ADSORBENȚI PE BAZĂ DE BENTONITĂ PENTRU ÎNDEPĂRTAREA PIRIDINEI DIN SOLUȚIILE APOASE
BENTONITE DERIVED ADSORBENT FOR SEQUESTERING PYRIDINE FROM AQUEOUS SOLUTIONS

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In this paper the adsorption of pyridine, a toxic pollutant, on naturally occurring clay, namely bentonite, was studied at a basic pH and room temperature. Sodium saturated bentonite as well as modified with a cationic surfactant were used and the results compared. The influence of contact time and of the initial pollutant concentration on the pyridine uptake was determined by GC-MS. The adsorbents were characterized before and after being in contact with the pyridine solution by BET specific surface area and porosity, XRD and FTIR analysis.

The hydroxyl groups of bentonite in contact with pyridine solution led to protonated pyridine forms which can be responsible for hydrogen bonds formation and electrostatic interactions with the clay and for surfactant removal. Chemical adsorption prevailed over the partition/physical adsorption in both cases and the process followed the pseudo-second-order kinetics with the Freundlich isotherm model representing well the equilibrium adsorption data. The equilibrium adsorptive efficiency was 82.88% for the surfactant modified bentonite and 97.82% for sodium bentonite, the latter being a better alternative for sequestering pyridine from solution.

Acest articol studiază adsorbția piridinei, un poluant al mediului, pe un material argilos natural şi anume bentonită, la un pH bazic şi la temperatura camerei. S-au folosit bentonita saturată cu sodiu şi bentonita modificată cu un surfactant cationic, iar rezultatele au fost comparate. S-a determinat influența timpului de contact şi a concentrației inițiale a poluantului asupra asimilării piridinei prin GC-MS. Adsorbenții au fost caracterizați înainte şi după contactul cu soluția de piridină prin următoarele metode: aria suprafeței specifice BET şi porozitatea, analiza XRD şi FTIR. Grupările hidroxil ale bentonitei în contact cu soluția de piridină formează compuşi protonați ai piridinei care generează legături de hidrogen şi interacții electrostatice argilă – piridină, putând duce la îndepărtarea surfactantului. Adsobția chimică este preponderentă față de adsorbția fizică/partiția în ambele cazuri, iar procesul decurge conform cineticii unei pseudo reacții de ordinul doi, modelul izotermei de adsorbție Freundlich reprezentând corect datele la echilibru. Eficiența de adsorbție la echilibru este de 82,88 % în cazul bentonitei modificate cu surfactant şi de 97,82 % pentru bentonita saturată cu sodiu, aceasta din urmă reprezentând o alternativă mai bună pentru înde-părtarea piridinei.

Keywords: bentonite, infrared spectroscopy, X-ray diffraction, kinetics, pyridine adsoption

1. Introduction

Due to the development of industrial activities environmental pollution has been considered a major concern in recent years. Pyridine and pyridine derivatives have attracted attention due to their presence in the environment as very toxic pollutants of surface and ground water [1]. A basic N-heterocyclic compound, with a great solubility in water, pyridine can be easily transported through soil and contaminated groundwater [2].

Therefore it is essential to monitor the levels of pyridine in waters. Several methods have been developed to remove pyridine from aqueous solutions among which adsorption, adsorption and electrosorption, biodegradation, ozonization, photocatalytic degradation, electrochemical oxidation and ion exchange [3, 4]. The most

frequently used technique is adsorption due to the fact that it is a convenient method, working at ambient temperature and pressure and that it does not generate hazardous by-products [3].

Bentonite, a naturally occurring clay mineral, consisting mainly of montmorillonite has a good performance in adsorbing contaminants from water [5 - 7]. Montmorillonite (Mt) is a dioctahedral clay composed of stacked alumino-silicate layers. The silica tetrahedral (T) and alumina octahedral (O) are thus interconnected as to generate a layered structure with the composition T-O-T [8 -10]. The aluminosilicate layers have a relatively low negative charge as a result of octahedral substitution of Al by Mg (II), Fe (II) or other divalent metal ions in a central octahedral sheet, charge which can be compensated by inorganic cations (Na^+, Ca^{+2}, etc) in the interlayer space [11]. Therefore bentonite has good performance in adsorbing cationic

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contaminants by cation exchange and organically modified clays have a high capability to remove hydrophobic pollutants from aqueous solutions [12, 13].

To remove pyridine from water and wastewater different adsorbents have been used such as activated carbon, ion exchange resins, zeolites, lignocellulosic-derived modified agricultural wastes, etc [1, 3, 14].

The present study reports a way for pyridine removal from diluted aqueous solutions at basic pH (8 -9) by adsorption on bentonite and organically modified bentonite. At the above given pH pyridine exists as a neutral form and the organic phase should generate a partition medium for capturing it from water but other interactions can occur in the adsorption of pyridine by the clay which will be evaluated by comparison considering the properties of the adsorbent-adsorbat system, the kinetics and adsorption isotherms as well as the efficiency of the separation system. This clay was chosen due to its high swelling potential, high occurrence and low cost.

2. Experimental

2.1. Materials and sample preparation

All the chemicals/reagents used in the present work were of analytical reagent grade, pyridine procured from Merck and cethyltrimethylammonium bromide from Carl Roth. Pyridine (Py), chemical formula: C_5H_5N is the adsobate under investigation and cethyltrimethylammonium bromide (CTAB), chemical formula: $(CH_3)_3N^+C_{16}H_{33}Br^-$ is the cationic surfactant used to modify the clay.

Bentonite was purchased from Gurasada province, Romania. It was purified and saturated with sodium by treating the clay with Na_2CO_3 (Na-Mt). It was mainly composed of polycationic montmorillonite.The cation exchange capacity (CEC) determined by methylen blue test was 45 meq/100g.

The Mt-CTAB was prepared by a conventional ion exchange reaction, by mixing the cationic surfactant and Na-Mt. The amount of CTAB used equals 2 times CEC of Na-Mt. CTAB was dissolved in a mixture of deionized water and ethanol and added to dry Na-Mt. The mass ratio of the mixture was 1 Na-Mt / 2 H_2O / 2 CEC CTAB / 1 EtOH [15]. The mixture was stirred, kept at 60^0C for 24 h, washed with deionized water to remove the free CTAB and then dried at 100^0C for 12 h. The solid product was ground to obtain a powder and marked Mt-CTAB.

The effect of contact time (5min, 10 min, 20 min, 40 min, 60 min, 120 min and 100 mg L^{-1} solution initial concentration) as well as of the adsorbat concentration (50 mg L^{-1}, 75 mg L^{-1},100 mg L^{-1}, 150 mg L^{-1}, 200 mg L^{-1}, 240 mg L^{-1}, 120 min contact time) on the removal of pyridine was determined.

All the adsorption experiments were performed at room temperature (25^0C) with 0.3 g Mt or Mt-CTAB into 100 ml pyridine solution, pH =8 - 9. The samples were mixed, the solid separated and the clear supernatant was analyzed for organics by GC-MS.

2.2. Charcaterization techniques

Nitrogen sorption isotherms at -196°C were recorded on a Micromeritics ASAP 2020 automated gas adsorption system. The samples were outgassed at 150°C for 4h before analysis. Specific surface areas (S_{BET}) were calculated according to the Brunauer-Emmett-Teller (BET) equation. The total pore volume (V_{total}) was estimated from the amount adsorbed at the relative pressure of 0.99. The average pore diameter and pore size distribution curves were obtained using Barrett–Joyner–Halenda (BJH) method from the desorption branch. The powders Na-Mt and Mt-CTAB as such and after pyridine adsorption (Mt-Py and respectively Mt-CTAB-Py) and separation from solution at different adsorption moments were characterized by XRD and FTIR spectroscopy. Powder X-ray diffraction patterns were recorded on a Rigaku's Ultima IV apparatus, with Cu Kα radiation (λ -1.54 Å), operating at 40 kV and 30 mA, 0.02° step size and 5°/min scan speed. Phase identification was performed using Rigaku's PDXL software, with Whole Pattern Fitting (WPF) module, connected to ICDD PDF-2 database. The interlayer distance, the basal spacing, was calculated by Bragg-reflections from data determined by X-ray diffraction. The FTIR samples spectra have been recorded as KBr pellet, with a Perkin Elmer Spectrum GX spectrometer, in the following conditions: range 4000 cm^{-1} to 400 cm^{-1}, 32 scan, resolution 4 cm^{-1}, gain 1. The concentration of pyridine left in the solution was determined in time by GC-MS analysis which was carried out using an Agilent 6890N/5975 B equipment. A HP-5MS 5% phenylmethyl siloxane capillary column was used for the separation of the sample components.

3. Results and discussion

3.1. Layered structure of Montmorillonite by X-ray diffraction

To study the introduction of organics (CTA$^+$ or /and pyridine) in the interlayer spaces of the adsorbent (Mt-CTAB and Mt) the basal spacing of the resultant solid was calculated as shown in Figure 1. For that purpose samples at 10 minutes contact time with a pyridine solution of 100 mg L^{-1} were chosen (Mt-CTAB-Py and Mt-Py) and compared with the parent Na-Mt and surfactant modified solid Mt-CTAB.

An increase of the d_{001} basal spacing for Mt-CTAB (19.66 Å) and Mt-CTAB-Py (21.22 Å)

amples compared to Na-Mt (12.70 Å) indicates that CTA$^+$ and respectively CTA$^+$ and pyridine were intercalated in the layered structure. The d_{001} value for Mt-Py (15.30 Å) shows the introduction of pyridine in the interlayer spaces even in the absence of surfactant.

With the increase of the organic loadings, the d_{001} diffraction peak shifts to lower 2θ region (6.95 - 4.16 θ) indicating the expansion of the interlayer space [6, 15, 16].
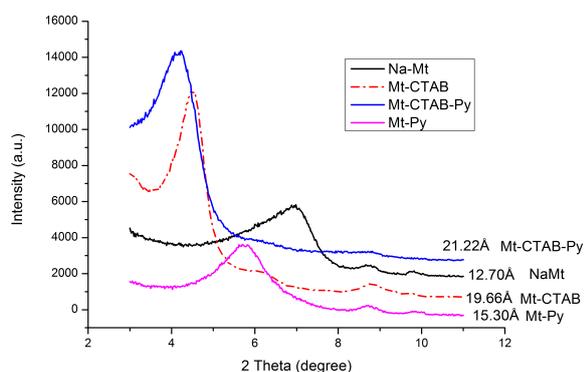
Fig. 1. - XRD patterns of Na-Mt and Mt-CTAB as such and for 10 min in contact with pyridine solution of 100 mg L^{-1} / *Tiparele de difracție de raze X ale Na-Mt și Mt-CTAB ca atare și după un contact de 10 min cu soluția de piridină 100 mg L^{-1}.*

3.2. Interaction of pyridine with the adsorbents reflected by FTIR spectra

FTIR spectra of the adsorbents in contact with pyridine solution 100 mg L^{-1} after 10 min (Mt-Py 10 and Mt-CTAB-Py 10) in comparison with the one of Mt-CTAB at initial time are presented in Fig. 2a. All spectra were normalized, base line correction was performed.

In the range 3500 – 3700 cm^{-1} (fig. 2b) all the samples exhibit multiple bands involving OH stretching of structural hydroxyl groups characteristic to clay [6, 16]. An intense band at approximately 3620 cm^{-1} is attributed to Al-OH groups in the clay structure (Fig. 2a) [17]. The broadness of the band in this region indicates a range of stretching frequencies due to hydrogen bonding either with adsorbed water or with neighboring hydroxyl group [18]. The samples modified by the hydrophobic surfactant have a lower moisture content [18]. In case of the CTAB containing samples, amphiphilic CTAB molecules, with a long hydrocarbon tail, give rise to two intense methylene modes of vibration $v_s(CH_2)$ at 2850 cm^{-1} and $v_{as}(CH_2)$ at 2932 cm^{-1} (Fig. 2a) [15, 16]. In the Mt-Py spectrum two large multiple bands appear in the 2400 - 2500 cm^{-1} and 3000 - 3300 cm^{-1} region which correlated can be attributed to intermolecular –NH and/or –OH association bonds (Fig. 2a) [19]. The band of water molecules appear at about 1648 cm^{-1}) [20] and Si-O streching vibrations at about 1100 cm^{-1}
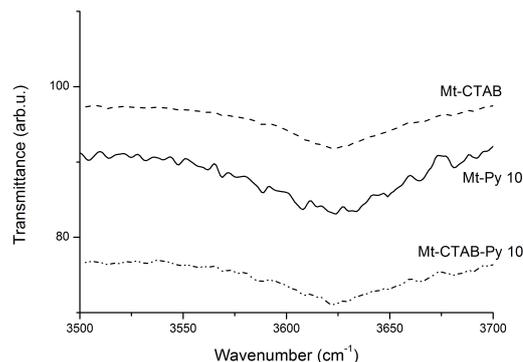
Fig.2a- FTIR spectra of Mt-Py10, Mt-CTAB-Py10 and Mt-CTAB/ *Spectrele FTIR ale Mt-Py10, Mt-CTAB-Py10 şi Mt-CTAB .*
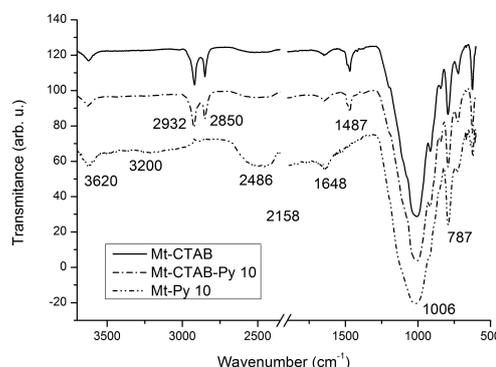
Fig. 2b - FTIR spectra of Mt-Py10, Mt-CTAB-Py10 and Mt-CTAB in the 3500-3700 cm^{-1} range/*Spectrele FTIR ale Mt-Py10, Mt-CTAB-Py10 şi Mt-CTAB în domeniul 3500-3700 cm^{-1} .*
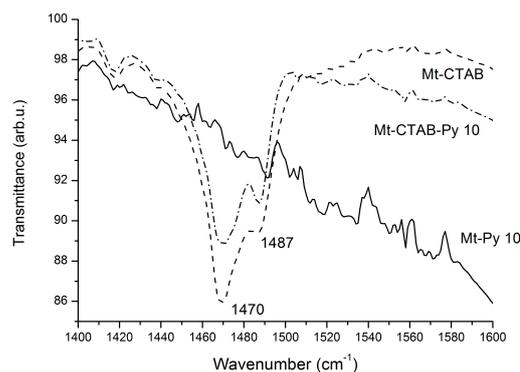
Fig. 2c - FTIR spectra of Mt-Py10, Mt-CTAB-Py10 and Mt-CTAB in the 1400-1600 cm^{-1} range/ *Spectrele FTIR ale Mt-Py10, Mt-CTAB-Py10 şi Mt-CTAB în domeniul 1400-1600 cm^{-1} .*

and 787 cm^{-1} confirm the presence of the inorganic clay (Figure 2a) [6, 16, 17].

The skeletal modes of pyridine should be observed in the 1400 - 1600 cm^{-1} region (Fig. 2c) which in case of Mt-Py sample are represented by a multiple large band [21, 22]. In the spectra of the

CTAB containing samples only the two bands at 1487 cm^{-1} and 1470 cm^{-1} generated by the asymmetric deformation mode of CTAB head group ($\delta_{as}CH_3$-N$^+$) predominate [23].

3.3. BET specific surface area and pore distribution of bentonite and organically modified bentonite

The adsorption isotherms of Na-Mt and Mt-CTAB as well as the pore distribution are represented in Figure 3. Both adsorption-desorption isotherms are type IV, accompanied by a H3 type hysteresis loop, according to IUPAC classification [24]. In the case of NaMt sample, a bimodal pore size distribution can be observed, with maxima at 2.9 and 6.2 nm, while S_{BET} and V_{tot} are 37 m^2/g and 0.115 cm^3/g, respectively. Compared to NaMt, the Mt-CTAB sample exhibits a drastic decrease of textural parameters (S_{BET} = 5 m^2/g, V_{tot} = 0.047 cm^3/g) while the isotherm retains almost the same profile, but the amount of adsorbed nitrogen is much lower.
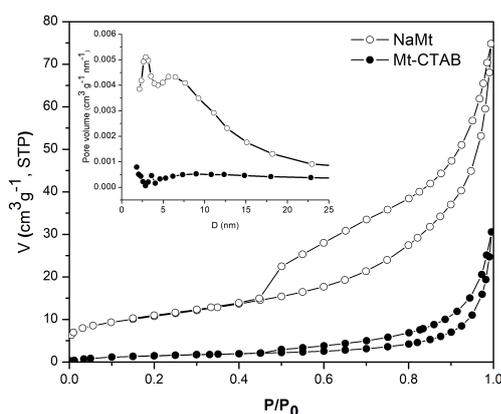
Fig. 3 - Adsorption isotherm and pore distribution of bentonite and organically modified bentonite/*Izotermele de adsorpţie şi distribuţia de pori pentru bentonită şi bentonită modificată organic.*

3.4. Effect of contact time on adsorption of pyridine on bentonite and process kinetics

The profile of pyridine adsorption on Mt and Mt-CTAB as a function of time was studied under reaction conditions: initial adsorbat concentration = 100 mg L^{-1}, adsorbent quantity (m) = 0.3 g/100 ml solution, room temperature, time = 5 min- 120 min.

The adsorption profile shows a quick uptake of pyridine in the first 5 min of interaction time with an adsorptive efficiency of 82.88% for Mt-CTAB and 97.42% for Mt.

This was due to the high concentration gradient between pyridine concentration in solution and on the adsorbent surface and to greater availability of sites on the solid surface. From this time on the pyridine adsorption rate was slower until its concentration in solution reached approximately the value it had after the first 5

minutes. Consequently it was considered that quasi-equilibrium was reached after 120 min. At this moment, the equilibrium concentration of pyridine in case of Mt-CTAB-Py and Mt-Py systems was 17.28 mg L^{-1} and respectively 2.18 mg L^{-1}, the lower uptake of the surfactant modified clay being due to a lower BET surface area and pore volume, as shown above and to a different adsorption mechanism.

Table 1.
The concentration of CTAB in solution at different contact times between Mt-CTAB and the 100 mg L^{-1} pyridine solution / *Concentraţia CTAB în soluţie la timpi de contact diferiţi între Mt-CTAB şi soluţia de piridină de 100 mg L^{-1}*

Contact time (min)/ *Timp de contact (min)*	CTAB in solution (%) *CTAB în soluţie (%)*
5	35.66
10	17.29
20	15.99
40	17.04
60	63.39
120	44.72

In the Mt-CTAB supernatant, CTAB was chromatographically detected besides pyridine as Table 1 illustrates. As previously described [6], the adsorption mechanism represents a synergistic effect of ion exchange, physical adsorption/partition, hydrogen bonding and electrostatic interactions. The protonated pyridine complexes [PyH]$^+$ evidenced by previous studies [21, 25] generate hydrogen bonding and electrostatic interactions with Mt resulting in more efficient adsorption and interlayer penetration in case of the clay as such and CTAB expulsion and a lower uptake in case of organically modified clay.

Partition adsorption of pyridine on montmorillonite has a less important contribution than chemisorption in the process as the following kinetic model will point out.

The adsorption kinetics shows the evolution of the adsorption process with time improving our understanding of the adsorption mechanism. A pseudo-second order model expressed as equation (1) was applied for analysis of kinetic data of adsorption of pyridine on Mt and Mt-CTAB [26, 27]. It is based on plotting *t/q* versus *t* which should give a linear relationship as shown in Fig. 4.

$$t/q = 1/(k_2 q_e^2) + (1/q_e)\, t \quad (1)$$

Where k_2 is the pseudo-second order rate constant, q_e is the sorption capacity at equilibrium, q is the sorption capacity at the moment t. k_2 and q_e can be obtained from the intercept and respectively the slope of the plot. The parameters obtained in equation (1) as well as the correlation coefficient (R^2) are given in Table 2.

Table 2

Kinetic parameters and correlation coefficient for pyridine sorption onto clay and surfactant modified clay considering a pseudo-second order model / *Parametrii cinetici şi coeficientul de corelaţie pentru adsorbţia piridinei pe argilă şi pe argilă modificată cu surfactant considerând modelul unei pseudo reacţii de ordinal doi*

Parameters	Mt-CTAB	Mt
q_e (mg g^{-1})	27.52	32.34
k_2 (g mg^{-1} min^{-1})	-0.0545	0.0291
R^2	0.999	0.998
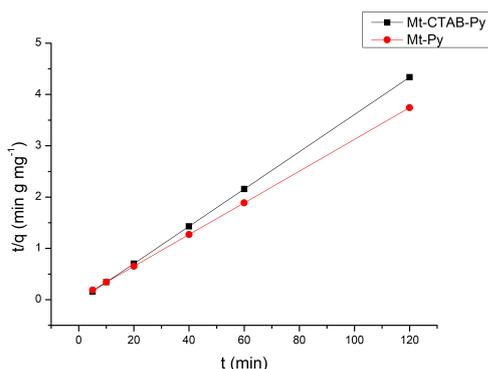
Fig. 4 - Pseudo-second order plots of pyridine adsorption on Mt-CTAB and Mt / *Graficele pseudo reacţiei de ordinul doi pentru adsorbţia piridinei pe Mt-CTAB şi Mt.*

Table 3

Freundlich isotherm parameters for pyridine uptake onto adsorbents/ *Parametrii izotermei Freundlich pentru adsobţia piridinei*

Sorbent	K_f	n	R^2
Mt-CTAB-Py	0.348	1.022	0.999
Mt-Py	0.392	1.045	0.999

The results in Table 2 indicate a less efficient adsorption process for Mt-CTAB, the rate constant has a slightly negative value. This is in accordance with the experimental results regarding pyridine separation from solution determined by chromatography as mentioned above. The sorption capacity at equilibrium (q_e) is very close to the experimental data, which are 27.57 (mg g^{-1}) for Mt-CTAB sorbent and 32.6 (mg g^{-1}) for Mt sample, data obtained for an initial pyridine concentration of 100 mg L^{-1}, 0.3 g adsorbent in 100 ml solution and 120 min contact time.

It can be assumed that pyridine is adsorbed in the interlayer spaces and on the surface sites mainly through a reaction mechanism, the rate-limiting step may be chemisorption for both studied sorbents [26].

3.5. Effect of initial pyridine concentration and adsorption isotherm

Freundlich isotherm model is commonly used to describe non-ideal and reversible adsorption characteristics, inferring multilayer

sorption on the surface. Based on this model, the ratio of solute on a given mass of adsorbent to the solute concentration in the solution differs at different solution concentrations [6, 28]. Freundlich isotherm can be depicted by equation (2):

$$\ln q_e = \ln K_f + 1/n \ln C_e \quad (2)$$

Where : q_e (mg g^{-1}) and C_e (mg L^{-1}) are adsorbent uptake capacity and adsorbate content at equilibrium time, K_f (mg$^{1-1/n}$ L$^{1/n}$ g^{-1}) and n are connected with the capacity of adsorption and adsorption intensity, respectively. The plot $\ln q_e$ against $\ln C_e$ should give a straight line and K_f and n can be determined from the intercept and respectively the slope of the plot.

The experimental parameters taken into consideration for isotherm study were the following: pyridine concentrations of 50 mg L^{-1}, 75 mg L^{-1}, 100 mg L^{-1}, 150 mg L^{-1}, 200 mg L^{-1}, 240 mg L^{-1}, 0.3 g adsorbent (Mt-CTAB or Mt) in 100 ml solution, 120 min equilibrium time. The pyridine concentration in solution was chromatographically determined after the above mentioned period and q_e was calculated.

The fitting parameters derived from Freundlich model along with the correlation coefficient (R^2) are presented in Table 3.

As the correlation coefficient (R^2) values show, the experimental data match well with the Freundlich model suggesting a heterogeneous distribution of active sites on both adsorbents [29]. The n values achieved represent beneficial adsorption [27, 30].

4. Conclusions

The removal of pyridine from aqueous solutions was achieved by adsorption on Na-montmorillonite as well as by cationic surfactant modified montmorillonite at basic pH. The basal spacing of the adsorbents proved that pyridine was intercalated in the layered spaces of the adsorbents in the presence as well as in the absence of surfactant, meaning that pyridine was separated from solution not only through partition but also due to other adsorption mechanisms. Pyridine protonation in the presence of the hydroxyl groups of the clay could generate cationic complex species which by hydrogen bonding and electrostatic interaction with montmorillonite led to a better separation from solution in case of bentonite as such and to surfactant removal from the clay and to a lower separation efficiency in case of organically modified bentonite. The experimental results indicated that Freundlich isotherm model and pseudo-second-order kinetic described well the sorption processes on both studied adsorbents. The sorption capacity of pyridine at equilibrium was 27.55 mg g^{-1} for Mt-CTAB and 32.6 mg g^{-1} for Mt showing that the

removal efficiency is not improved by surfactant modification. The performance is comparable with the one of modified agricultural wastes, for instance : bentonite has an adsorption efficiency of 97.42% after 5 minutes contact time, 0.3 g adsorbent/100 ml pyridine solution of 100 mg/L concentration, while the lignocellulosic derived material [3] has an adsorption efficiency of 88.28% after 2 minutes contact time, 0.5 g adsorbent/100 ml pyridine solution of 300 mg/L concentration.

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