

# Adsorption of Lead (II) Ions on Rejuvenated NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Spent Hydrodesulfurization Catalyst

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## Abstract

Spent NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> hydrodesulfurization catalyst was rejuvenated using n-hexane to remove the soluble coke and the oxalic acid to remove the foulant elements and insoluble coke by calcinating it at under the temperature of 500°C for 4 hr. It was then structurally characterized using AFM techniques, and finally, the lead ion was separated from its aqueous solution via the adsorption batch method with varying concentrations of the lead ions, and then, the absorption efficiency was calculated. The results indicated that the removal efficiency of more than 99% was resulted when the rejuvenated NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts were used, compared with 51 % removal when a none rejuvenated one was used.

**Keywords:** Adsorption, Lead (II), rejuvenation, NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> spent catalyst.

## Introduction

It is well known that the problems of the ecosystem have been increasing with developing technology. Heavy metal pollution has been one of the main problems (Uzun et al., 2000). Consequently, the removal of the heavy metals from waste water and industrial waste has become a very important environmental issue (Awan et al., 2003).

Lead is one of the toxic elements which is released to the environment through several sources. Lead and its compounds are poisonous to animals and humans, when eaten or inhaled. The permissible amount of lead in drinking water has been indicated to be 0.015 mg/L. Chemical precipitation, co-precipitation, adsorption, flocculation, reverse osmosis, ion exchange, electro deposition and filtration have been the mostly used methods to remove lead from the aqueous solutions (Li & Bai., 2006). The majority of these methods have several cons such as their chemical requirements, time consuming procedure, production of large amount of sludge, low efficiency, and less cost effectiveness (Gupta et al., 2011). Among these, the adsorption method has been

regarded as more efficient, cost effective and without sludge formation (Cheng et al., 2012).

In order to treat wastes, metal oxide adsorbents have been applied abundantly. Currently, applying metal oxide nanoparticles as ideal adsorbents of heavy metal ions has been increasingly taken into consideration because of their larger surface area filled by the smaller particle size in comparison to the bulk materials (Savage and Diallo., 2005).

The catalysts are usually deactivated as time passes, and the spent catalysts finally take the shape of solid wastes (Marafi and Stanislaus., 2008). The amount of the spent catalysts released in different processing units is largely dependant on the quantity of the fresh catalysts used, their life and the deposits formed on them while they were used in the reactors. In most refineries, hydroprocessing units produced the largest portion of the spent catalyst wastes. Recently, the environmental laws regarding the spent catalyst disposal are getting increasingly rigid. The Environmental Protection Agency in the USA has categorized the spent hydroprocessing catalysts as dangerous wastes (Marafi and Stanislaus., 2003). Molybdenum (Mo), cobalt (Co), nickel (Ni) and/or vanadium (V) on an alumina (Al<sub>2</sub>O<sub>3</sub>) carrier are included in the spent HDS catalysts. These catalysts have been considered as the major catalysts for recycling these metals because of their large quantities and metal values, and also the environmental concerns if they are disposed off (Zeng et al., 2009)

Various catalysts get deactivated, and this is an ever-present problem that causes the catalytic rate, activity and/or selectivity to decrease with time, it also makes big problems in the industrial catalytic processes. The total cost of replacing catalysts and the process shutdown has been estimated to be billions of dollars per year. The time scales for catalyst deactivation are remarkably different; for example, considering the cracking catalysts, the catalysts get deactivated in seconds, contrarily in ammonia synthesis, the iron catalyst may survive for 5–10 years. Afterall, the decay of all the catalysts is inevitable (Thomas and Thomas., 2014). A huge amount of the useful spent catalysts and hydrodesulfurization (HDS) one in particular is delivered from the petrochemical and petroleum refining industries after several regeneration cycles. One of these, is NiMo/Al<sub>2</sub>O<sub>3</sub> spent HDS catalyst which is used in HDS of heavy petroleum products (Pereira et al., 2011).

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The aim of the present investigation was to rejuvenate the NiMo/γAl<sub>2</sub>O<sub>3</sub> spent catalyst, and use it as the adsorbent to remove lead (II) ions from their aqueous solution.

### Experimental Details

#### Materials and Instruments

Analytical grade materials were used without any further purification in addition to the deionized water, n-hexane, (C<sub>6</sub>H<sub>14</sub>), oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>), lead chloride PbCl<sub>2</sub>, and commercial spent NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst in Baji refinery company in Iraq.

Atomic force microscopy was used to study the surface of the samples through AFM model AA3000 SPM 220 V- angstrom Advanced INC, USA where the average grain size of the surface nanoparticles was measured (Kumar and Rao., 2011).

#### NiMo/γAl<sub>2</sub>O<sub>3</sub> spent catalyst rejuvenation procedure

The spent Ni-Mo/γ-Al<sub>2</sub>O<sub>3</sub> catalyst from Baji refinery company with specification given in table (2) was used. It was first cleaned from the contaminants by being washed with distilled water several times, and then dried in an oven at ~100°C for three hours, and finally processed through three-steps of pre-treatment.

- *Extraction of the soluble coke from the spent Ni-Mo/γAl<sub>2</sub>O<sub>3</sub>*

(9g) of the spent NiMo/γAl<sub>2</sub>O<sub>3</sub> catalyst were introduced into a Soxhlet apparatus and treated with n-hexane (50ml) for 6 h under the reflux at the temperature of (75-85 °C) and stirring rate of (200 rpm), in order to extract the soluble coke, then it was filtered to remove the solvent, and dried in an oven at (110 °C) for three hours, and then the recovered organic matter was weighed.

- *Leaching of the foulant elements from the treated Ni-Mo/γAl<sub>2</sub>O<sub>3</sub>.*

(5g) of the spent NiMo/γAl<sub>2</sub>O<sub>3</sub> treated with n-hexane were introduced into a Soxhlet apparatus, and (50 mL) of the aqueous oxalic acid (0.08 mol L<sup>-1</sup>) was added and extracted for 1hour at a temperature of (75-85 °C), the stirring rate was fixed at 200 rpm. Then the leached catalysts were filtered, washed with the distilled water for several times, dried in oven at 150 °C for 3 hours, and then cooled down in the desiccator, and finally weighed.

**Table 1-** Granularity cumulating distribution and average diameter of regenerated NiMo/γAl<sub>2</sub>O<sub>3</sub>

Avg. Diameter:67.48 nm								
Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)	Diameter (nm)<	Volume (%)	Cumulation (%)
55.0	3.98	3.98	70.00	18.58	59.29	85.0	7.08	100.0
60.0	18.58	22.57	75.00	18.58	77.88			
65.0	18.14	40.71	80.00	15.04	92.92			

- *Removal of the insoluble coke from Ni-Mo/γAl<sub>2</sub>O<sub>3</sub>*

(0.3g) of the catalysts (the original spent catalysts, the one treated with n-hexane only and the other treated with (oxalic acid and n-hexane) were placed in crucibles, and introduced in a furnace. The insoluble coke was burned under the temperature of 500 °C for (4 hours). The oxidized samples were cooled down in the furnace, and transferred into a dessicator, and then it was weighed.

#### Study of the adsorption

A standard stock solution of Pb (II) ions (1000 mg/L) were prepared from PbCl<sub>2</sub> in deionized water. Several concentrations (50,100,150,200,250 mg/L) were prepared from this standard stock of lead (II) ions. The absorbance of these solutions were measured at a wavelength (λ<sub>max</sub>) of 238.3 nm for lead to determine its concentrations by the atomic absorption.

There were many volumetric flasks containing 50 ml of Pb(II) ion with 100 mg/L at pH of 6, then 0.1 g of the regenerated NiMo/γAl<sub>2</sub>O<sub>3</sub> was added into each flask, and they were placed in a water bath shaker device with the speed of 150 rpm at room temperature (298 K) under different time intervals 5,10,15 and 20 min. Then, the samples were filtered before the analysis to prevent the nanoparticles' interference with the analysis. The concentrations of the metal solutions were determined using the atomic absorption. The factors influencing the adsorption of (NiMo/γAl<sub>2</sub>O<sub>3</sub>) were studied, namely, the contact time, the initial concentration, the adsorbent quantity, and the temperature. The lead metal percentage removal was calculated using the equation below (Onundi et al., 2010; Rozaini et al., 2010).

$$R \% = \frac{(C_o - C_e) * 100}{C_o} \tag{1}$$

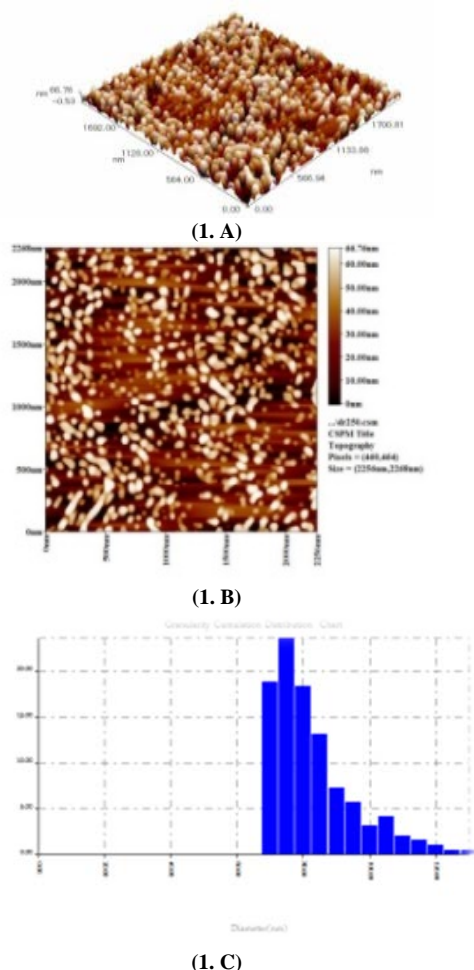
In which (R%) is percentage removal of Pb(II) ions, (C<sub>o</sub>) is the initial concentration of the lead ions (mg/L), (C<sub>e</sub>), is the concentration of the lead ions after the equilibrium (mg/L).

### Results and Discussion

#### Characterization of the regenerated NiMo/γAl<sub>2</sub>O<sub>3</sub>)

- *Atomic force microscope*

**Fig (1) and Table (1)** indicate the images of AFM for the regenerated NiMo/γAl<sub>2</sub>O<sub>3</sub> catalysts with (size =2256, 2268nm), and the ability of the analytical (pixel=460,464). **(1A)** shows AFM images in three dimensions (3D), it explains the structural shape of a grain, and **(1B)** represents AFM images in two dimensions (2D), it has been found that the average roughness was (16.4) nm , and the Root mean square (RMS) was (19) nm , also **(1C)** represents the particle size distribution, which has also been explained in table (1), where the average diameter was 67.48 nm ,and the particle size in less than 10 % of the total particles was 55 nm, in less than 50 % , it was 65 nm, and in less than 90%, it was 75 nm .



**Fig. 1:** AFM images of the regenerated NiMo/γAl<sub>2</sub>O<sub>3</sub>

#### Catalysts regeneration

The results of regeneration has been given in table (2). As can be seen, the spent catalyst was composed of (4.327) wt.% of the soluble coke being removed by hexane, and that the main foulant elements and materials removed from the oxalic acid included Fe, Ca, As and sulfate, composing approximately about (7.158) wt.%, while the insoluble coke being removed by the calcination was only (12.766) wt.% of it. What was gained from the catalyst regeneration was the recovery of its original properties such as the percentage of the active components like, nickel and molybdenum and the alumina support. As well, the surface area was lost as a result of sintering and fouling. This enhanced the lead ions' removal to a reasonable amount approaching 99% by using a regenerated catalyst compared with 51% removal through using the spent one.

**Table 2-** Physical and Chemical Properties of Commercial, Spent and Regenerated NiMo/γAl<sub>2</sub>O<sub>3</sub> Catalysts.

Property	Commercial	Spent	Regenerated
NiO	3.00 % wt	2.18 % wt	3.03
MoO <sub>3</sub>	15.00 % wt	10.91 % wt	15.15
Al <sub>2</sub> O <sub>3</sub>	81.00 % wt	58.92 % wt	81.82

Na <sub>2</sub> O	< 0.06	With foulant	0.0
Fe	< 0.06		0.0
SO <sub>4</sub> <sup>-2</sup>	< 1.06		0.0
Soluble coke	0.0	4.33	0.0
Insoluble coke	0.0	15.77	0.0
Fouling elements, Fe, Ca, As	0.0	7.89	0.0
Normal size	1.5-2.5mm	< 1.5-2.5mm	< 1.5-2.5mm
Form	Extrudates	Extrudates	Powder
Bulk density, kg/L	0.67	0.68	0.68
Surface area, m <sup>2</sup> /gm	180	120	175
Pore volume, cm <sup>3</sup> /gm	0.50	0.40	0.50

#### Adsorption of lead (II) ions on HDS catalysts

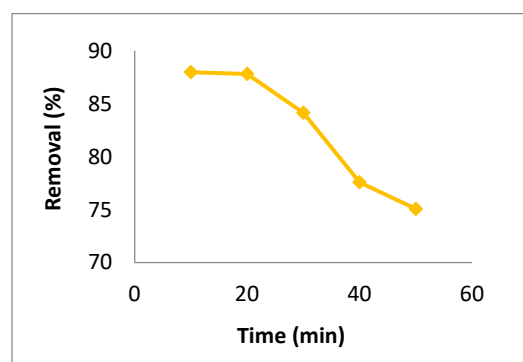
##### • The adsorption of spent NiMo/γ-Al<sub>2</sub>O<sub>3</sub> Catalyst

The adsorption of the lead (II) ion from the aqueous solution on the spent NiMo/γ-Al<sub>2</sub>O<sub>3</sub> Catalyst before the treatment was examined using the solution concentration of (100 mg/L), pH of 6, (0.2g), at 298 K for 20 min. The removal efficiency of Pb<sup>+2</sup> was 51%, and, the experiment was repeated after the treatment in same condition. The removal of Pb (II) was more than (99%).

##### • The Effect of the contact time on the adsorption

The effect of the contact time on the removal of pb (II) ions on the regenerated (NiMo/γAl<sub>2</sub>O<sub>3</sub>) was examined with the contact time of (5,10,15 and 20) min at 298 K, the lead ions' concentration of 100 mg/L, and pH of 6.

Fig. (2) indicates the change of the percentage of removal in the various contact times. As can be seen, the equilibrium time required for the adsorption of ions was almost (20 min). The effect of the contact time on the removal of the ions using (NiMo/Al<sub>2</sub>O<sub>3</sub>) explained the increase in the percentage of removal at the beginning of the contact time, then there was a gradual decline in the percentage of removal of ions, the rapid initial rate increase followed by a slow rate at the later stages could be due to the availability of the excessive adsorption sites on the adsorbent (Saeed et al., 2005). The ion exchange might cause the initial high adsorption rate which was slowed down by the chemical reaction of the metal ions (Alfa et al., 2012), and the remaining empty surface sites were difficult to be occupied because of the repulsive forces (Srivastava et al., 2006).



**Fig. 2.** Effect of contact time of Pb (II) ion in regenerated NiMo/γAl<sub>2</sub>O<sub>3</sub> at 298K.

• Effect of the adsorbent quantity on the adsorption

The quantity of the adsorbent on Pb (II) ions' adsorption on the regenerated NiMo/γAl<sub>2</sub>O<sub>3</sub> was studied using several quantities of (0.06, 0.08, 0.10, 0.12, 0.15 ,0.20 and 0.25 g) at 298 K, the lead ions' fixed concentration of (100 mg/L), pH of 6, with the contact time of 20 min. The influence of the adsorbent quantity on the removal of Pb<sup>+2</sup> ions has been shown in Fig. (3). It could be observed that with increasing the quantity of NiMo catalysts, the lead ions' removal was increased too, the increase in the percentage removal could be explained by the increasing surface area, where the adsorption took place, and the optimum adsorbent quantity that could be used in lead (II) removal was (0.2 g) (Han et al., 2006).

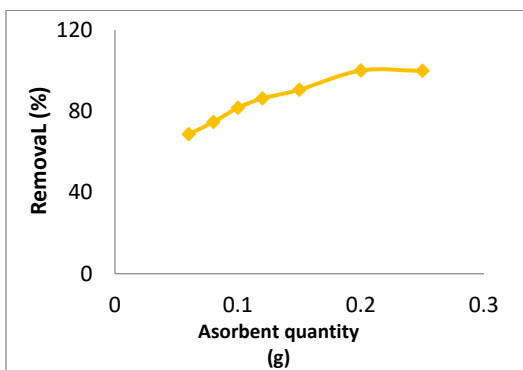


Fig. 3. Effect of adsorbent quantity of Pb (II) ion in regenerated NiMo/γAl<sub>2</sub>O<sub>3</sub> at 298K.

• Effect of temperature on adsorption

In this section, the effect of temperature on the extent adsorption of the lead on the regenerated NiMo/γAl<sub>2</sub>O<sub>3</sub> at four different temperatures of (298, 308, 318 and 323) K and pH of 6.03, with the initial concentration of 100 mg/L of Pb (II), the adsorbent quantity of (0.2 g), and the constant contact time of 20 min was examined. The general shape of the adsorption of lead(II) ions on the (regeneration NiMo/γAl<sub>2</sub>O<sub>3</sub>) given in Fig (4), showed that the removal percentage was decrease with the increase in temperature, which proved that the removal of Pb ions on the (regeneration NiMo/γAl<sub>2</sub>O<sub>3</sub>) surface was exothermic, the reduction in the rate of the adsorption with the increase in temperature may be weakening the interaction force between the active sites of the adsorption surface and the metal ions (Sheela et al., 2012).

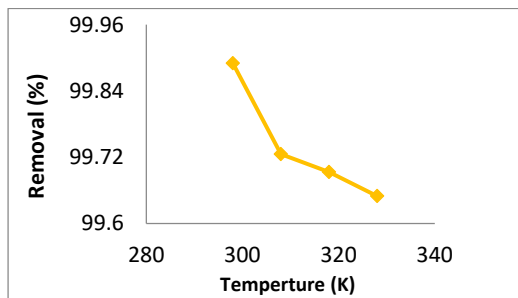


Fig. 4. Effect of temperature of Pb (II) ion in regenerated

• The effect of initial concentration

The adsorption of the lead metals from an aqueous solution on the regenerated NiMo/γAl<sub>2</sub>O<sub>3</sub> was studied first at the optimum conditions, using different initial concentrations of the aqueous solution of (50,100,150,200 and 250) mg/L for Pb(II). The results of the impacts of the initial concentration as shown in Fig. (5), indicated little decrease in the removal with increasing the initial concentration of Pb(II) ions on the surface. The Pb<sup>+2</sup> ion adsorptivity (% removal) depended on the initial Pb<sup>+2</sup> ions concentration. Where the adsorptivity decreased with the increasing initial Pb (II) concentration. This was the result of the increase in the driving force from the concentration gradient (Farghali et al., 2013).

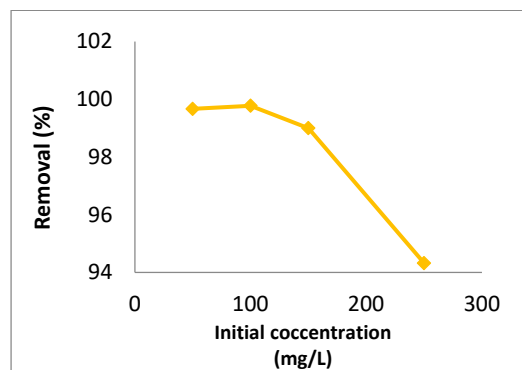


Fig. 5. Effect of initial concentration adsorption of Pb(II) ion in regenerated NiMo/γAl<sub>2</sub>O<sub>3</sub>.

Table 3- The effect of temperature on the equilibrium constant for the adsorption of Pb (II) ions in the regenerated NiMo/γAl<sub>2</sub>O<sub>3</sub>

Metals	T(K)	1/T K <sup>-1</sup>	C <sub>e</sub> mg/L	Q <sub>e</sub> mg/g	k	Ln k
Pb (II) ions	298	0.00335	0.1098	24.9725	909.7449	6.8131
	308	0.00324	0.2744	24.9314	363.4314	5.8955
	318	0.00314	0.3068	24.9233	324.9452	5.7836
	328	0.00304	0.3502	24.9124	284.5505	5.6509

• The thermodynamic study of the adsorption

The Thermodynamic functions related to the adsorption of the pesticides, like, Gibbs free energy change (ΔG<sup>\*</sup>), enthalpy change (ΔH<sup>\*</sup>) and entropy change (ΔS<sup>\*</sup>), were examined. The change in free energy could be determined from the following equations (Sirichote et al., 2002).

$$\Delta G = -RT \ln k \tag{2}$$

$$\ln k = (-\Delta H / RT) + (\Delta S / R) \tag{3}$$

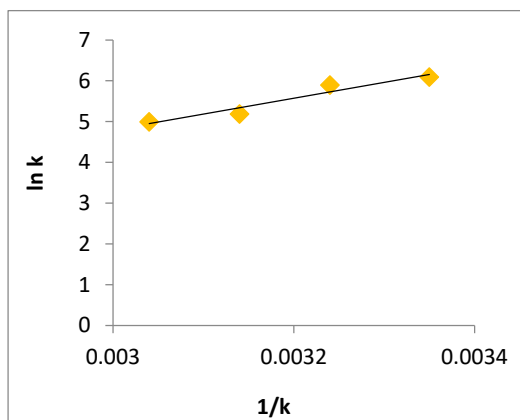
$$\Delta G = \Delta H - T\Delta S \tag{4}$$

Which is:

R is the gas constant (8.314 × 10<sup>-3</sup> k J/mol.deg), k is the adsorption equilibrium constant which was calculated at each temperature (T) from the following equation (Taqe et al., 2015).

$$k = \frac{Q_e \cdot W_g}{C_e \cdot V (L)} \quad (5)$$

Which:  $Q_e$  is the adsorption capacity of the metal ions, (**mg/g**),  $m$  is the quantity of NiMo catalysts, (**g**),  $C_e$  is the concentration of the equilibrium after the removal lead (II), (**mg/L**),  $v$  is the volume of the aqueous solution containing Pb (II) ions, (**L**). The results obtained have been given in Table (3) and Figure (6). ( $\Delta G^*$ ), ( $\Delta H^*$ ) and ( $\Delta S^*$ ) values were listed in Table (4).



**Fig. 6.** The Van 't Hoff Plot for adsorption of Pb (II) ions on regenerated NiMo/ $\gamma$ Al<sub>2</sub>O<sub>3</sub>.

**Table 4-** The values of the thermodynamic functions for the adsorption of Pb (II) on NiMo/ $\gamma$ Al<sub>2</sub>O<sub>3</sub> surfaces at different temperatures

Metals	T/ K	$\Delta G^*$ kJ/mol	$\Delta H^*$ kJ/mol	$\Delta S^*$ J/mol. K
Pb (II) ions	298	-16.8799	-29.4024	-43.6850
	308	-15.0966		
	318	-15.2911		
	328	-15.4099		

The free energy ( $\Delta G^*$ ), enthalpy ( $\Delta H^*$ ), and entropy ( $\Delta S^*$ ) changes have been recorded in Table (3.22). The negative  $\Delta G$  values at different temperature meant that the adsorption process was thermodynamically spontaneous. The value of  $\Delta H$  was negative, indicating the exothermic nature of the adsorption. This meant that the thickness of the boundary decreased with the rise in the solution temperatures, thus as a result of an increase in the kinetic energy of the adsorbate species at high temperatures, a decrease in the adsorption was observed, and  $\Delta S$  negative value showed the decreasing randomness at solution– sorbate interface during the adsorption process. On the other hand, from the values of  $\Delta H$ , it was obvious that physical adsorption took part in the adsorption process (Ali et al., 2016).

## Conclusion

The spent NiMo/Al<sub>2</sub>O<sub>3</sub> catalyst which is treated with n-hexam and oxalic acid, was used to remove the soluble coke and fluoride element. The amount of the soluble coke was (4.327) %, and the

amount of the fluoride element which was removed by this acid was (7.158) %. Thus, the sample obtained was structurally characterized using AFM techniques, and the results showed that the particle size was less than 100 nm. And finally, the adsorption batch was used to separate the lead ions from their aqueous solution. The results indicated that the removal efficiency of more than 99% when rejuvenated NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts was used, compared with 51 % removal when a non-rejuvenated one was applied at the optimum condition of: pH of 6, the contact time of 20 minutes, the temperature of 25 °C, the NiMo/Al<sub>2</sub>O<sub>3</sub> weight of 0.2gm, and the adsorbate concentration of 100ppm. The negative values of the thermodynamic functions of  $\Delta G$ ,  $\Delta H$  and  $\Delta S$  for the adsorption of Pb<sup>+2</sup> ion in regeneration NiMo/ $\gamma$ Al<sub>2</sub>O<sub>3</sub> on the adsorbents indicated that the adsorption processes were spontaneous, exothermic, and there was less randomness at the solid– solution interface.

## References

- Alfa, Y. M., Hassan, H., and Nda-Umar, U. I. (2012). Agricultural waste materials as potential adsorbent for removal of heavy metals from aqueous solutions. *International Journal of Chemical Research*, 2 (2): 48-45.
- Ali, R. M., Hamad, H. A., Hussein, M. M., and Malash, G. F. (2016). Potential of using green adsorbent of heavy metal removal from aqueous solutions: adsorption kinetics, isotherm, thermodynamic, mechanism and economic analysis. *Ecological Engineering*, 91: 317-332.
- Awan, M. A., Qazi, I. A., and Khalid, I. (2003). Removal of heavy metals through adsorption using sand. *Journal of Environmental Sciences*, 15(3): 413-416.
- Cheng, Z., Tan, A. L. K., Tao, Y., Shan, D., Ting, K. E., and Yin, X. J. (2012). Synthesis and characterization of iron oxide nanoparticles and applications in the removal of heavy metals from industrial wastewater. *International Journal of Photoenergy*, 2012: 1-5.
- Farghali, A. A., Bahgat, M., Allah, A. E., and Khedr, M. H. (2013). Adsorption of Pb (II) ions from aqueous solutions using copper oxide nanostructures. *Beni-Suef University Journal of Basic and Applied Sciences*, 2(2): 61-71.
- Gupta, V. K., Agarwal, S., and Saleh, T. A. (2011). Synthesis and characterization of alumina-coated carbon nanotubes and their application for lead removal. *Journal of hazardous materials*, 185(1) :17-23.
- Han, R., Li, H., Li, Y., Zhang, J., Xiao, H., and Shi, J. (2006). Biosorption of copper and lead ions by waste beer yeast. *Journal of Hazardous Materials*, 137 (3): 569-1576.
- Kumar, B.R., and Rao, T.S. (2011). Effect of substrate temperature on structural properties of nanostructure zinc oxide thin films prepared by reactive DC magnetron sputtering. *Digest Journal of Nanomaterials and Biostructures*, 6(3) :1281-1287.
- Li, N., and Bai, R. (2006). Highly enhanced adsorption of lead ions on chitosan granules functionalized with poly (acrylic acid). *Industrial & engineering chemistry research*, 45(23) :7897-7904.

- Marafi, M., and Stanislaus, A. (2003). Options and processes for spent catalyst handling and utilization. *Journal of hazardous materials*, 101(2): 123-132.
- Marafi, M., and Stanislaus, A. (2008). Spent hydroprocessing catalyst management: A review: Part II. *Advances in metal recovery and safe disposal methods. Resources, Conservation and Recycling*, 53(1-2) :1-26.
- Onundi, Y.B., Mamun, A.A., Al Khatib, M.F., and Ahmed, Y.M. (2010). Adsorption of copper, nickel and lead ions from synthetic semiconductor industrial wastewater by palm shell activated carbon. *International Journal of Environmental Science and Technology*, 7 (4): 751-758.
- Pereira, A. L. D. S., Silva, C. N. D., Afonso, J. C., and Mantovano, J. L. (2011). The importance of pre-treatment of spent hydrotreating catalysts on metals recovery. *Química Nova*, 34(1): 145-150.
- Rozaini, C.A., Jain, K., Oo, C.W., Tan, K.W., Tan, L.S., Azraa, A. & Tong, K.S. (2010). Optimization of nickel and copper ions removal by modified mangrove barks. *International Journal of Chemical Engineering and Applications*, 1(1): 84-89.
- Saeed, A., Akhter, M. W., and Iqbal, M. (2005). Removal and recovery of heavy metals from aqueous solution using papaya wood as a new biosorbent. *Separation and Purification Technology*, 45(1): 25-31.
- Savage, N., & Diallo, M. S. (2005). Nanomaterials and water purification: opportunities and challenges. *Journal of Nanoparticle research*, 7(4-5): 331-342.
- Sheela, T., Nayaka, Y. A., Viswanatha, R., Basavanna, S., and Venkatesha, T. G. (2012). Kinetics and thermodynamics studies on the adsorption of Zn (II), Cd (II) and Hg (II) from aqueous solution using zinc oxide nanoparticles. *Powder Technology*, 217: 163-170.
- Sirichote, O., Innajitara, W., Chuenchom, L., Chunchit, D., and Naweekan, K. (2002). Adsorption of iron (III) ion on activated carbons obtained from bagasse, pericarp of rubber fruit and coconut. *Songklanakarin J. Sci. Technol.* Vol. 24 No. 2 Apr.-Jun. 2002, pp.235-242.
- Srivastava, V. C., Mall, I. D., & Mishra, I. M. (2006). Equilibrium modelling of single and binary adsorption of cadmium and nickel onto bagasse fly ash. *Chemical Engineering Journal*, 117(1) :79-91.
- Taqe, R. M. M. (2015). Removal of some water pollutants using newly synthesis organoclays. Iraq: M.Sc. thesis, College of Science, University of Al- Mustansiriyah.
- Thomas, J. M., and Thomas, W. J. (2014). Principles and practice of heterogeneous catalysis. John Wiley and Sons.
- Uzun, I., and Güzel, F. (2000). Adsorption of some heavy metal ions from aqueous solution by activated carbon and comparison of percent adsorption results of activated carbon with those of some other adsorbents. *Turkish Journal of Chemistry*, 24(3): 291-298.
- Zeng, L., and Cheng, C. Y. (2009). A literature review of the recovery of molybdenum and vanadium from spent hydrodesulphurisation catalysts: Part I: Metallurgical processes. *Hydrometallurgy*, 98(1-2) : 1-9.