



**ΠΑΝΕΛΛΗΝΙΟ
ΕΠΙΣΤΗΜΟΝΙΚΟ
ΣΥΝΕΔΡΙΟ
ΧΗΜΙΚΗΣ
ΜΗΧΑΝΙΚΗΣ**

**ΑΘΗΝΑ
23-25
ΜΑΙΟΥ
2013**

η συμβολή της
χημικής μηχανικής
στην **αειφόρο ανάπτυξη**

Πρακτικά Συνεδρίου

Χορηγοί



ΑΝΑΛΥΤΙΚΕΣ ΣΥΣΚΕΥΕΣ Α.Ε.
Δρ Κ.Ι. ΒΑΜΒΑΚΑΣ - ΕΠΙΣΤΗΜΟΝΙΚΟΣ ΕΞΟΠΛΙΣΜΟΣ

INGENIA



ΚΛΕΩΣ



THERMANSYS

ΑΝΑΓΓΕΛΙΑ & ΠΡΟΣΚΛΗΣΗ ΣΥΜΜΕΤΟΧΗΣ

9^ο Πανελλήνιο Επιστημονικό Συνέδριο Χημικής Μηχανικής **«Η Συμβολή της Χημικής Μηχανικής στην Αειφόρο Ανάπτυξη»**

Αθήνα, Πολυτεχνειούπολη Ζωγράφου, 23 - 25 Μαΐου 2013

Αγαπητά Μέλη της Ελληνικής Χημικο-Μηχανικής Κοινότητας:

Εκ μέρους της Οργανώτριας Σχολής των Χημικών Μηχανικών του Εθνικού Μετσόβιου Πολυτεχνείου, έχω την τιμή και τη χαρά να σας προσκαλέσω να συμμετάσχετε στο 9^ο Συνέδριο της επιτυχημένης σειράς των Πανελληνίων Επιστημονικών Συνεδρίων Χημικής Μηχανικής, το οποίο θα πραγματοποιηθεί σε χώρους της Πολυτεχνειούπολης Ζωγράφου του ΕΜΠ, στο τριήμερο Πέμπτης 23/5 – Σαββάτου 25/5/2013.

Όπως και στα προηγούμενα 8 Συνέδρια της σειράς, ο σκοπός του 9ΠΕΣΧΜ θα είναι η *παρουσίαση των αποτελεσμάτων της έρευνας*, που διεξάγεται σε Πανεπιστήμια, ερευνητικά κέντρα, επιχειρήσεις και άλλους οργανισμούς, κι εντάσσεται στις επιστημονικές περιοχές του πεδίου της Χημικής Μηχανικής. Όμως, η σημερινή συγκυρία μας οδήγησε στην προσθήκη ενός δεύτερου στόχου, αυτού της *συμβολής στην Αειφόρο Ανάπτυξη της πατρίδας μας*. Επομένως, θα θέλαμε οι ερευνητικές ομάδες να δώσουν κατά το δυνατόν προτεραιότητα στις εργασίες τους με αναπτυξιακές προοπτικές κάθε είδους.

Ένας άλλος τομέας, όπου το 9ΠΕΣΧΜ θα προσπαθήσει να εκμεταλλευτεί την συσσωρευμένη εμπειρία των 8 προηγούμενων Συνεδρίων, είναι στην ενεργοποίηση της συμμετοχής όλων των κατηγοριών συνέδρων, και ειδικότερα:

- στον *εκπαιδευτικό χαρακτήρα* της παρακολούθησης του Συνεδρίου για τους φοιτητές μας, π.χ. μέσω της ελεύθερης (δωρεάν) συμμετοχής τους στις συνεδριάσεις
- στην *αριστεία* των εργασιών των *νέων ερευνητών* μας, π.χ. μέσω της θεσμοθέτησης βραβείων και διακρίσεων σε όλες τις κατηγορίες (Διπλωματικές, Διδακτορικά, poster, κ.α.)
- στην *ενίσχυση και αξιοποίηση της συμμετοχής των έμπειρων συναδέλφων* μας, π.χ. ως ειδικών ομιλητών, σε ρόλους rapporteur, και ως μελών των επιτροπών βράβευσης του Συνεδρίου.

Έτσι, ο τρίτος στόχος του 9ΠΕΣΧΜ είναι η δημιουργία μιας ζωντανής και δημιουργικής «*κυψέλης*» *αλληλεπίδρασης* ατόμων, θεωριών και εφαρμογών.

Η επίτευξη των ανωτέρω στόχων θα εξαρτηθεί από τη συμμετοχή σας, αναλυτικά στοιχεία για την οποίαν θα βρείτε στην ειδική ιστοσελίδα του Συνεδρίου (<http://9pesxm.chemeng.ntua.gr/>). Ειδικότερα, καλούμε τις ενδιαφερόμενες για την ανακοίνωση των εργασιών τους ερευνητικές ομάδες να υποβάλουν *περιλήψεις των εργασιών αυτών μέσω των ιστοσελίδων του 9ΠΕΣΧΜ, το αργότερο ως τις 28/2/2013*. Η Επιστημονική Επιτροπή του Συνεδρίου θα ενημερώσει, το αργότερο ως τις 15/3/2013, τους συγγραφείς των εργασιών για την αποδοχή τους και τη θέση τους στο πρόγραμμα, δίνοντας οδηγίες για την συγγραφή των κειμένων τους. Ταυτόχρονα, καλούμε τους συγγραφείς των εργασιών που βασίζονται σε *Διπλωματικές Εργασίες ή Διδακτορικές Διατριβές* να δηλώσουν τις υποψηφιότητές τους για βράβευση στις σχετικές ιστοσελίδες.

Ελπίζουμε, με τη βοήθεια όλων σας, σε ένα Συνέδριο αντάξιο του δυναμικού και των επιτευγμάτων της Ελληνικής Χημικο-Μηχανικής Κοινότητας.

Αθήνα, 31-12-2012

Ο ΠΡΟΕΔΡΟΣ ΤΗΣ ΟΡΓΑΝΩΤΙΚΗΣ ΕΠΙΤΡΟΠΗΣ



Ε.Γ. Κούκιος, Καθηγητής ΕΜΠ - Πρόεδρος Σχολής ΧΜ

ON THE KINETICS AND THERMODYNAMICS OF MERCURY(II) REMOVAL FROM AQUEOUS SOLUTIONS WITH MAGNETIC GRAPHENE OXIDE AND MAGNETIC CHITOSAN

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Keywords: Thermodynamics, Kinetics, Mercury(II), Modeling, Magnetic chitosan, Magnetic graphene oxide

EXTENDED ABSTRACT

Contamination of aquatic systems is a serious environmental problem given the pollution of natural waters by heavy metal ions. Mercury is one of the most toxic heavy metals since it is not biodegradable and causes a lot of toxic effects in the human body. Its presence is due to a combination of natural processes (volcanic action, erosion of mercury-containing sediments) and anthropogenic activities (mining operations, tanneries, metal plating facilities) as well. Adsorption is considered to be one of the most effective and economical treatment methods for mercury removal of effluents. In order to focus on the kinetics and thermodynamics of the mercury(II) adsorption, two main adsorbents were selected: magnetic chitosan and magnetic graphene oxide.

Chitosan is a multifunctional polymer that has primary and secondary hydroxyl groups, as well as highly reactive amino groups. It has been regarded as a useful starting support for adsorption purposes. Numerous investigations on chemical activation of chitosan have been carried out to increase its adsorption capacity for metals. In the past, magnetic chitosan has emerged as a new generation of materials for environmental decontamination, since magnetic separation simply involves applying an external magnetic field to extract the adsorbents. Graphene, a new class of two dimensional carbon nanostructure with one atom thickness and with a two-dimensional honeycomb sp^2 carbon lattice, receives extensive research interest due to its unique properties and applications in catalysis, biomedical fields, adsorption and separation etc. The π -electron rich structure renders graphene potential applications as adsorbent. Graphene oxide produced from graphite after chemical oxidation, is one of the most important derivatives of graphene. It is characterized by a layered structure with oxygen functional groups bearing on the basal planes and edges. However, its small particle size and the high dispersibility in aqueous solutions, make difficult its separation from solution after adsorption process via filtration and/or centrifugation. A solution to this problem is the development of magnetic adsorbents, which can ensure the convenient magnetic separation after adsorption. Many procedures were applied to magnetic graphite oxide fabrication including in-situ co-precipitation, and covalent bonding, methods are generally multistep, hard to control and they also require some rigorous conditions. Electrostatic self-assembly has proved to be an effective method for fabricating metal oxides composites especially with carbon based materials.

In the present study, a full thermodynamic analysis was realised for the adsorption of mercury(II) onto both magnetic graphene oxide and magnetic chitosan (Table 1). The parameters determined were the change of Gibbs free energy (ΔG^0 , kJ/mol), change of enthalpy (ΔH^0 , kJ/mol) and entropy change (ΔS^0 , kJ/mol K). The equations for the calculation of the above parameters are briefly expressed below and based on theory (where C_s (mg/L) is the amount adsorbed on solid at equilibrium and R (=8.314 J/mol K) is the universal gas constant):

$$K_c = \frac{C_s}{C_e} \quad (1)$$

$$\Delta G^0 = -R T \ln(K_c) \quad (2)$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (3)$$

$$\ln(K_c) = \left(-\frac{\Delta H^0}{R} \right) \frac{1}{T} + \frac{\Delta S^0}{R} \quad (4)$$

The values of ΔG^0 were calculated from Eq. (2), while the values of ΔH^0 and ΔS^0 were calculated from the slope and intercept of the plot between $\ln(K_c)$ versus $1/T$ (Eq. (4)). For both adsorbents, the decrease of negative values of ΔG^0 with the increase of temperature from 25 to 65 °C revealed that the adsorption process was more favourable at higher temperatures. The latter can be explained by (i) the enhancement of the mobility/motion of adsorbate Hg(II) ions in the solution with increase of temperature, and (ii) the higher affinity of adsorbate on the adsorbent at high temperatures. Furthermore, the positive values of ΔH^0 implied the endothermic nature of the process for all cases studied. The positive values of ΔS^0 emphasized the increased randomness at the interface of solid/solution interface with possible micro-structural changes of the adsorbate and adsorbent.

Adsorbent	C ₀ (mg/L)	T (K)	Q _e (mg/g)	K _c	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol K)
GOm	20	298	14.02	2.33	-2.10		
		318	15.06	3.00	-2.90	+18.38	+0.068
		338	16.980	5.67	-4.87		
	100	298	56.02	1.27	-0.60		
		318	60.08	1.50	-1.07	+6.10	+0.023
		338	62.99	1.70	-1.50		
	500	298	123.10	0.33	-0.11		
		318	145.04	0.41	-1.44	+5.78	+0.010
		338	150.03	0.43	-2.44		
CSm	20	298	15.11	3.00	-0.50		
		318	16.02	4.00	-0.80	+13.27	+0.054
		338	17.08	5.67	-3.09		
	100	298	58.12	1.38	-0.20		
		318	61.99	1.63	-0.85	+6.21	+0.024
		338	65.03	1.86	-2.52		
	500	298	130.07	0.35	-0.17		
		318	139.89	0.39	-2.03	+5.70	+0.010
		338	158.01	0.46	-2.80		

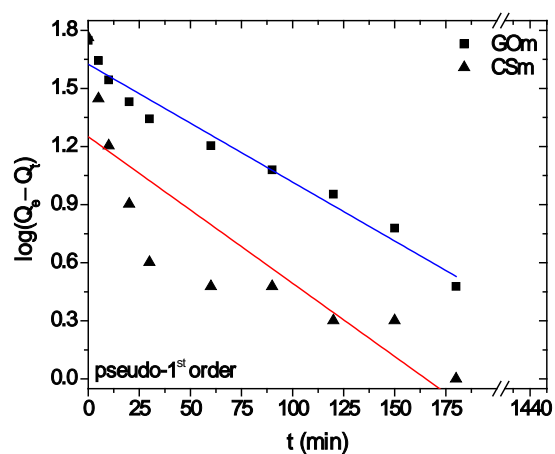
A deep kinetic study was realized in order to examine the adsorption dynamics of the process. The experimental results were fitted to the pseudo-first, -second order and Elovich equation:

$$\log(Q_e - Q_t) = \log(Q_e) - \left(\frac{k_1}{2.303} \right) t \quad (5)$$

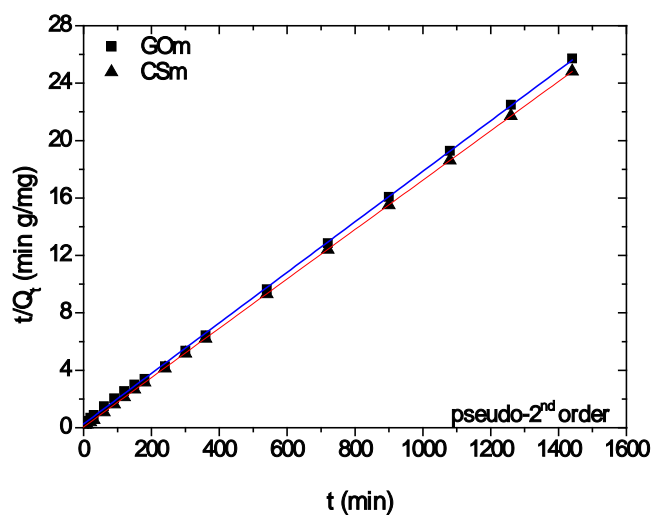
$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \left(\frac{1}{Q_e} \right) t \quad (6)$$

$$Q_t = \frac{1}{\beta_{el}} \ln(a \cdot \ln t) + \frac{1}{\beta_{el}} \quad (7)$$

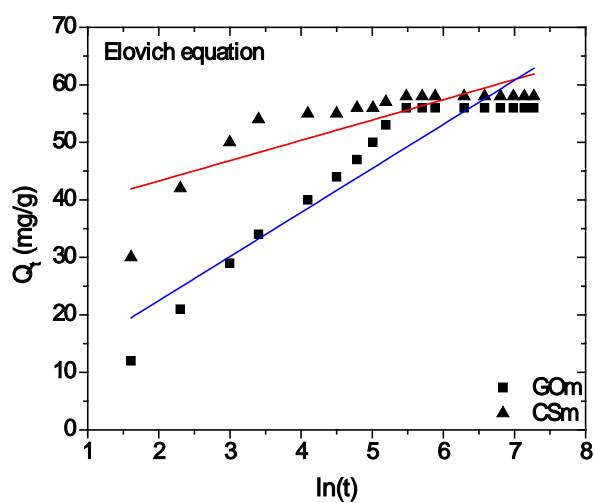
In the case of pseudo-first order equation (Eq. (5)), the slope ($k_1/2.303$) and intercept $\log(Q_e)$ of plot $\log(Q_e - Q_t)$ versus t were used to calculate the parameters of k_1 and $Q_{e,cal}$. In the case of pseudo-second order equation (Eq. (6)), the slope ($1/Q_e$) and intercept ($1/k_2 Q_e^2$) of plot (t/Q_t) versus t were used to calculate the parameters of k_2 and $Q_{e,cal}$. In the case of Elovich equation (Eq. (7)), the slope ($1/\beta_{el}$) and intercept ($\ln(a \cdot \beta_{el})/\beta_{el}$) of plot Q_t versus $\ln(t)$ were used to calculate the parameters of a and β_{el} . The linear fitness revealed the perfect connection between theoretical points exported from the pseudo-second order model and experimental data. R^2 (correlation coefficients) in all cases (both chitosan and graphene oxide) was 0.999. The fitness success can be easily confirmed from the nearly same adsorption capacities (calculated and experimental) $Q_{e,cal} = Q_{e,exp}$. All above confirmed the second order kinetic trend of the experimental results (Fig. 1).



(a)



(b)



(c)

Fig. 1. Effect of contact time on adsorption of Hg(II) onto GOM and CSM: fitting to (a) pseudo-first order equation; (b) pseudo-second order equation; (c) Elovich equation.

ON THE KINETICS AND THERMODYNAMICS OF MERCURY(II) REMOVAL FROM AQUEOUS SOLUTIONS WITH MAGNETIC GRAPHENE OXIDE AND MAGNETIC CHITOSAN



George Z. Kyzas, Nikolina A. Travlou, Konstantinos A. Matis, Eleni A. Deliyanni

Division of Chemical Technology, Department of Chemistry, Aristotle University of Thessaloniki, Greece

Aim

- Kinetic and Thermodynamic evaluation of adsorption
- Adsorbents: Magnetic graphene oxide (GOM)
Magnetic chitosan (CSm)
- Removal of Hg(II) from aqueous solutionst

Adsorption Experimental

Kinetic experiments were performed by mixing 0.02 g of adsorbent with 20 mL of metal aqueous solution ($C_{0,Hg(II)}=100$ mg/L). The suspensions were shaken for 24 h at pH=5 in water bath at 25 °C (N=160 rpm). Samples were collected at fixed-time intervals (from 5 min to 24 h). Pseudo-first, pseudo-second order, and Elovich equations were used to fit the kinetic experimental data.

The effect of temperature on adsorption was determined by mixing 0.02 g of adsorbent with 20 mL of metal aqueous solutions of different initial concentrations ($C_{0,Hg(II)}=0-500$ mg/L). The suspensions were shaken for 24 h at pH=5 in water bath at 25, 45, 65 °C (N=160 rpm). The resulted equilibrium data were fitted to the Langmuir model and Freundlich equation.

$$Q_e = \frac{Q_{\max} K_L C_e}{1 + K_L C_e} \quad Q_e = K_F (C_e)^{1/n}$$

where Q_e (mg/g) is the equilibrium metal concentration in the solid phase; Q_{\max} (mg/g) is the maximum amount of adsorption; K_L (L/mg) is the Langmuir adsorption equilibrium constant; K_F ($\text{mg}^{1-1/n} \text{L}^{1/n}/\text{g}$) is the Freundlich constant representing the adsorption capacity; n (dimensionless) is the constant depicting the adsorption intensity.

The thermodynamic parameters determined were the change of Gibbs free energy (ΔG^0 , kJ/mol), change of enthalpy (ΔH^0 , kJ/mol) and entropy change (ΔS^0 , kJ/mol K). The equations for the calculation of the above parameters are briefly expressed below and based on theory (where C_s (mg/L) is the amount adsorbed on solid at equilibrium and R ($=8.314$ J/mol K) is the universal gas constant):

$$K_c = \frac{C_s}{C_e} \quad \Delta G^0 = -R T \ln(K_c) \quad \Delta G^0 = \Delta H^0 - T \Delta S^0 \quad \ln(K_c) = \left(-\frac{\Delta H^0}{R} \right) \frac{1}{T} + \frac{\Delta S^0}{R}$$

The values of ΔG^0 were calculated from first eq. while the values of ΔH^0 and ΔS^0 were calculated from the slop and intercept of the plot between $\ln(K_c)$ versus $1/T$ (last eq).

Synthesis of Adsorbents

Synthesis of magnetic cross-linked chitosan (CSm)

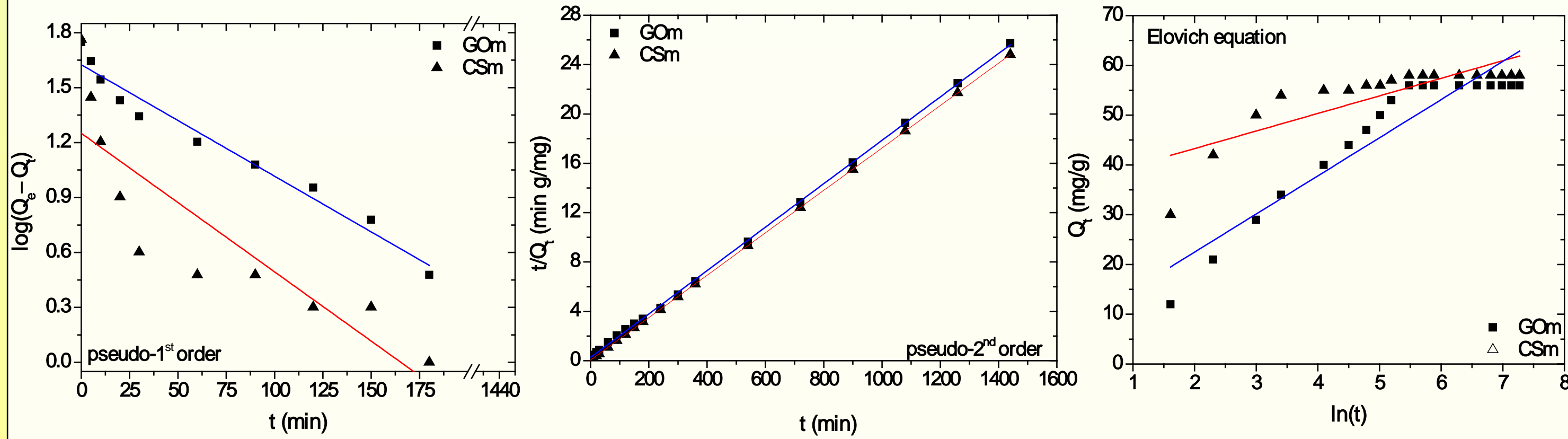
Initially, the preparation of magnetic nanoparticles was carried out mixing 3.5 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$, 9.5 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 400 mL of double distilled water and stirring in a water bath at 60 °C under nitrogen for 1 h. Ammonia solution was added dropwise, purged with nitrogen until pH=10. The precipitate obtained was decanted in a dialysis tubing cellulose membrane (Sigma Co.) and the latter was placed in a bath filled with distilled water. The chloride ions presented in the initial suspension were slowly removed by osmosis through the membrane. The existence of Cl^- ions in the water bath was tested with a solution of AgNO_3 (0.1 M). The water of the bath was replaced several times, until no more chloride ions were detectable in it. The resulting cake on the membrane surface after decanting was freeze-dried in a bench freeze drier (Christ Alpha 1-4). 2 g of CSP was dissolved in 400 mL of acetic solution (2% v/v). 0.75 g of the prepared magnetic nanoparticles were added in the above chitosan solution and the mixture was sonicated for 30 min. Then, GLA was added to mixture solution in order to cross-link chitosan. So, 15 mL of GLA (similarly as CS, the ratio was 2:1 aldehyde groups (-CHO) of GLA per initial amino groups (- NH_2) of chitosan) were added into reaction flask to mix with the solution and was vigorously stirred at 60 °C for 2 h. The precipitate was washed with ethanol and distilled water in turn and dried in a vacuum oven at 50 °C. The obtained product was the magnetic cross-linked chitosan derivative (CSm).

Synthesis of Magnetic Graphene oxide (GOM)

In a typical synthesis, GO (0.3 g) was dispersed in 150 mL water by sonication for 30 min in order graphene oxide to be formed. Then, 0.825 g $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.322 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ were dissolved in 25 mL of water and the solution was added dropwise to GO solution at room temperature under a nitrogen flow with vigorous stirring. After completing ion exchange, 28% ammonia solution was added dropwise to make the pH of solution 10 for synthesis of magnetite nanoparticles. The temperature of the solution rose to 80 °C. After stirring for about 45 min, the black precipitate was centrifuged, washed with ethanol several times, and finally was freeze-dried.

Kinetics

The fitting was performed using pseudo-first, -second order and Elovich equations. First figure shows the plot of linearization of pseudo-first order model, where the slope ($-k_1/2.303$) and intercept $\log(Q_e)$ of plot $\log(Q_e - Q_t)$ versus t was used to determine the pseudo-first order constant k_1 and the equilibrium adsorption density $Q_{e,cal}$. However, the experimental data deviated considerably from the theoretical data. The correlation coefficients (R^2) obtained were not as high as those for pseudo-second equation. Also, the adsorption equilibrium values ($Q_{e,cal}$) found gave significant deviation for both adsorbents. These findings suggest that this adsorption system is not a pseudo-first order reaction. Furthermore, the experimental data fitted to the pseudo-second order equation (2nd figure), calculating the respective parameters. The slope ($1/Q_e$) and intercept ($1/k_2 Q_e^2$) of plot (t/Q_t) versus t were used to calculate the parameters of k_2 and $Q_{e,cal}$. The straight lines in plots showed an excellent agreement of experimental data with this model. The correlation coefficients for all adsorbents were equal to 0.999. Also, the calculated $Q_{e,cal}$ values are completely the same with those exported from the experimental data. These findings indicate that the adsorption system studied belongs to the second-order kinetic model. 3rd figure shows a plot of linearization of Elovich model. The slope and intercept of plots of Q_t versus $\ln(t)$ were used to determine the constant B_{el} and the initial adsorption rate α . However, the experimental data deviated considerably from the theoretical data. The correlation coefficients for the Elovich kinetic model obtained at all the studies concentrations were low ($R^2_{CSm}=0.658$ and $R^2_{GOM}=0.884$). This suggests that this adsorption system is not an acceptable for this system.



Thermodynamics

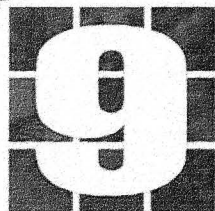
For both adsorbents, the decrease of negative values of ΔG^0 with the increase of temperature from 25 to 65 °C revealed that the adsorption process was more favourable at higher temperatures. The latter can be explained by (i) the enhancement of the mobility/motion of adsorbate Hg(II) ions in the solution with increase of temperature, and (ii) the higher affinity of adsorbate on the adsorbent at high temperatures. Furthermore, the positive values of ΔH^0 implied the endothermic nature of the process for all cases studied. The positive values of ΔS^0 emphasized the increased randomness at the interface of solid/solution interface with possible micro-structural changes of the adsorbate and adsorbent.

dsorbent	C_0 (mg/L)	T (K)	Q_e (mg/g)	K_c	ΔG^0 (kJ/mol)	ΔH^0 (kJ/mol)	ΔS^0 (kJ/mol K)
GOM	20	298	14.02	2.33	-2.10	+18.38	+0.068
		318	15.06	3.00	-2.90		
		338	16.980	5.67	-4.87		
	100	298	56.02	1.27	-0.60	+6.10	+0.023
		318	60.08	1.50	-1.07		
		338	62.99	1.70	-1.50		
	500	298	123.10	0.33	-0.11	+5.78	+0.010
		318	145.04	0.41	-1.44		
		338	150.03	0.43	-2.44		
CSm	20	298	15.11	3.00	-0.50	+13.27	+0.054
		318	16.02	4.00	-0.80		
		338	17.08	5.67	-3.09		
	100	298	58.12	1.38	-0.20	+6.21	+0.024
		318	61.99	1.63	-0.85		
		338	65.03	1.86	-2.52		
	500	298	130.07	0.35	-0.17	+5.70	+0.010
		318	139.89	0.39	-2.03		
		338	158.01	0.46	-2.80		

Conclusions

$\Delta H^0 > 0$ suggested the endothermic nature of the process, $\Delta G^0 < 0$ suggested the spontaneity of the process, and $\Delta S^0 > 0$ showed the increased randomness at the solid/liquid interface.

The best fitting was done using the pseudo-second order kinetic equation for both adsorbents. Low correlation coefficients for pseudo-first order and Elovich equations.



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**ΑΘΗΝΑ
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2013**

ΒΕΒΑΙΩΣΗ

Βεβαιώνεται ότι ο / η

Γ.Ζ. Κύζας

συμμετείχε στο **9^ο Πανελλήνιο Επιστημονικό Συνέδριο Χημικής Μηχανικής** - «*η Συμβολή της Χημικής Μηχανικής στην Αειφόρο Ανάπτυξη*».

Το 9^ο ΠΕΣΧΜ διοργανώθηκε από τη Σχολή Χημικών Μηχανικών του Εθνικού Μετσόβιου Πολυτεχνείου στην Πολυτεχνειούπολη Ζωγράφου στην Αθήνα από 23 έως 25 Μαΐου 2013.

Ο Πρόεδρος της Οργανωτικής Επιτροπής

Καθηγητής Εμμανουήλ Γ. Κούκιος

Ο Αντιπρόεδρος της Οργανωτικής Επιτροπής

Καθηγητής Δημήτρης Γ. Κέκος

Εθνικό Μετσόβιο Πολυτεχνείο, Πολυτεχνειούπολη Ζωγράφου, Αθήνα