Kinetic Studies on Enhanced Mercury Adsorption in Zeolite Nay and Waste Fcc Catalyst

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ABSTRACT: The mercury (II) removal was studied using two adsorbents: waste FCC Catalyst and NaY zeolite, those materials were characterized under test such as TGA, XRD, IR, immersion enthalpy and N_2 adsorption isotherms. The zeolite superficial area is 773 m^2/g and that of the FCC catalyst is 135 m^2/g. The maximum mercury adsorption capacity was 1.8561mg/g for the FCC catalyst and 2.6845 mg/g for the zeolite. The equilibrium isotherms were described with the Langmuir and Freundlich linear models. Besides, the kinetics was described with the Lagergren and Pseudo-second order, the latter fit better in the experiments. After the use of the adsorbents, they were regenerated, acquiring their superficial areas as 675 and 87 m^2/g for the NaY zeolite and the FCC catalyst, respectively.

Key Words: Mercury removal, Adsorption Kinetics, NaY Zeolite, waste FCC Catalyst.

1 INTRODUCTION

Without earth`s water, no living organism can grow or reproduce if there is scarcity of this recourse, besides the water availability is necessary not only for the Industry but also for the human life. Heavy metals, as mercury, are contaminant pollutants that have to be treated to prevent environmental and community disasters.

The present investigation compares the mercury (II) adsorption kinetics using two materials, the NaY zeolite and the waste FCC catalyst, the latter provided by petroleum Colombian Company (ECOPETROL). These materials were characterized with nitrogen adsorption isotherm at 77K, XRD (X-ray diffraction), FTIR (Infrared spectra), TGA (Thermo gravimetric analysis) and immersion calorimetric test.

The adsorption process was studied from two kinds of solutions ($HgCl_2$+H_2O and $HgCl_2$+H_2O +$CaCl_2$) [1], with different conditions such as temperature (298.55K and 308.15K), residence time and pH. The linear models of Langmuir and Freundlich were used to describe the mechanism, and both fit differently based on each experiment. Adsorption kinetics was analyzed with the Lagergren and Pseudo-second order, the latter represents better the adsorption system.

2 MATERIALS Y METHODS

2.1. Materials

The adsorbents were (A) Waste FCC catalyst which is a complex material composed by Y zeolite, Kaolin and other additives. After the process in ECOPETROL this adsorbent has from 0.2 %wt to 0.4%wt of Coke[2], and (B) the NaY zeolite, its structure has low density, catalytic and adsorbent properties and a

high hydration level. All the chemicals used in this investigation were not purified, and all the solutions were diluted with distillate water.

2.2. Methods

2.2.1. Material Characterization

Both adsorbents were subject to a different characterization tests presented next:

1. *BET model:* It starts with the development of the polarization theory of DeBoer y Zwicker, which is based on the dipolar moments happening when the adsorption layers are forming, it permits know the surface area of the material within other characteristics[3].
2. *X-ray diffraction:* It shows the crystalline structure of the solids. When the ray is directed towards the solid, it will generate a diffraction pattern based on Bragg`s law.
3. *Infrared spectra:* when the electrons absorb radiation, they pass from a low energy level to a higher one, increasing their energy. This process results in vibrations of different intensity showed in specific regions of the spectra [4].
4. *TGA and DTA:* TGA test determine the weight changed and the structure degradation in the solid being subject to temperature ramps under an inert atmosphere. While DTA compare between two materials temperature variations and behaviors.
5. *Immersion Enthalpy:* A solid immersed into an inert liquid generates heat; this immersion heat is related to a layer formation over the solid surface. The immersion enthalpy is an enthalpy change at constant temperature that develops when the solid is submerged into the liquid and it does not react or dissolve [5].

2.3. Quantification of mercury

This method is based on the radiation absorption at 253.7 nm that mercury atomic vapour suffers; in order to do this is necessary to use cold vapour without flame. With this process the mercury is reduced to its elementary state following these reactions:

$$2MnO_4^- + 16H^+ + 5Hg^0 \rightarrow 2Mn^{2+} + 5Hg^{2+} + 8H_2O \quad (1)$$

$$MnO_4^- + 8H^+ + 5Hg^+ \rightarrow Mn^{2+} + 5Hg^{2+} + 4H_2O \quad (2)$$

$$Sn^{2+} + Hg^{2+} \xrightarrow{H^+} Hg^0 + Sn^{4+} \quad (3)$$

The mercury vapour is drag by an inert gas along an absorption cell made of quartz: this cell is aligned with the spectrophotometer light beam. This experiment produces a signal proportional to the number of free atoms in the cell [6].

2.4. Adsorption process

2.4.1. Equilibrium studies

The aqueous isotherms were made at two different temperatures (298.55K and 308.15K), controlling pH at 9- 10.5 to be sure that the Ion 2+ is, actually, present in the solutions. The mercury concentrations used were varied from 50 to 700 ppm and the adsorbent doses were between 40 and 200 mg.

1. *Langmuir model:* this model was formulated in 1918, and was the first model trying to interpret the adsorption phenomena, it has the following assumptions [7]: First, The whole surface has the same adsorption activity, and then is a flat surface and energetically homogeneous. Each particle is going to be adsorbed just for one active site. Second, There is not interaction between the adsorbed particles. Finally, The process is directed by just one mechanism and it happens in the monolayer.
The Langmuir Isotherm is presented next:

$$\theta = \frac{KC_e}{1-KC_e} \tag{4}$$

2. *Freundlich model:* Generally this model is used in aqueous adsorption processes and has the following assumptions: The adsorption process is not happening only in the monolayer, The active sites energy is not the same and the adsorption and desorption velocities varies with the force or the energy of each site. The Freundlich model is represented by the following equation:

$$v_{ad} = K_f C_e^{1/n} \tag{5}$$

K_f is the Freundlich adsorption coefficient and n is an empirical coefficient. Suggestions about better process fit have been made: with some systems is best the Freundlich model [8].

2.4.2. Kinetics studies

With an initial concentration of 400 ppm was carried out the experimentation, each sample was taken every 30 minutes during 4 hours. The results were approached to the equation of Lagergren first order:

$$Log(q_e - q) = Log(q_e) - \frac{K_{ad}t}{2.303} \tag{6}$$

Where q and q_e are the amount of mercury adsorbed (mg/g) at some time t (min) and at the equilibrium time, respectively. In a logarithmic scale should be prepared a figure with (q_e-q) on the y-axis and t on the x-axis, this, in order to calculate the adsorption constant, K_{ad} [9].
Second, the pseudo-second order was determined along with its constant, K_2 (7th equation). As well as the first order, q (mg/g) is the amount adsorbed at some time t (min), and q_e is the amount adsorbed at the equilibrium time [10].

$$\frac{t}{q} = \frac{1}{K_2 q_e^2} - \frac{t}{q_e} \tag{7}$$

3 RESULTS AND DISCUSSION

3.1. Materials characterization

1. *N_2 adsorption isotherm:* The analysis conditions are shown on Table 1. The adsorbate was nitrogen and the bath temperature was 77.4 K for both adsorbents. The Isotherms for the materials are shown in Figure 1 and 2, for the waste FCC catalyst and NaY zeolite, respectively. The FCC isotherm is described by the isotherm type II because of its small area, and its micropores volume, besides the isotherm shows a fast saturation on the monolayer. On the other hand, the NaY zeolite is correlated with the isotherm adsorption type I, and the reason is that the monolayer saturation occurs at a higher relation between the pressures, P/Po.

Table 1. Analysis Conditions for the nitrogen adsorption.

Conditions	Waste FCC	NaY Zeolite
Weight sample	0.1242 g	0.0895 g
Degasification temperature	250 °C	250 °C
Degasification time	23.0 hrs	12.0 hrs
Analysis time	622.2 min	191.2 min

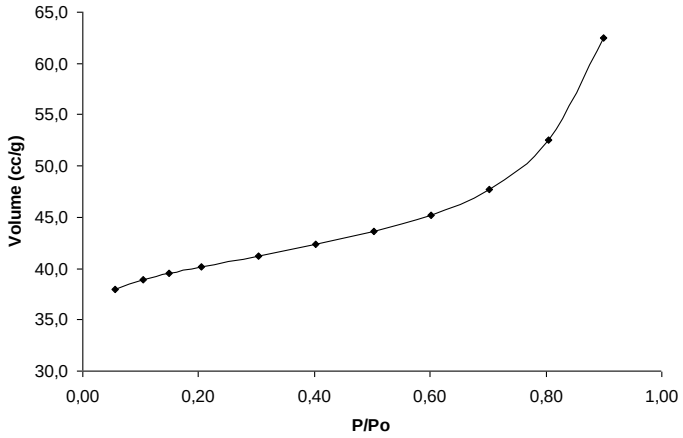

Figure 1. N_2 adsorption isotherm, waste FCC catalyst.

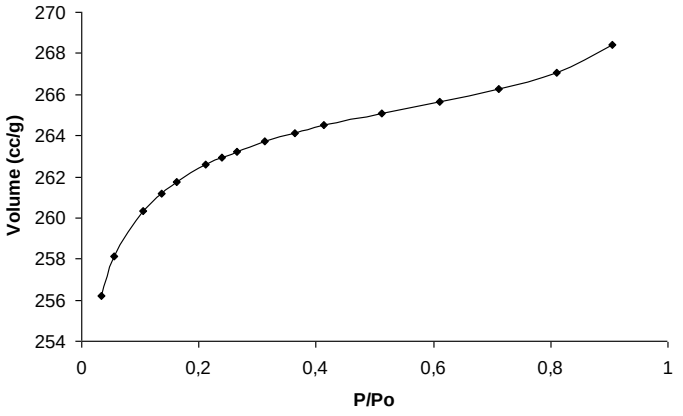

Figure 2. N_2 adsorption isotherm, NaY zeolite.

The surface area was calculated. Is 135 m²/g for the waste FCC catalyst, and 773 m²/g for the NaY zeolite, this let conclude that the mercury adsorption should be more in the zeolite structure than in the structure of the catalyst. Moreover the pore diameter of the two materials are 12.0 Å (NaY) and 14.2 Å (FCC) and this allows the mercury Ion (diameter: 2.2 Å) to enter in the structure of the two adsorbents. The hysteresis for the two adsorbents shows the possible presence of mesopores. But in both structures the micropores proportion is more than the mesopores volume. It is possible that the micropores were not filled in completely at the relative partial pressure used, and then the mesopores could be filled before the complete filled of the micropores.

2. *X-ray diffraction:*

In XRD pattern of the waste FCC catalyst are some aluminum oxides peaks at 2-theta angles of 6, 11, 12, 16, 21, 25, 28 and 39 and comparing between the standard pattern is possible to find the Faujasita structure [11]. The standard peaks of the NaY zeolite are: 2-theta= 6, 10, 12, 15, 17, 21, 24, 31 and 35 [12] present on the pattern obtained in XRD pattern of the NaY zeolite. The highest peak in the FCC pattern is at 26.85 Bragg angle, while the NaY zeolite is 6.22. Those angles are typical for an amorphous structure (FCC) and a crystalline structure (NaY). Besides, the crystalline percentage is 28 for the waste FCC, and 95.7 for the zeolite [12, 13].

3. *Infrared spectra:* The infrared spectra of the waste FCC has the following characteristic bounds: at 3443 cm^{-1} wavelength are O-H stretching vibrations, at 1634 cm^{-1} C=N stretching, at 1402 cm^{-1} NOx vibrations, at 1012 cm^{-1} flexion of the bound C-OH, at 789 cm^{-1} C-Cl stretching, and at 460 cm^{-1} can be presence of sodium. The presence of the sulfur compounds in the waste FCC can be an advantaged to the mercury adsorption due to the affinity between those compounds [14]. For the NaY zeolite, the broad bands observed at 3420, 1631, 1082.76 cm^{-1} are due to stretching of O-H, C=S and C-O bounds, respectively. The other visible bands in the up corner of the figure are at 835.76, showing characteristic bounds of C=C-R flexion, and at 612.93 cm^{-1} C-S stretching.

4. *Thermal analysis:* the waste FCC catalyst´s TGA shows the high thermal stability of the structure and permits recognize the low amount of water molecules present on the FCC, moreover the DTA shows that the waste material suffers an exothermic process while is heated between 100 to 1000°C The TGA for the NaY zeolite shows the high degree of hydration of the compound, because the weight lost that suffers is about 25% of its initial weight, before the 400ºC ramp. There is a lose of water molecules, and let know that the structure will not lose another kind of molecules different from water ones, at the same time is developed an endothermic process, that turns into an exothermic process when the most water molecules had been lost. After the flat region occurs an exothermic process; this allows a degradation of the zeolitic structure after the 800ºC ramp. In this investigation the highest temperature, except the recuperation one, was 35ºC and then there was not structural degradation for neither of the two materials.

5. *Immersion Entalphy:* this test was made to probe that the process was going to be physical. And effectively, the immersion process was physical for both materials, these can be observed with the low heats produced when the solid was wet with both solvents. With this experiment is possible to appreciate that both adsorbents have the capacity to accept the mercury Ions because its diameter is 2.2 Å, and the diameter of the dichloromethane is 3.3 Å and 6.0 Å the one of the tetrachloride, both bigger than the diameter of the mercury. Furthermore, the immersion enthalpy developed let know that the surface area

of the NaY zeolite is bigger than the one of the waste FCC catalyst due to the proportionality between the heat of immersion and the surface area. It also shows the difference in adsorption capacity of the two adsorbents.

3.2. Adsorption Process

The adsorption isotherms and the kinetics experiments were performed according to Table 2:

Table 2. Experimental conditions.

Condition	Meaning	1	2	3	4	5	6	7	8
Tempera-	25.4 ºC	X	X	X	X				
	35ºC					X	X	X	X
pH	between 9 and 10.5	X	X	X	X	X	X	X	X
Solution	H_2O + $HgCl_2$(S1)	X	X			X	X		
	H_2O+ $CaCl_2$+$HgCl_2$(S2)			X	X			X	X
Adsorbent	FCC	X		X		X		X	
	NaY		X		X		X		X

3.2.1. Adsorption Isotherms

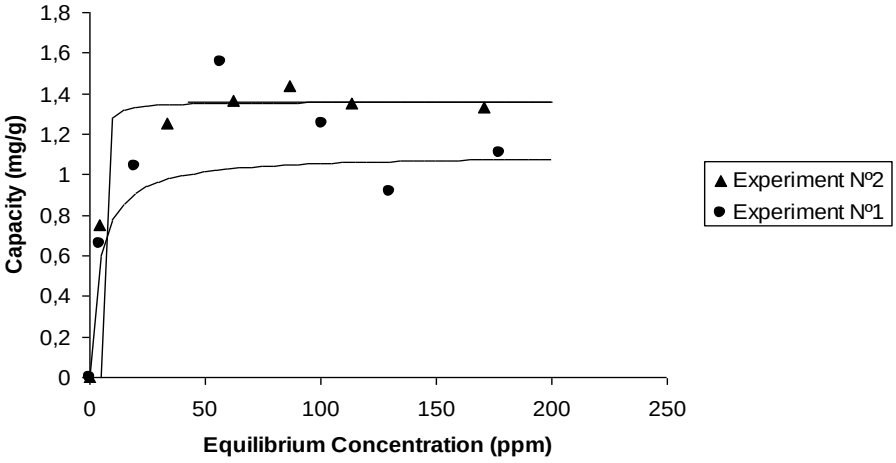

Figure 3. Two of the Aqueous Isotherm, T=25ºC, pH = 9-10.5.

Table 3. Adsorbent´s capacity for each experiment.

Experiment	Q(mg/g)
1	1.4671
2	1.0946
3	1.8561
4	1.4550
5	1.3301
6	2.4162
7	2.0629
8	2.6845

To verify the adsorbent behavior for each experiment was made a duplicated and for the analysis was taken into account the pH, solution, temperature and doses of the adsorbent effects.

Effect of pH: In the experimentation two pH´s, below 2 and above 9, were going to be used [15]; this to guarantee the mercury Ion form (Hg^{2+}) in the solutions. But below pH=3 the structure of the adsor-

bents collapsed and no profitable results were obtained, reason for which there are not results of that kind presented in this paper and all the experimentation process were carried out with pH values between 9 and 10.5. Th pH value was controlled with HCl and NaOH solutions.

Effect of temperature: At 25.4ºC the capacity for the waste FCC catalyst was 1.4671 mg/g and 1.0946 mg/g for the NaY (S1), while at 35ºC the capacity of the FCC decrease 9.33% and the zeolite capacity increased 54.7%. So, the capacity of the NaY increases with temperature but is important to not carry out the process with high temperatures in order to not accelerate the desorption process.

Effect of the solution type: The adsorption was higher using the $CaCl_2$ solution. At 25ºC the capacity of both adsorbents increased 43% with the waste FCC and 24.8% for the NaY. While at 35ºC the difference between solutions were increased 8.7% for the zeolite and 35.4% For the catalyst this can be advantageous for the process due to no contaminant pollutant is alone in the wastewater, and is necessary to involve other species in the removal of this toxic compounds.

Effect of doses and type of adsorbent: How it was mentioned in the effect of the temperature the waste FCC is best at lower temperatures (1.4671 – 1.8561 mg/g), on the contrary the zeolite mercury removal was higher at higher temperatures. The removal could be higher if were used more adsorbent quantity, although for investigation experimentation is not necessary use to much adsorbent. These conditions can be improved for the process scale up.

3.2.2. Adsorption mechanism

A good linear approach is given by a correlation coefficient $R^2 > 0.98$, however in this process was not possible to obtain $R^2>0.9$ for Freundlich, except for the first experiment that has a $R^2= 0.7853$. There were experiments where Freundlich adjust better than Langmuir and vice versa. Reason for which the adjustments were individually for each experiment, in other words, the Isotherms were adjusted with the model that has higher correlation coefficient. Some approximations are showing next:

Table 4. Langmuir and Freundlich parameters for the experiments.

	Langmuir			Freundlic		
Experi-	**K(g/l)**	**V_m(mg/g**	**R^2**	**K_f**	**n**	**R^2**
1	1,4	1,3564	0,997	0,9	12,936	0,7
2	0,2	1,0866	0,987	0,5	7.8452	0,9
3	0,0	1.5873	0,797	0,0	0,9576	0,9
4	0,0	2,2872	0,897	0,0	1,3493	0,9
5	0.7	1,6326	0,943	0,2	2,5322	0,9
6	1.9	3,0959	0,873	0,0	1,0333	0,9
7	1,7	0,0325	0,281	0,0	0,9401	0,9
8	0,0	5,8445	0,925	0,1	1,6725	0,9

3.2.3. Adsorption Kinetics

As well as 25.4ºC experiments the 35ºC experiments have a strong adsorbate-adsorbent interactions, besides when the zeolite is used in the batch procedure the Lagergren graphics (Y-Axis) has larger differences values, while the pseudo-second order has not that differences (less than 0.95%). For that fact and due to the coefficient correlation obtained in the calculations has been chosen the pseudo-second order kinetics to model the system. The Kinetics approaches are showed in Figure 4 and 5:

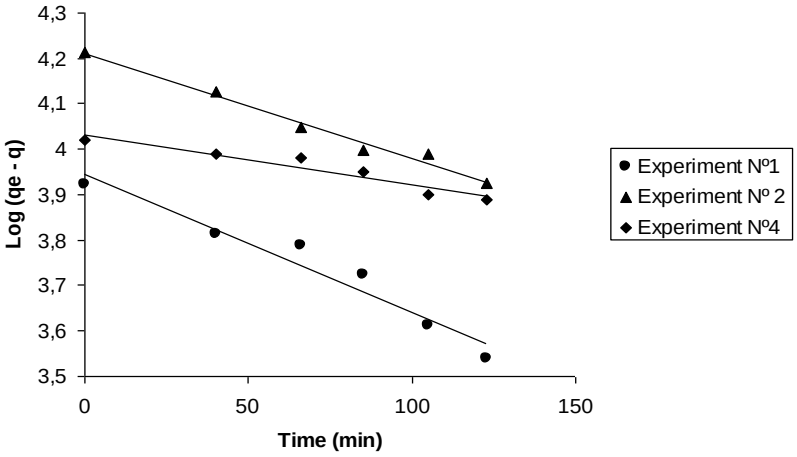

Figure 4. Lagergren approaches for some experiments.

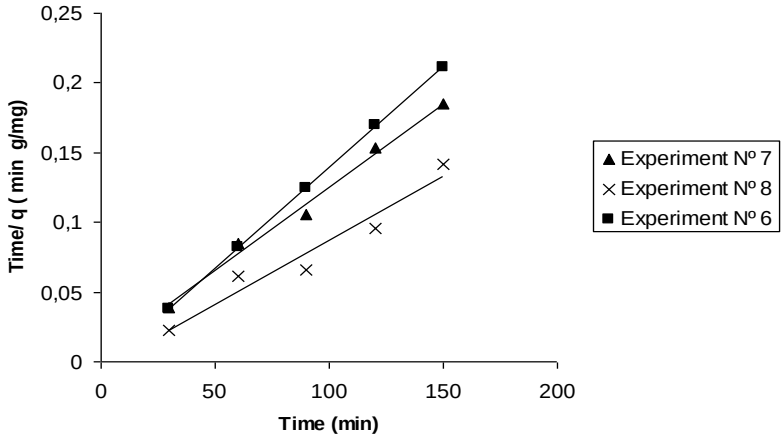

Figure 5. Pseudo-second order approaches for some experiments.

Table 5. Lagergren y Pseudo-second order parameters for the Hg(II) adsorption.

Order		**Lagergren**		**Pseudo**	**second**	
Experiment	**$K_1(min^{-1})$**	**q_e (mg/g)**	**R^2**	**$K_2(min^{-1})$**	**q_e (mg/g)**	**R^2**
1	0.069	2.209	0.9838	0.058	1.523	0.9456
2	0.052	1.625	0.9482	0.042	1.00	0.8834
3	0.043	1.604	0.9104	0.038	1.565	0.8830
4	0.025	2.107	0.9235	0.019	1.004	0.9376
5	0.009	1.262	0.8196	0.008	2.431	0.9896
6	0.006	2.176	0.8309	0.010	3.768	0.9457
7	0.011	1.21	0.9552	0.009	1.111	0.9464
8	0.006	2.288	0.8846	0.011	3.633	0.9898

4 CONCLUSIONS

The mercury removal capacity for the waste FCC does exceed neither the zeolite capacity, nor other materials in other studies; this is because of its low surface area. Although, the sulphur compounds in the waste FCC catalyst, could helped in the adsorption process.

The Pseudo-second order can model the mechanism well to scale up the process.

Finally, is important for this type of process to know the ionic charge of the surface and give an accurate treatment to the solution involved in the adsorption.

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