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Arsenic removal by clay and Y zeolite samples: a kinetic and thermodynamic study

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Abstract: *This study dealt with the removal of As(V) by a clay sample (KO2) from Burkina Faso, and two sodic and protonic Y type zeolite samples. The clay sample contained both kaolinite and illite phases. The kinetic study exhibited that adsorption was significantly faster for zeolites than for clay sample because of ease of access to porosity. The role of extra-framework Na+ cation in the restriction of As(V) to zeolite porosity was also highlighted. Despite differences in adsorption kinetics adsorption capacities were fairly close for the studied samples. The concentration of active site on the clay surface was higher than the concentration of active sites in zeolites micropores. Framework aluminol groups were mainly involved in As(V) complexation by zeolites.*

Keywords*: clay, zeolite, As(V), removal, water, Burkina Faso.*

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I. Introduction

Arsenic is a toxic element for human and environment. In water it is responsible for dermatitis, skin cancer [1], neurological and cardiology diseases, enlargement of liver, heart diseases and internal cancers [2-6]. The occurrence of arsenic in groundwater is widespread [7-12] with concentrations above the limit of 10 µg/L recommended by WHO and US-EPA [13-14]. Several techniques have been implemented for arsenic removal from water such adsorption on oxides and activated carbon [15-21], anion exchange [22], reverse osmosis [23] or coagulation methods [24-25]. The adsorption over both natural [26-27] and synthetic zeolites [28-30] was widely investigated. Natural clay samples were also studied for arsenic removal in water [31-33]. Zeolites and clays showed interesting adsorption capacities due to the presence of aluminol and silanol hydroxyl groups in their structures.

In the present study the removal of arsenic (V) in water was studied for a clay sample from Burkina Faso and two synthetic Y type zeolites, HY(33.93) and NaY(2.5). Both kinetic and thermodynamic aspects were considered for the adsorption of As(V) on zeolite and clay samples.

II. Experimental

HY sample was provided by par Zeolyst International and NaY sample by IFP (Institut Français du Pétrole). The framework Si/Al ratios were respectively 33.93 and 2.5 for HY and NaY. The clay sample was collected in the locality of Koro in the western region of Burkina Faso (West Africa). The localization of the collection site was 11˚09' North latitude and 4˚11' West longitude. The clay sample was referenced as KO2. The analytical grade arsenic (V) was provided by Sigma Aldrich as $Na_2HAsO_4,7H_2O$. The As(V) solutions were prepared with Milli-Q ultrapure water. The adsorption experiments were realized at 30°C. The pH of the solutions was 7.5. As(V) concentrations were determined by a Perkin Elmer AA300 atomic absorption spectrometer with graphite furnace technique.

The physico-chemical characteristics of samples were obtained by several techniques. The surfaces and volumes were determined by nitrogen adsorption-desorption experiments performed at 77K with a Micromeritics ASAP 2010 analyzer. The different clay phases were identified by X-ray diffraction using a Bruker D5005 diffractometer, and by thermal analysis using a TA Instruments SDT-Q600 DTA-TGA analyzer. Thermal analysis were performed under air flow at 60 $mL\cdot min^{-1}$, the temperature varying from room temperature to 900˚C.

Kinetic experiments were realized over HY, NaY and KO2 samples for an As(V) initial concentration fixed at 10 $mg.L^{-1}$. 50 mg of adsorbent was in contact with 20 mL of sorbate in stirring batch reactor. A few amount (≈ 1 µL) of supernatant solution was withdrawn regularly for analysis until its concentration remained constant.

III. Results and discussion

3.1 Sample characterization

The diffractogram of KO2 clay sample is presented on figure 1.

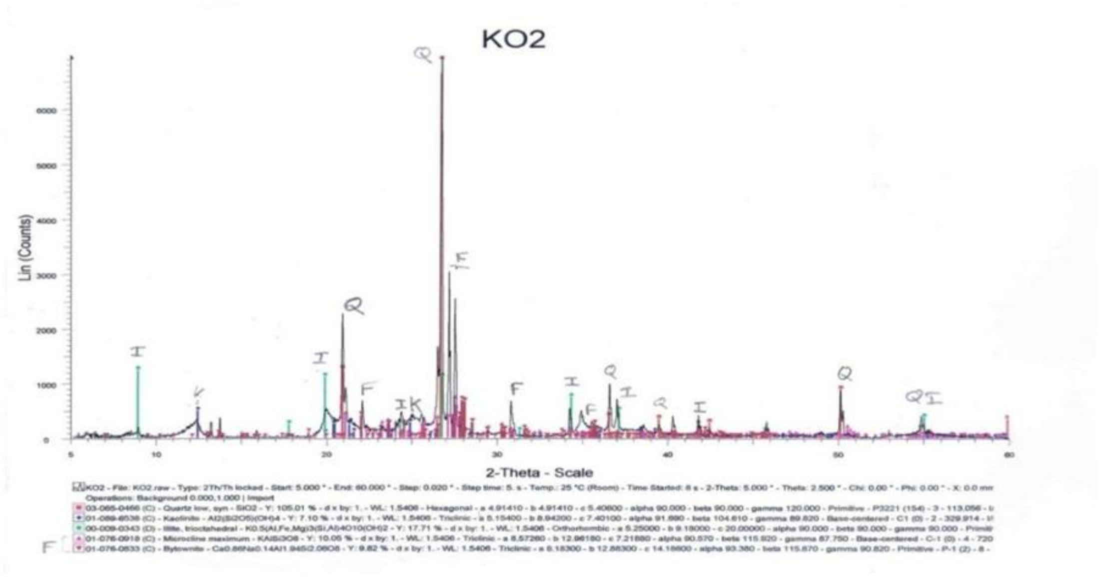

Figure 1: *Diffractogram of KO2 sample*

It appears that KO2 sample is composed by quartz α, feldspar, kaolinite and illite phases. This is confirmed by TGA-DTA results. Indeed, a pick at 455°C associated to kaolinite dehydroxylation [34-35], another one at 449°C associated to illite dehydroxylation [36] and a last one at 573°C indicating a transformation of quartz α into quartz β [37], exhibit the presence of kaolinite, illite and quartz in the KO2 sample.

The surface and porous volume data from nitrogen adsorption-desorption experiments are reported in Table 1.

Table 1: Surface and volume determined N_2 adsorption-desorption at 77K for HY, NaY and KO2 samples.

Samples	Surfaces		Porosity		
	Specific area (m².g^{-1})	Microporous area (m².g^{-1})	Microporous volume (cm^3.g^{-1})	Mesoporous volume (cm^3.g^{-1})	Total volume (cm^3.g^{-1})
KO2	42	7.4	0.0027	-	0.0034
HY	825	791	0.325	0.118	0.449
NaY	852.5	810.2	0.283	0.033	0.3190

The specific area (42 m².g^{-1}) for the KO2 clay sample is significantly lower than the one of zeolite samples (825 and 852.5 m².g^{-1} respectively for HY and NaY). In the case of zeolites the microporous surface is more important than external surface while in the case of clay sample the external surface (34.6 m².g^{-}1) is higher than microporous area (7.4 m².g^{-1}). The specific surface is higher for NaY than for HY. The microporous volume of HY (0,325 cm^3.g^{-1}) is higher than the one of NaY (0,283 cm^3.g^{-1}). The same trend is observed for mesopores. As Na^+ cations are bigger than H^+ protons a reduction of internal porosity access occurs for NaY zeolite, inducing a decrease of accessible pores volumes.

3.2 Kinetic study

The adsorption kinetic of As(V) over KO2, HY and NaY samples was studied. The percentage of adsorbed As(V) versus time is represented on figure 2.

After 3 minutes, 99.98% of As(V) are adsorbed by HY sample. For NaY sample, only 80% are adsorbed after 3 minutes and 100% after 40 minutes. In the case of KO2, 60% are adsorbed after 3 minutes and 100% after 60 minutes.

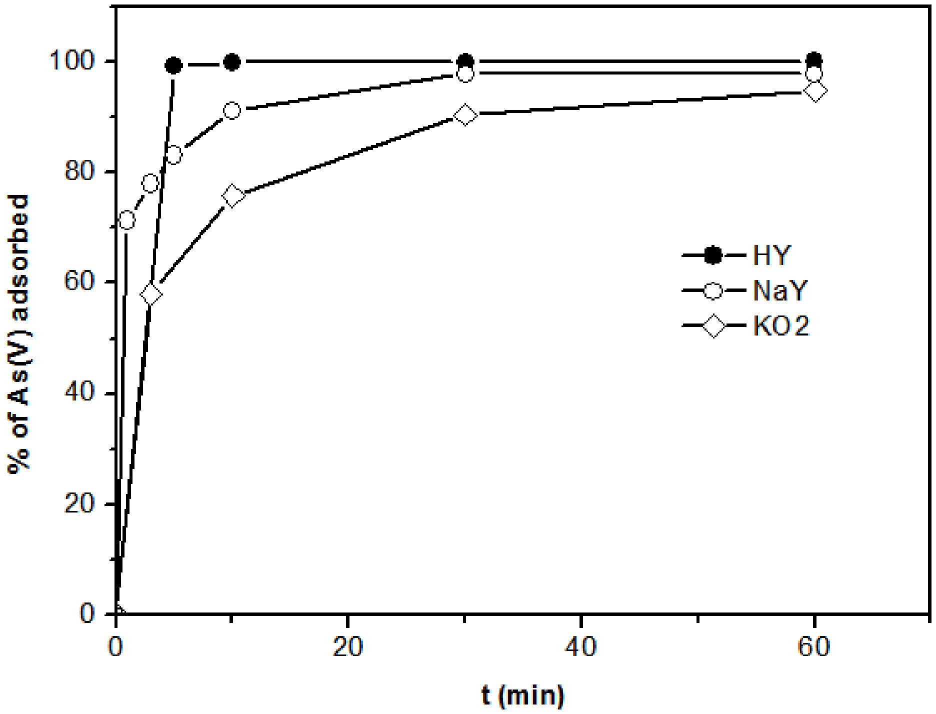

Figure 2: *Adsorption kinetic of As(V) for HY, NaY and KO2 samples*

Adsorption is faster for zeolites than for clay sample. Indeed the interplanar spacing of kaolinite is about 7 Å and the one of illite is about 10 Å. In contrast, the inner cavity of Y zeolites is about 13 Å [38]. So As(V) ions reach the active sites easier and faster for zeolites than for KO2 clay sample. Adsorption rates increase significantly for zeolites by comparison with KO2.

In the case of zeolites, active sites are mainly aluminol sites [30]; most of Al atoms are in the framework, and some are extra-framework [39]. Na^+ cations reduce the access to zeolites micropores where are most of the active sites; this results in a reduction of adsorption kinetic for NaY sample.

The diffusion coefficients were determined by Fick's equation [40]. They are reported in Table 2.

Table 2: Diffusion coefficients determined from Fick's equation.

Sample	Diffusion coefficients (s^{-1})
HY	0.0057
NaY	0.0007
KO2	0.00045

The values of diffusion coefficients show that the diffusion is 10 times faster on HY than on NaY; this can be explained by the steric hindrance due to the size of Na^+ cations. The diffusion is 100 times faster for HY by comparison with KO2 clay sample. As KO2 contains kaolinite and illite phases where interfoliaceous space is maximum 10 Å (illite) and the pores opening of α cages is about 13 Å for HY zeolite, diffusion appears easier on HY sample.

3.3 Isothermal study

The adsorption isotherms were determined for HY, NaY and KO2 samples. Experimental points were well fitted by Langmuir model [41]. The adsorption isotherms are represented on figure 3 where theoretical points from Langmuir modeling are in solid lines.

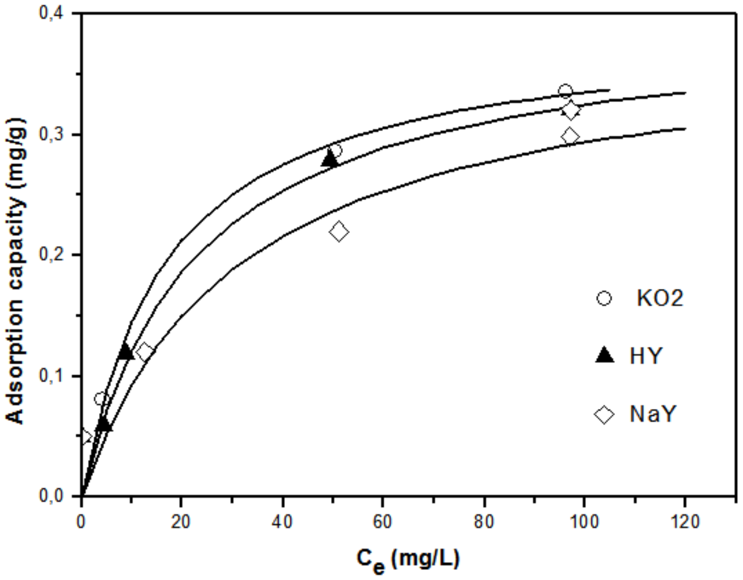

***Figure 3**. As(V) adsorption isotherms on KO2, HY and NaY samples*

Isotherms are type I according to IUPAC classification [42], exhibiting a monolayer adsorption in micropores, without lateral interactions between adsorbed species. According to Langmuir assumptions adsorption occurs also on localized iso-energetic sites. On kaolinite and illite these sites are identified as hydroxyl groups (aluminols and silanols present on the surface [43]. In the case of zeolites aluminols groups are responsible of arsenic uptake [30]; indeed, it was shown [44-45] that adsorption capacity of silanol surface groups in silicon oxide is substantially lower. The determination of BrØnsted acidity according to protocol described by Yonli et al [46] for both HY and NaY samples indicated a concentration of 133 µmol.g^{-1} for HY and no BrØnsted acidity for NaY; on an other hand, Lewis acidity for HY (44 µmol.g^{-1}) was lower than the one for NaY (1039 µmol.g^{-1}). It is well known [46] that BrØnsted acidity is associated to framework Al atoms and Lewis acidity is linked to extra-framework Al atoms. This suggests that As(V) anions are preferentially adsorbed on framework Al atoms rather than extra-framework Al atoms. Adsorption occurs by complexation of terminal aluminols and arsenate oxyanions [30].

Adsorption capacities and sorbent-adsorbent interactions coefficients were determined from Langmuir modeling. Data are reported on Table 3.

Table 3: Langmuir parameters determined for KO2, HY and NaY samples

Sample	Maximum adsorption capacity	Sorbate-adsorbant interaction coefficient
	Q_m (mg/g)	K (L.g^{-1})
KO2	0.392	0.0595
HY	0.399	0.0438
NaY	0.386	0.0318

Unlike diffusion coefficients maximum adsorption capacities are very close for the studied samples. This exhibits that even the adsorption rates are different at equilibrium the uptake level is close. The specific surfaces are very different (42 m^2.g^{-1}, 825 m^2.g^{-1} and 852.5 m^2.g^{-1} respectively for KO2, HY and NaY) when adsorption capacities are close: this suppose that the concentration of hydroxyl active sites on the surface is higher for KO2 clay sample than for zeolites. The specific surface is higher for NaY than for HY and the adsorption capacity is greater for HY sample. This confirms that for Y type zeolites the adsorption capacity depends more on framework Al atoms quantity than specific surface value. Framework Al atoms are in micropores so the greater microporous volume of HY sample favors the As(V) adsorption on this sample.

The adsorption capacity is about 0.392 mg/g for KO2 sample. This value is superior to the adsorption capacity determined for a kaolinite sample by Mohan et al (0.23 mg/g) [47] or Sanou et al (0.67 µg/g) on a lateritic sample of Burkina Faso [48], Maji et al (0.18 mg/g) [49] for a lateritic soil from Bangladesh.

The adsorption capacities for Y zeolites are respectively 0.399 mg/g and 0.386 mg/g for HY and NaY. Mohan et al [47] found 10.49 mg/g for an aluminum loaded shirazu-zeolite, exhibiting the role of Al atoms on the As(V) uptake by zeolites.

The sorbate-adsorbent interaction coefficient K is greater for KO2 (0.0595 L.g^{-1}) as the concentration of aluminol sites is higher on the surface of this sample, and the interfoliaceous space is low, inducing a greater confinement of arsenate ions between the clay layers. Due to the attraction between framework Al atoms and arsenate ions the K value is higher for HY (0.0438 $L.g^{-1}$) than for NaY (0.0318 $L.g^{-1}$): sorbate-adsorbent interaction is greater for HY than for NaY zeolites.

IV. Conclusion

The study of adsorption kinetic showed that adsorption is faster for zeolites than for clay sample due to an easier access to active sites in the case of zeolites. Moreover, the access was favoured for HY sample because of the lack of Na^+ extra-framework cations restricting the access to the porosity. There are significant differences regarding the diffusion coefficients of the samples; the diffusion was 10 times faster on HY than on NaY, due to the steric hindrance of Na^+ cations. The diffusion was 100 times faster for HY than for KO2 clay sample, due to smaller size of interplanar space when compared to the size of HY α cages. Despite significant differences in kinetics, adsorption capacities for KO2, NaY and HY samples were quite close. The active sites identified as hydroxyl groups appeared more concentrated on the surface of KO2 clay sample than in the micropores of zeolites. Framework Al atoms appeared as preferential As(V) adsorption sites in the case of zeolites. For clay samples both silanols and aluminols groups were involved in adsorption of arsenic oxyanions where for zeolites mainly aluminols groups were concerned.

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