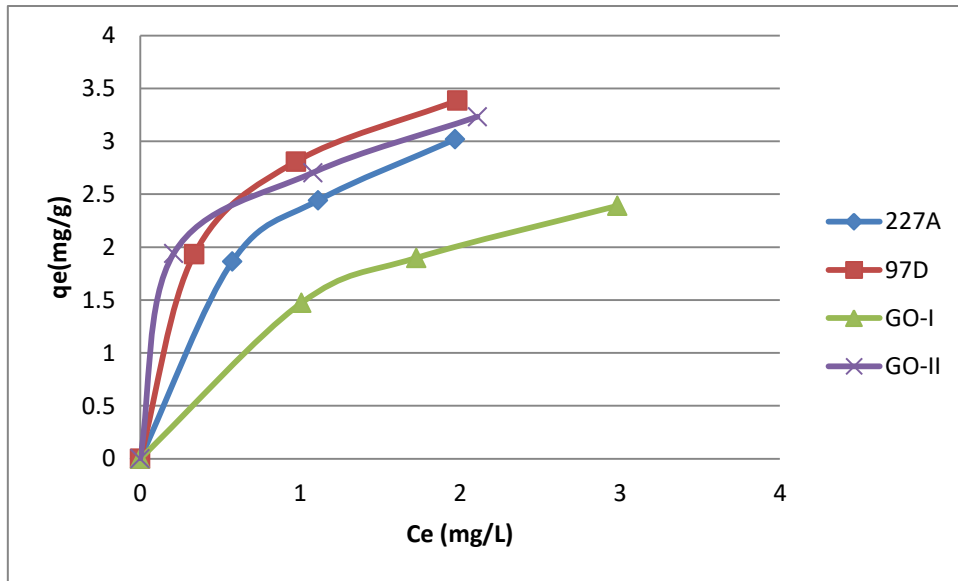


Fig. 18 Adsorption isotherms of Cd²⁺ for each adsorbent. Adsorbent concentration= 2 g/L at pH=6, t=1h, except for 97D t=3h. (n=3).

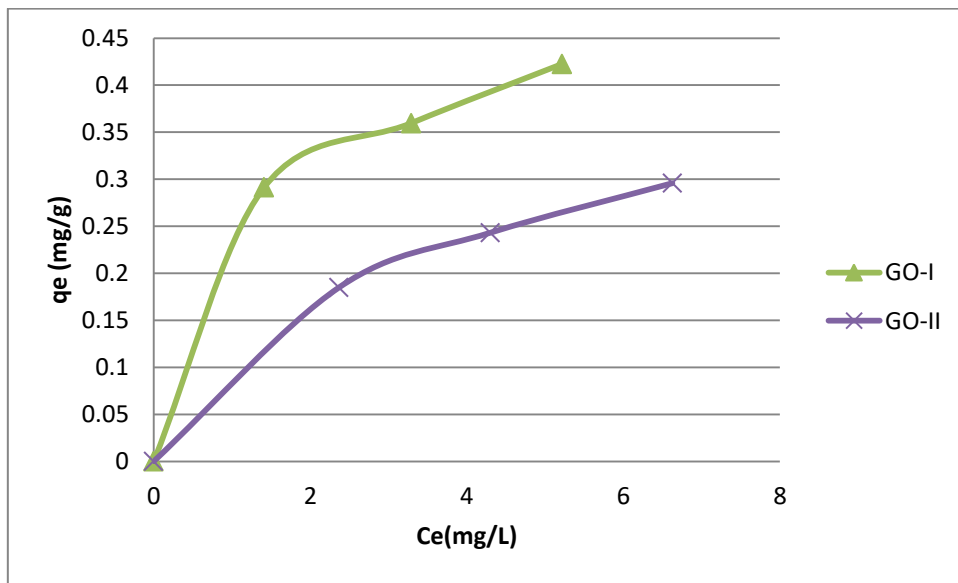


Fig. 19 Adsorption isotherms of CrO₄²⁻ for each adsorbent. Adsorbent concentration= 10 g/L at pH=2, t=3h. (n=3).

The **Langmuir** model assumes monolayer adsorption, where adsorption can only occur at a finite number of definite localized sites that are identical and equivalent, with no lateral interaction between the adsorbed molecules, even on adjacent sites. The linear Langmuir model is presented by **Eq. 3**:

$$\frac{C_e}{q_e} = \frac{1}{q_{max} \cdot K_L} + \frac{1}{q_{max}} C_e \quad \text{Eq. 3}$$

Where:

q_{\max} : maximum adsorption capacity (mg/g)

K_L : Langmuir constant (L/mg)

The essential characteristic of the Langmuir isotherm can be explained by the equilibrium separation factor (R_L) defined as follows:

$$R_L = \frac{1}{1 + C_0 K_L} \quad \text{Eq. 4}$$

The R_L value indicates the adsorption nature to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$) or irreversible ($R_L = 0$).

The **Freundlich** model can be applied to multilayer adsorption, with non-uniform distribution of adsorption over the heterogeneous surface. The linear Freundlich model is expressed by **Eq. 5**:

$$\ln q_e = \ln k_F + \frac{1}{n} \ln C_e \quad \text{Eq. 5}$$

Where:

q_e : amount of metal adsorbed at equilibrium (mg/g)

C_e : equilibrium concentration (mg/L)

K_F : Freundlich constant

The **Temkin** model is usually used for heterogeneous surface energy systems. The linear Temkin model is expressed by **Eq. 6**:

$$q_e = B \ln A + B \ln C_e \quad \text{Eq. 6}$$

Where:

A: Temkin constant (L/mg)

B: Temkin constant related to heat adsorption (J/mol)

The slope and the intercept of each linear model are used to calculate Langmuir, Freundlich and Temkin parameters, and the isotherm constants and correlation coefficients for each metal are summarized in **Table 1, 2 and 3**.

The adsorption experimental data of Cu^{2+} fitted well to the Langmuir isotherm model with high determination coefficient (R^2) in the case of 227A, 97D and GO-II sorbents, the only exception is the GO-I sorbent, which fitted better with the Freundlich isotherm model. In the case of Cd^{2+} , the experimental data of all the adsorbents fitted with the Langmuir model with determination coefficients higher than 0.96. In the case of CrO_4^{2-} , the best fit of the experimental data is to the Langmuir model for GO-I and to Freundlich model for GO-II. In general, the Langmuir isotherm model, which assumes a monolayer adsorption, fitted well with the experimental data obtained for Cu^{2+} , Cd^{2+} and CrO_4^{2-} for most of the four adsorbents. Furthermore, as it can be observed, the dimensionless constants R_L have a value inside the favourable limit ($0 < R_L < 1$).

The q_{max} value is the maximum adsorption capacity, maximum adsorption ranging from 2.6 to 5.4 mg/g were obtained for Cu^{2+} and Cd^{2+} with results. This q_{max} was a lower for CrO_4^{2-} , obtaining values of 0.44 and 0.5 mg/g, depending of the adsorbent. These results explain the fact that a higher concentration of adsorbent was required to obtain a similar adsorption percentage in the case of CrO_4^{2-} .

The results obtained with the different isotherm models didn't provide enough information to explain the difference in the equilibrium time between 97D (3 hours) and the other graphenes (1 hour). However, the differences observed in thermogravimetric curves between 97D and the rest of the adsorbents, show that the lack of functional groups such as epoxy or carbonyl in the surface of 97D sorbent resulted in a lower kinetics.

Table 1 Results obtained by applying the Langmuir, Freundlich and Temkin models to the experimental data of Cu²⁺ for each adsorbent.

Cu ²⁺		227A	97D	GO-I	GO-II	
Langmuir	q _{max} (mg/g)	2.6	4.6	5.4	4.3	
	K _L (L/mg)	28.6	1.4	1.8	9.4	
	R ²	0.984	0.975	0.951	0.983	
	R _L	C ₀ =5mg/L	0.0069	0.12	0.099	0.021
		C ₀ =7.5mg/L	0.0046	0.087	0.069	0.014
C ₀ =10mg/L		0.0035	0.066	0.052	0.010	
Freundlich	n	8.8	2.7	2.3	5.4	
	K _F	2.6	2.6	3.3	3.7	
	R ²	0.925	0.927	0.979	0.881	
Temkin	A (L/mg)	1.8	16.4	62.4	7.9	
	B (J/mol)	4.2	1.0	0.8	1.8	
	R ²	0.891	0.924	0.943	0.850	

Table 2 Results obtained by applying the Langmuir, Freundlich and Temkin models to the experimental data of Cd²⁺ for each adsorbent.

Cd ²⁺		227A	97D	GO-I	GO-II	
Langmuir	q _{max} (mg/g)	4.0	3.5	3.9	3.5	
	K _L (L/mg)	1.5	0.71	2.8	5.0	
	R ²	0.984	0.969	0.993	0.991	
	R _L	C ₀ =5mg/L	0.12	0.22	0.067	0.038
		C ₀ =7.5mg/L	0.082	0.16	0.046	0.026
C ₀ =10mg/L		0.063	0.12	0.035	0.020	
Freundlich	n	2.6	2.3	3.2	4.6	
	K _F	2.3	1.5	2.8	2.7	
	R ²	0.958	0.947	0.969	0.988	
Temkin	A (L/mg)	8.8	3.3	9.6	4.4	
	B (J/mol)	1.1	1.2	1.3	1.9	
	R ²	0.959	0.947	0.971	0.975	

Table 3 Results obtained by applying the Langmuir, Freundlich and Temkin models to the experimental data of CrO_4^{2-} for each adsorbent.

CrO_4^{2-}		GO-I	GO-II	
Langmuir	q_{\max} (mg/g)	0.50	0.44	
	K_L (L/mg)	0.90	0.30	
	R^2	0.989	0.986	
	R_L	$C_0=5\text{mg/L}$	0.18	0.40
		$C_0=7.5\text{mg/L}$	0.13	0.31
$C_0=10\text{mg/L}$		0.099	0.25	
Freundlich	n	3.6	2.2	
	K_F	0.3	0.13	
	R^2	0.982	0.989	
Temkin	A (L/mg)	1.0	1.0	
	B (J/mol)	10.7	9.4	
	R^2	0.960	0.982	

Ethics and sustainability

The solution manipulation and residue treatment has been performed considering the sustainability criteria applied in chemical analysis laboratories. Generally, residues have been disposed in their corresponding container. Solutions containing heavy metals have been disposed in their appropriate container for further treatment. Given its high toxicity, Cr^{6+} residues have been collected in a separate container. In order to avoid the generation of high volumes of wastes, the volumes and concentrations of the different solutions needed to perform the experiments (including the replicates) were previously calculated.

No living organism has been hurt during the realization of this research work.

This manuscript was originally written and plagiarism is avoided. The findings made by other authors are reported by including the corresponding reference in order to avoid confusion with our findings.

Conclusions

In this project, the sorption capacity of four different graphene-based adsorbents to Cu^{2+} , Cd^{2+} and CrO_4^{2-} has been studied. The adsorbents were firstly characterized and then the experiment conditions were optimized, considering different factors such as contact time, pH of the aqueous solution, adsorbent concentration or initial metal concentration.

The thermogravimetric curves of the adsorbents help understanding the different kinetics of 97D (3 hours) in comparison with the rest of the graphenes (1 hour). The lack of functional groups such as epoxy or carbonyl in the surface of 97D results in lower kinetics.

Cu^{2+} and Cd^{2+} presented similar behaviour in the adsorption, the experiments could be done at pH=6 and with an amount of adsorbent of 4 g/L. In the case of CrO_4^{2-} , the required pH was lower (pH=2) and a higher adsorbent concentration (10 g/L) is required to obtain significant adsorption percentage of this metal. These acidic conditions for CrO_4^{2-} suggest that the interaction with the graphene may be through an electrostatic interaction (ion-exchange mechanism) with the adsorbent surface.

The experimental data of almost all the sorption systems studied fitted well with the Langmuir isotherm, with only two exceptions (GO-I for Cu^{2+} and GO-II for CrO_4^{2-}). Maximum adsorption values (q_{max}) ranging from 2.6 to 5.4 mg/g were obtained for Cu^{2+} and Cd^{2+} with results. This q_{max} was a lower (~ 0.5 mg/g) for CrO_4^{2-} .

The results obtained suggest that these adsorbents can be effectively used to remove metallic cations, such as Cu^{2+} or Cd^{2+} , as well as anions, such as CrO_4^{2-} from aqueous solutions. Having single metal or multi-metal composition as there is not competition for the adsorbent in the experimental conditions tested.

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