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Adsorption of a dye and a real rejection of textile on sludge from drinking water treatement

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Abstract

The characterization of sludge from the production of drinking water shows that it is silico-aluminous clays with the dominance of mineralogical phases kaolinite muscovite. Our job is to valorize this sludge as an adsorbent material for the discoloration of methylene blue and and reducing the pollutant load of a real rejection of textiles. The effect of different experimental parameters such as adsorbent mass, pH and contact time were studied. We also studied the effect of chemical sludge activation on treatment. The adsorption kinetics of methylene blue are better described by the pseudo-second order model. The adsorption isotherms are satisfactorily described by the Langmuir model with adsorption capacities of 11.364 mg/g for raw sludge and 65.1 mg/g for activated sludge with 2M sulfuric acid under pH conditions 9, concentration of 20mg/L, mass of 1.5g/L and contact time of 60min. For the treatment of the rejection of the textile industry the raw and activated sludge gave good yields of réduction of pollution parameters.

Keywords: Sludge, potabilization, activation, discoloration, COD, textile rejection.

1. Introduction

Textile rejects are complex and difficult to biodegrade [1], they constitute a real danger for man and the environment because of their high content of dyes, organic matter, suspended matter and salts [2-3]. Methylene blue is the most used dye in the textile field, it is used for dyeing cotton, wood and silk. This dye has a harmful effect on human health, it can cause eye burns that cause permanent injuries to humans and animals. Inhalation may cause breathing difficulties and ingestion through the mouth produces a burning sensation, nausea, vomiting, sweating and heavy cold sweat [4]. Methylene blue is toxic to algae and small crustaceans from concentrations of 0.1 mg/L and 2 mg/L respectively [5]. For the treatment of textile rejects several treatment processes have been applied. Biological processes [6], physico-chemical such as coagulation flocculation [7-8], advanced oxidation [9], membrane processes [10]. These processes in addition to their very expensive costs give unsatisfactory results since the textile rejects contain non-biodegradable dyes [11-13]. Adsorption on various media is an emerging solution to the problems of pollution in receiving environments. Adsorption remains a relatively easy and less expensive technique. Coal is the most used adsorbent, it has a high adsorption capacity [14] but remains very expensive and difficult to regenerate. Several researchers are oriented towards finding new low-cost and effective adsorbents from natural substances or waste, among these adsorbents are clays which have shown a high adsorption capacity of textile dyes [15], sawdust [16-17], sugar cane waste [18], date kernels [19-20], eucalyptus [21] and eggshells [22]. Hydroxide sludges from drinking water treatment are known for their depolluting power, they are used for the extraction of coagulant for the treatment of waste [23], they are used as additives to improve the coagulation flocculation [24]. Sludge from potabilization is also used for the adsorption of metal pollutants [25], textile dyes [26-27] and organic matter in leachates [28]. This study examines the use of raw and activated sludge as an adsorbent for the treatment of methylene blue and a real rejection of the textile industry.

2.Material and method

1- Materials used

The sludge samples are taken directly from the decanters of the drinking water treatment plant of the Bin el Ouidane Dam (Beni Mellal region). The liquid sludge is decanted, dried and then placed in an oven at a temperature of 105°C. We used the raw and activated material. Acid activation of sludge is carried out at a temperature of 25°C with sulfuric acid at concentrations of 0.5M, 1M and 2M. The analysis of the oxide composition is carried out by X-ray fluorescence spectrometry. The mineralogical composition is determined by X-ray diffraction and infrared spectroscopy. The microscopic observation of the sludge is carried out by transmission electron microscopy (TEM).

2- Methylene blue solution to be treated

The dye used is the methylene blue dye marketed under the C.I: BLUE 274 dye, with a density of 1.134 mg/L and a pH of 8.26. Methylene blue (cationic dye) (Figure 1). The methylene blue solution is prepared by dissolving 1 g of the dye per liter of distilled water.

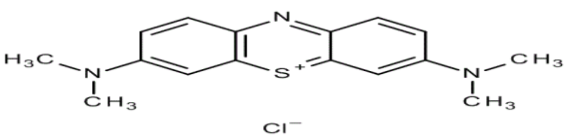

Figure 1: Disposition in the space of the methylene blue molecule

3.Experimental protocol

Methylene blue adsorption experiments on hydroxide sludge were performed by introducing varying amounts of sludge into small reactors containing the methylene blue solution. The solid liquid separation is carried out by centrifugation at 5000 rpm for 5 minutes. The filtrate is analyzed by UV-visible spectrometry at a wavelength of 661 nm. The adsorbed amount is calculated using the following formula:

Qads = (C0 - Ct). V / M

Or: Qads: amount adsorbed at time t in (mg/g).; V: volume of the solution in (m/L).; C0 and Ct: are, respectively, the initial concentration and the concentration at time t of the dye in (mg/L).; M: mass of the adsorbent in (g).

4.Results and discussion

1-Chemical characterization of drinking water sludge

1-1-Chemical Analysis by Fluorescence X

Table 1 X-Fluorescence Analysis of Sludge of the Bin El Ouidane Dam station

Element	**SiO_2**	**Al_2O_3**	**Perte au feu**	**Fe_2O_3**	**MgO**	**CaO**	**K2O**	**TiO_2**	**Na_2O**	**SO_3**	**P_2O_5**	**MnO_2**
Conc%	37.5	30.4	17.6	4.38	3.13	3.02	2.25	0.429	0.408	0.378	0.162	0.142
Element	**Cl**	**BaO**	**SrO**	**ZnO**	**I**	**ZrO2**	**Rb**	**Br**	**Y_2O_3**	**Ac**	**Nb**	**Sum**
Conc%	0.084	0.028	0.021	0.015	0.014	0.01	0.008	0.008	0.004	0.003	<<	100

Important aluminum values (30.4%) for sludge are due to the use of alumina sulfates in water treatment operations and to the nature of clay sludge. The high silica content may be due to the nature of the lands crossed by the water supply of the water purification plants. Sludge is also rich in iron. The analyzed sludge is rich in calcium and magnesium oxides. The low concentrations of heavy metals recorded indicate that the station's water supply is far from anthropogenic pollution. The sludge is composed mainly of silica oxides, alumina, iron, calcium, and magnesium. They are therefore silico-aluminous clays.

2-Mineral characterization of drinking water sludge

2-1 X-Ray Diffraction Analysis (XRD)

The mineralogical composition of the sludge was determined by X-ray diffraction of a powder dried at a temperature of 105 °C for 2h. The analysis of the diffractograms (Figure. 2) allows us to observe a strong presence of free silica in the form of quartz identified by its characteristic line (d = 3.34 Å, 2θ = 26.75 °). We also identified Calcite (d = 3.01 Å, 2θ = 29.60 °) and Talc (d = 9.25 Å, 2θ = 9.55 °). Regarding the phyllitous phases, the analysis shows that the sludge has kaolinite and muscovite, so these two sludges have a kaolinitic- Muscovite character. The sludge analysis results by X-ray diffraction correlate with the chemical composition determined by X-ray fluorescence spectrometry.

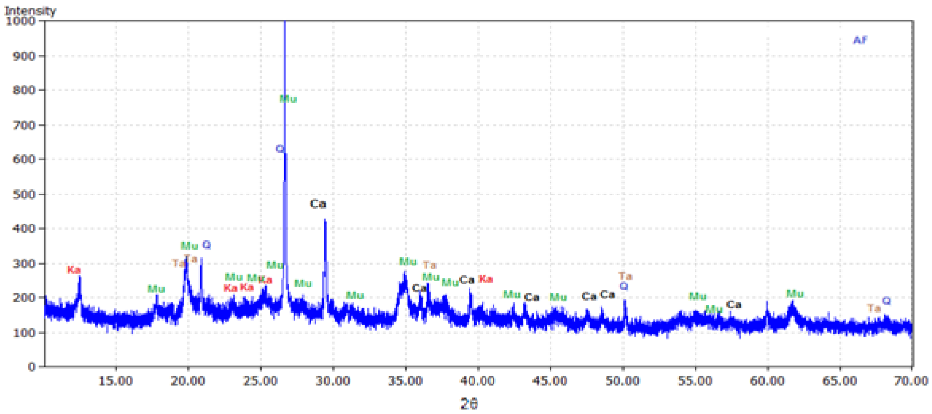

Fig2. XRD spectrum of the sludge of the Bin El OuidaneDamstation (Mu: Muscovite, Ka: Kaolinite, Ca: Calcite, Ta: Talc and Q: Quartz)

2-2- Infrared spectroscopy analysis

Infra-Red spectroscopy is known for its sensitivity to detect hydrated minerals with high thermal instability. This method is used to complete the X-ray diffraction analysis.

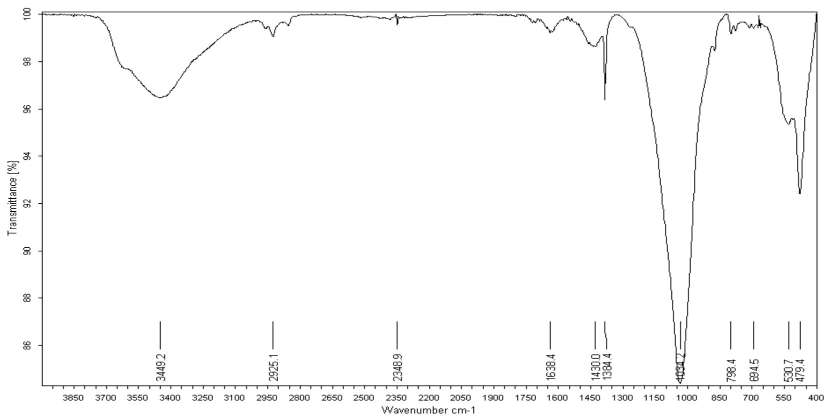

Fig3. Infrared spectrum of the sludge of the Bin El Ouidane Dam station dried at 105 ° C.

Table 2: Main IR bands characteristic of the sludge of the Bin El Ouidane Dam station

Radical	Number of waves (frequencies) cm^{-1}
	Bin El Ouidane Dam Station
O-H	3650-3449.2- 1638.4 [29, 30]
CO_2^-	2650 – 2348.9 [31]
CO_3^{2-}	1430 – 1384.4 – 850 [32]
SiO_4	1250 [35]
SiO de la kaolinite	1034.2 [29]
Al-O-H	910 [29]
Si-O du quartz	798.4 – 694.5 – 479.4 [29]
Si-O-Al	530.7 [29]

Infrared spectroscopy results confirm the results of X-ray diffraction analysis.

3-Microscopic characterization of drinking water sludge

3-1- Analysis by MET

The MET analysis was done to complete the mineralogical characterization of the sludge; it allows the determining of the micro texture, the structure of the phases present as well as the arrangement of the particles of sludge.

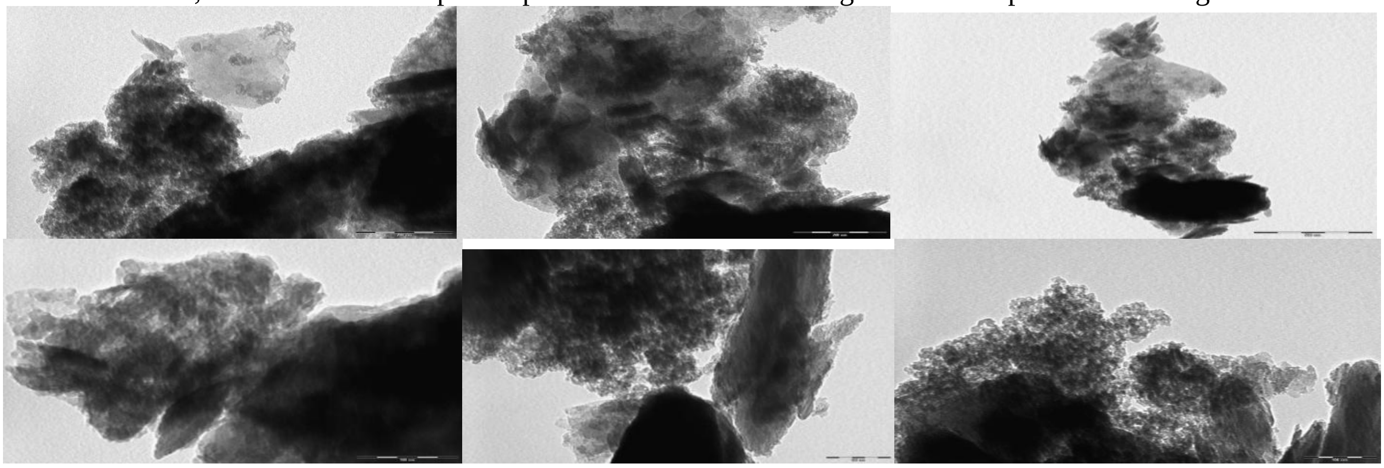

Fig4. MET sludge photo of the Bin El Ouidane Dam station

The photos taken by MET (Figure 4), show that the sludge is a heterogeneous mixture of irregularly shaped particles in sheet and granular forms composed of rounded minerals.

The characterization of sludge shows that they are very rich in silica, aluminum, and iron. Mineralogical analysis by X-ray diffraction approved the same composition; the hydroxide sludge is composed of silico-aluminous clays, so this sludge can be used as a support for adsorption of pollution.

2-Adsorption of methylene blue on sludge

2-1- Effect of contact time on the removal of methylene blue

We contacted 20mg/L of methylene blue with 1.5g of sludge to determine the equilibrium time.

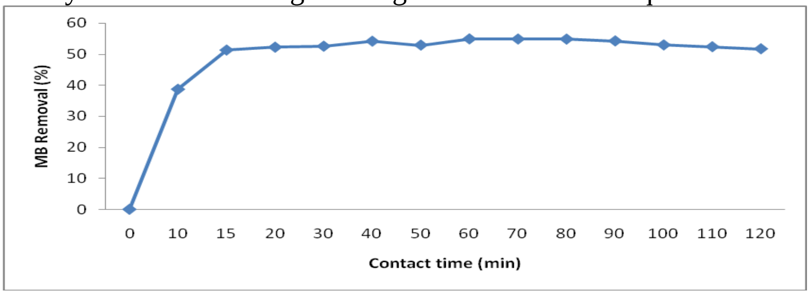

Figure 6: Adsorption kinetics of methylene blue on the raw hydroxide sludges (Ci of BM = 20 mg/L, mass of adsorbent 1.5 g/L, T ° = 25 ° C., initial pH of the solution = 8. 26)

The adsorption kinetics of methylene blue is very fast in the first 10 minutes, this may be due to the availability of free sites on the surface of the material and the strength of the interactions between sludge and methylene blue. Subsequently, the adsorption becomes slower and the adsorbed quantity is relatively low, this may be due to the molecular diffusion of methylene blue towards the less accessible adsorption sites because of their progressive saturation [32]. The equilibrium time taken in the sequel is 60min. Similar results were found by Rashed et al (2016) [27] and Poormand et al (2017) [33]. Mouni et al (2018) [34] have found that the equilibrium time of the adsorption of methylene blue on kaolinite is 120 min.

2-2- Effect of the mass of the adsorbent

The experiments were carried out using 100 ml of methylene blue at a concentration of 20mg/L, at which different amounts of raw sludge were added in order to estimate the optimum amount.

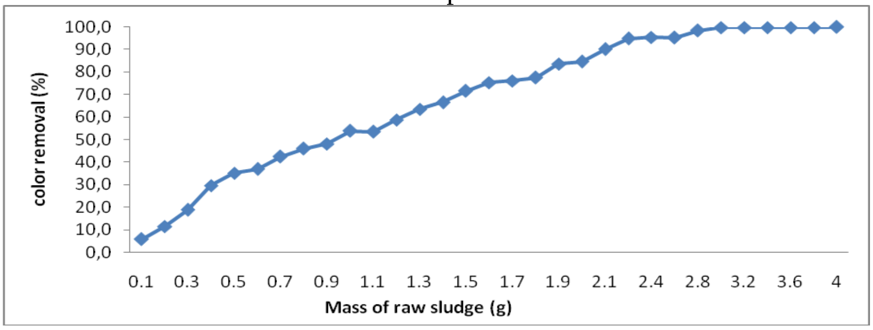

Figure 7: Effect of raw sludge mass on the adsorption of methylene blue (BM = 20mg/L, contact time = 60min, T ° = 25 ° C, initial pH of the solution = 8.26)

Figure 7 shows that the amount of adsorbed dye increases with the addition of adsorbent to mass 3 g/L. From 3 g of sludge, the adsorbed amount of the dye remains constant. This is due to the increase of the adsorption sites with the increase of the adsorbent mass which at a mass of 3g/L becomes stable [35]. The optimum mass is 3 g/L with a yield of 99.7%. Subsequently, a mass of 1.5 g was used to study the effect of other methylene blue adsorption parameters on raw sludge. Rashed et al (2016) found that the optimum mass for the adsorption of methylene blue at a concentration of 50 mg/L on sludge is 0.25 g/100 mL [27]. Karim et al (2010) showed that the adsorbed quantity of methylene blue is maximal at a mass of 40 mg/100 ml of purified clay [36]. Mouni et al (2010) found that a mass of 1 g/L of kaolinite gives a yield of 97% [34].

2-4- pH effect

The pH has a very important effect on the adsorption, the adsorption of the methylene blue on the hydroxide sludge was studied on a range of pH 4-11. The tests were carried out by adding 0.15 g of sludge to 100 ml of the methylene blue solution at 20 mg/L. The pH of the solution was adjusted to the desired values by the addition of H_2SO_4 or NaOH. The solutions are stirred for 60 minutes. After centrifugation, the filtrate is recovered and analyzed. Figure 9 shows that the adsorption increases with increasing pH, this can be explained by the increase in OH^- ions and the change in the surface charge of the adsorbent. A good discoloration yield of methylene blue is observed at pH 9. Similar observations have been reported by Mouni et al (2018) [34]. Rashed et al (2016) found that adsorption of methylene blue on sludge is optimal at pH 7 [27]. Poormand et al (2017) found that the optimum pH for the adsorption of methylene blue on sludge beads is pH8 [33]. The adsorption of BM in a pH of 4 and 5 is low, which may be due to the competition of H^+ ions with BM.

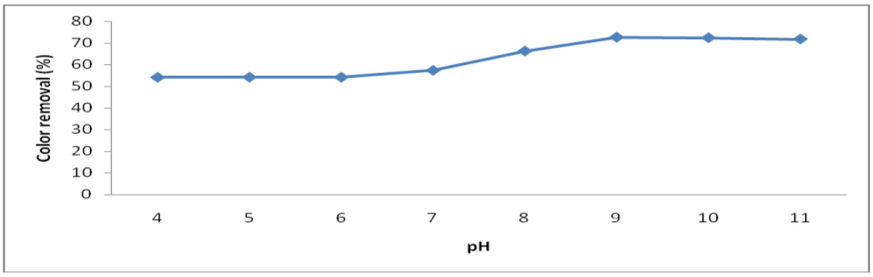

Figure 8: Effect of pH on adsorption of methylene blue on raw sludge (BM = 20mg/L, contact time = 60min, T ° = 25 ° C, sludge mass = 1.5)

2-6-Effect of Chemical Activation of Sludge

In order to determine the effect of sludge activation on the discoloration yield of methylene blue, we proceeded to the activation of sludge by sulfuric acid at different concentrations (0.5M, 1M and 2M and 5M) at 25 ° C.

In methylene blue solutions with a concentration of 20mg/L and at pH 9 we added 1.5g masses of each sludge. From Figure 12 it is noted that activated sludge with a concentration of 2M sulfuric acid gives the best efficiency of adsorption of methylene blue. The acid attack of the sludge is intended to extract some of the oxides of the sludge layers to increase the number of active sites.

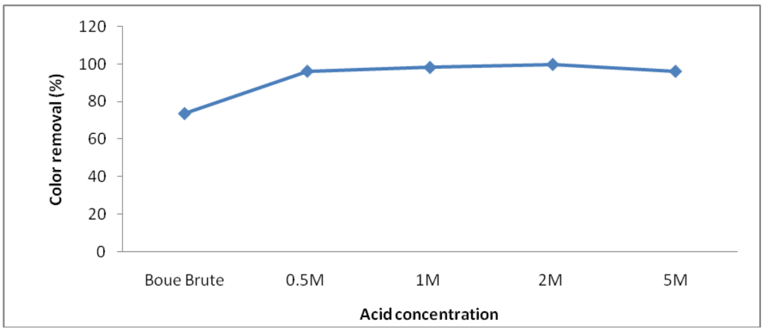

Figure 9: Effect of chemical activation of the sludge on the adsorption of methylene blue (Ci of BM = 20mg/L, contact time = 60min, T° = 25 °C, sludge mass = 1.5, pH9)

2-7- Effect of the mass of activated sludge on adsorption

The effect of activated sludge mass with a concentration of 2M sulfuric acid was studied at the initial pH of the solution, at room temperature and at a speed of 120 rpm. Figure 10 shows that there is an improvement in the adsorption efficiency of methylene blue with the activation of sludge, it is noted that a mass of 1.6 g gives a fading yield of 93.5%. This improvement in yield is due to the presence of the active sites on the adsorbent surface. The chemical activation with sulfuric acid causes the reorganization of the sludge structure which leads to the formation of the voids and the valences of the ions found there become unsaturated and consequently they tend to fix other particles which are in solution [37].

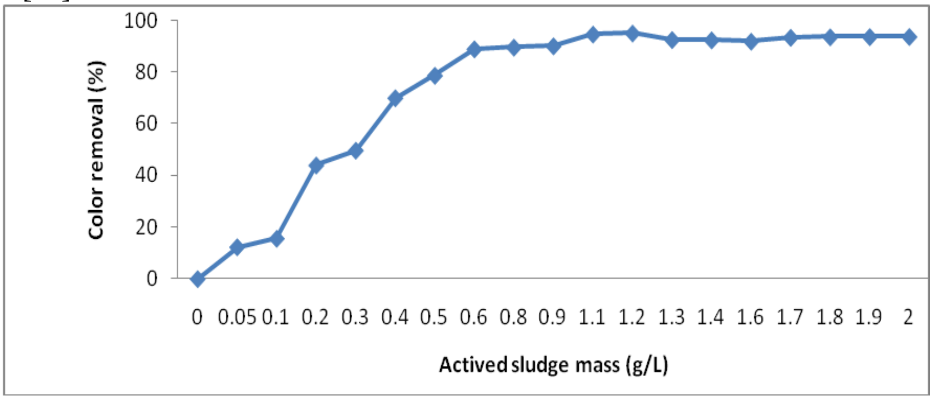

Figure 10. Effect of Activated Sludge Mass on Adsorption of Methylene Blue (Ci of BM = 20mg/L, Contact time = 60min, T ° = 25 °, initial pH of the solution = 8.26)

Modélisation de la cinétique d'adsorption:

Modeling of adsorption kinetics

Kinetic model of the first order (Lagergren equation)

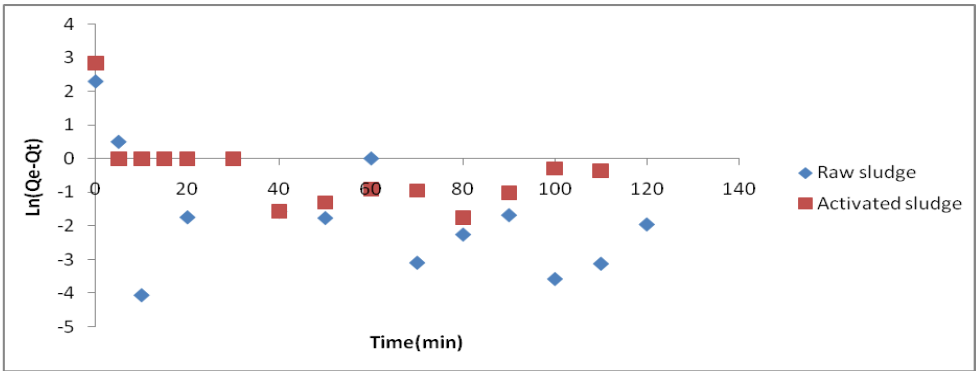

Figure11. Determination of first-order rate constants of adsorption of methylene blue by raw and activated sludge

Qt: Amount adsorbed at time t (mg/g) and Qe: Quantity adsorbed at equilibrium (mg/g)

The figure shows that Log (Qe-Qt) as a function of time is nonlinear. The adsorption kinetics of methylene blue on the raw and activated sludge cannot be described by pseudo-first-order kinetics.

4-8-2-Kinetic model of the second order

The calculated values of the adsorbed quantities Qe, the pseudo-second-order constants K and the regression coefficients R are given in Table 3. The results show that the values of R are very high and are all of the order of 99.9% and exceed those obtained with the pseudo-first-order model. Quantities fixed at equilibrium Qe are very close to the values found experimentally. So the adsorption process follows the pseudo-second-order model well.

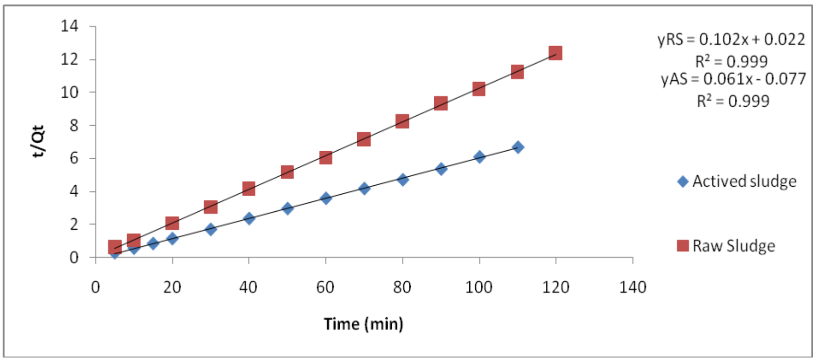

Figure 12. Determination of 2nd order rate constants of adsorption of methylene blue by raw and activated sludge.

Table 3: Kinetic parameters according to the second order

SLUDGE	Pseudo-second order			
	K_2 (g/mg/min)	Qe calculated (mg/g)	R (%)	Qe experimental (mg/g)
Raw sludge	0.473	9.804	99.9	9.82
Activated sludge	0.048	16.39	99.9	17.11

2-9-Isothermes d'adsorption

The Langmuir model better describes the adsorption of BM on sludge with its correlation factor of 92.6 for raw sludge and 99.3% for activated sludge. The maximum adsorbed quantities for the crude and activated sludge are respectively 11.364 mg.g-1 and 65.1 mg.g-1. The adsorption of MB on the sludge is favorable since the separation factors R_L are between 0 and 1. These results are in agreement with those found by Reshed et al (2016)[27]. The adsorption of methylene blue on the sludge is in monolayer.

Table 4: Paramètres des isothermes de Langmuir et Freundlich

	Langmuir		Freundlich	
sludge	Raw sludge	Activated sludge	Raw sludge	Activated sludge
Qm, Qe	11. 364	65.1	3.97	11.35
K, K_F	0.606	0.005	4.10	9.87
N	-		3.55	2.53
R_L	0.65	0.99	-	
R2 (%)	92.6	99.3	88	82.2

3- Treatment of a real rejection of the textile industry

3-1- Effect of contact time on adsorption of textile rejection

Raw and activated sludge was used for the treatment of a real textile rejection. The experiments were carried out at the initial pH of the solution with a mass of 1.5 g of crude sludge with rapid stirring. The discoloration of the textile rejection is evaluated by measuring the absorbance and the organic matter is evaluated by measuring the COD.

Figure 13 shows that discoloration and COD increase with increasing contact time and discoloration kinetics is rapid relative to COD. The fading rate and the COD range from 25.76 to 55.48% and 32.23 to 40.1% respectively for a contact time of 5 to 120min, these yields are high compared to the values found by Zaharia et al (2012) who reported that the adsorption of a fly ash rejection for 500 min gave a 49.12% discoloration yield and 25% COD with a mass of 40g/L of adsorbent [38]. The discoloration and decay rate of COD became slower and slower at 120min, however, we used a 120min contact time to study the effect of other parameters on adsorption.

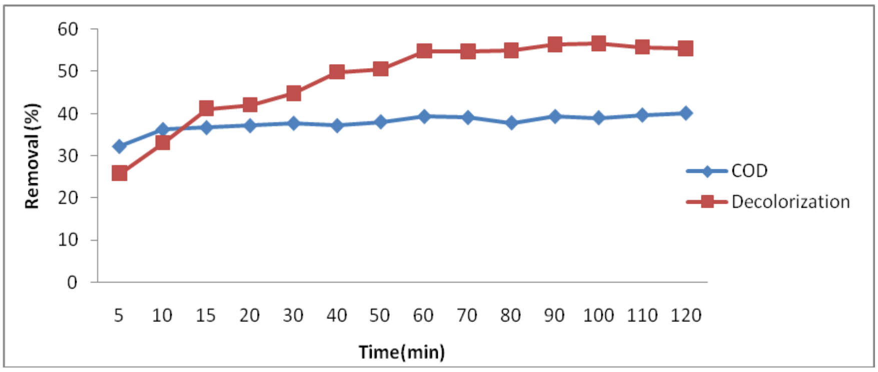

Figure13: Effect of contact time on the discoloration rate of textile discharge (T° = 25 °C, mass of sludge = 3, initial pH of the rejection)

3-2- Effect of quantity of sludge on adsorption of textile rejection

Discoloration and COD abatement values increase as the amount of adsorbent increases. These observations are consistent with those reported by Zaharia et al (2012)[38]. Discoloration efficiencies of 85.49% and COD reduction of 46.46% are achieved at a mass of 5g/L of raw sludge. The increase in the fading yield with the adsorbent mass is explained by the increase of the adsorption sites on the sludge.

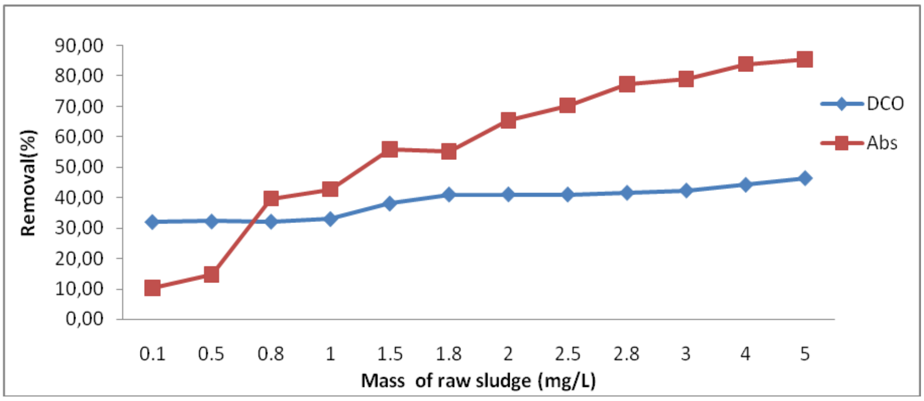

Figure 14: Effect of the sludge mass on the discoloration rate of the textile rejection (T ° = 25° C, contact time = 120min, initial pH of the rejection)

3-3- pH effect on adsorption of textile rejection on sludge

The pH has a very important effect on the treatment efficiency, it has an effect on the surface charge of both the adsorbent and the adsorbate [39]. For this purpose, we have varied the pH of the textile rejection at the same time. Using sulfuric acid and sodium hydroxide in a range of 2 to 12, the rejection is stirred with a mass of 5 g/L of sludge for 120 min. The discoloration curve shows that the discoloration depends on the pH and the degree of discoloration increases at acidic pH and decreases for pH between 6 and 8 and then increases for pH higher than 8. The COD does not very much with the pH, however, the best discoloration and COD abatement yields are obtained in very acidic pH, these results are in agreement with those found by Zaharia et al (2012) and Weng et al (2015) [38, 40]. The pH that gives the best yield of discoloration and COD reduction is pH2. The textile rejection must undergo a pH neutralization before release into the receiving medium.

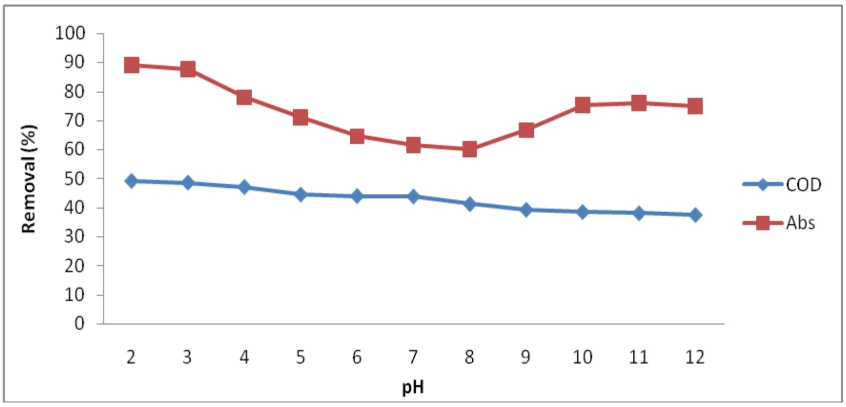

Figure 15: Effect of the initial pH on the discolouration of the textile rejection (T ° = 25 ° C, mass of sludge = 5g, contact time = 120min)

3-4- Effect of sludge activation

We proceeded by chemical activation with sulfuric acid at concentrations of 0.5M, 1M, 2M and 5M at 25 ° C. It is noted that the acidic activation of the sludge increases the adsorptive capacity of the sludge, the chemical activation by sulfuric acid leads to the reorganization of the structure of the sludge, the creation of the pores and the valences of the ions which are on the surface of the sludge. adsorbent becomes unsaturated, increasing their interaction with adsorbate molecules [41-45]. The figure shows that the COD discoloration and abatement efficiency increases with the increase

of the sulfuric acid concentration used for the activation, a fading reduction rate of 97.6% and COD reduction of 56.5% with sludge activated with 2M sulfuric acid. Note that when the sulfuric acid agreement exceeds 2M the yield drops.

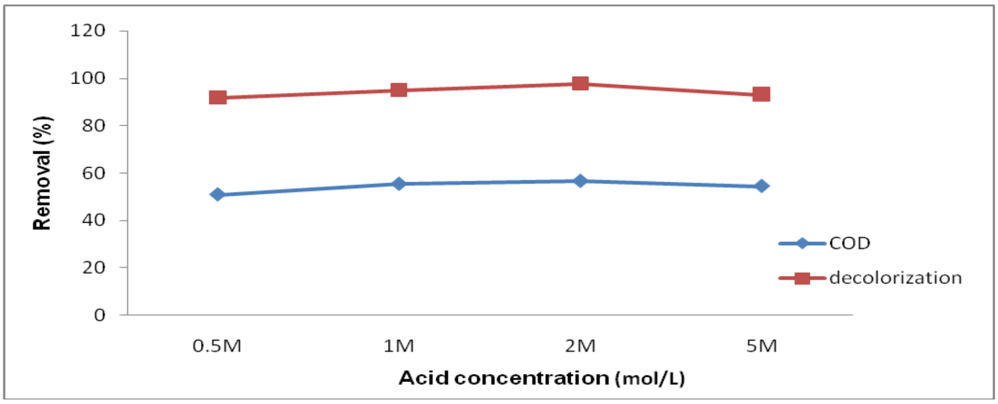

Figure 16: Effect of the chemical activation on the COD and the discoloration of the textile rejection (T ° = 25 ° C, mass of sludge = 5g, pH = 2 contact time = 120min)

3-4-Characterization of the textile rejection before and after adsorption on chemically activated sludge

The table shows the variation of the parameters of pH, electrical conductivity, COD, BOD_5 and discoloration by absorbance measurement of the rejection of the textile industry before and after adsorption treatment on the sludge resulting from the water purification, in conditions of pH9, contact time of 120min and a mass of 5g/L of sludge activated with 2M sulfuric acid. There is a large decrease in the pollution parameters analyzed, although the COD remains a little high compared to the specific limit values for the rejection of textile industries in Morocco [46].

Table 5. Characterization of the textile effluent before and after treatment

Paramètres	Textile effluent before treatment	Textile effluent after treatment	Specific Limit Values of Textile Industries Rejection [46]
pH	12.08	6.95	6.5-9
Electrical conductivity (ms/cm)	4.22	1.820	-
COD (mg/L)	1732	751	500
BOD_5 (mg/L)	150	80	140
suspended matter (mg/L)	1016	30.45	50
UV absorbance at 659nm	0.907	0.015	
UV absorbance at 311.5nm	1.796	0.1	

Conclusion

This study aims at recovering sludge from drinking water treatment for the treatment of methylene blue dye and a real rejection of the textile industry. The adsorption kinetics show that the adsorption of methylene blue on the sludge is fast and the equilibrium time is 60min. The adsorption mechanism can be described by pseudo-second-order kinetics. The adsorption isotherms of methylene blue are described by the Langmuir model and the maximum adsorbed

quantities are 11.364 mg/g for raw sludge and 65.1 mg/g for activated sludge. Sludge activation improves the adsorbent capacity of sludge.

In addition, adsorption treatment on the sludge of a real rejection of the textile industry allowed the discoloration of this rejection with a rate of 89%, the reduction of the COD with a rate of 48.6% for a pH 2. Chemical activation improves the adsorbent capacity of sludge, gives 97.3% textile discoloration yield and 56.5% COD reduction. The textile rejection must undergo a pH neutralization before release into the receiving medium.

This work aims at proposing a simple and fast efficient method for the treatment of discharges by the valorization of solid waste (sludge) for the decontamination of the liquid discharges.

References

[1] A. Jarmany , A. Kheribech , M. Mountadar, *Phys. Chem. News*. 6 (2002) 101-109.

[2] J. Perowski, L. Staislaw, *Ozone Sci. Engi*., 18 (1996) 73-85.

[3] H. Lin Shengh, Y. Lin Wen, *Environ. Teach.*, 15 (1994) 299-311.

[4] D. Ghosh,. K.G. Bhattacharyya, *Appl. Clay Sci.*, 20(2002) 295-300.

[5] J. Garcia, K. Takashima, *J Photoch Photobio A.*, 155 (2003) 215-222.

[6] S. Gatut, B. Keller-Lehmann, *J. Keller. J. Hazard. Mater.*, 138(2006) 160–168

[7] C.Allegre, M. Maisseu, F. Charbit, P. Moulin. *J. Hazard. Mater.*, 116 (2004) 57-64.

[8] A.Alinsafi, M. Khemis, M.N. Pons, J.P. Leclerc, A. Yaacoubi, A. Benhammou, A. Nejmeddine, *Chem. Eng. Proc.*, 44(2005) 461–470,

[9] I. Arslan, I.A. Balcioglu. *Dyes Pigm.*, 43(1999) 95–108.

[10] I. Petrinic, N.P. Raj Andersen, S. Sostar-Turk, A.M. Le Marechal, *Dyes Pigm.*, 74(2007) 512-518.

[11] Z. Dali-Youcef, H. Bouabdasselem, N. Bettahar, *C. R. Chim.* 9 (2006) 1295–1300

[12] M. El Krati, Etat de l'environnement de la ville d'El Jadida. Etude de la traitabilité des rejets liquides de textiles, thèse de doctorat d'Etat Chimie), Fac. Sci. El Jadida, Univ. Chouaïb Doukkali (2000).

[13] P. Sutarik, M. Hendou, TSM Etude, 3 (1997).

[14] G.M.Walker, L.R.Weatherley, *Water Res.*, 31(1997) 2093-2101

[15] E. Errais, Réactivité de surface d'argiles naturelles : étude de l'adsorption de colorants anioniques,thèse de doctorat, Université de Strasbourg, 2011.

[16] K. Belaid, S. Kacha, *RSE*, 242 (2011) 131–144

[17] H. Pekkuz., İ. Uzun, F. Güzel, *Bioresour. Technol.*, 99(2008) 2009-2017.

[18] A. Aarfane , S. Tahiri , A. Salhi , G. E. Boutchich , M. Siniti , M. Bensitel , B. Sabour , M. El Krati, *J. Mater. Environ. Sci.* 6 (10) (2015) 2944-2957

[19] S. Hazourli., M. Ziati, A. Hazourli, M. Cherifi. *Rev. Ener.Renouv.*, 07 (2007)187-192.

[20] A. Dbik, N. El Messaoudi et A. Lacherai, *J. Mater. Environ. Sci.*, 5 (S2) (2014) 2510-2514

[21] M. Abdallah, A. Hijazi, M. Hamieh, M. Alameh, J. Toufaily, H. Rammal, *J. Mater. Environ. Sci.*, 7 (11) (2016) 4036-4048.

[22] N. Y. Mezenner., Z. Bensaadi, H. Lagha, A. Bensmaili, *Larhyss Journal*, 11(2012) 7-16.

[23] A. Suman, T. Ahmad, K. Ahmad, *Environ. Dev. Sustain.*, 2016(2018)15–1625

[24] S. Jangkorn, S. Kuhakaew, S. Theantanoo, H. Klinla-or, T. Sriwiriyarat, *J. Environ Sci.*, 23(4) (2011)587–594

[25] S. A. Abo-El-Eneina, A. Shebl, S.A. Abo El-Dahab, *Appl. Clay Sci.* 146 (2017) 343–349.

[26] W. Chu, *Water Res.* 35 (13) (1999) 3147–3152.

[27] M. N. Rashed, M. A. E. El Taher, S. M. M. Fadlalla, *Water Sci Technol.*, 74.8(2016)

[28]H. Elmontassir, K. Zaki, B. Wassate, N. Gouzouli, M. Afdali, Y. Karhat, *Scientific Study & Research, Chemistry & Chemical Engineering, Biotechnology, Food Industry*, 20(2019) 089 – 102.

[29] M. Farias., R.V. de la villa, R. Garcia., M.I. Sanchez de Rojas, T.A. Baloa., J. Am. *Ceram. Soc.*, 1-8 (2013).

[30] G. Maglione., M. Carn., *Cah. ORSTOM. sér.Géol.*, 7(1) (1975) 3-9.

[31] G. Pivnyak, V. Bondarenko, , I. Kovalevs'ka, , M. Illiashov, Mining of mineral deposits, ed., Leiden, The Netherlands : CRC Press/Balkema, 2013.

[32] S. Bouzid, Adsorption de polluants organiques sur une argile échangée aux phosphoniums, Thèse De Doctorat, Univ. Sci. Technol. d'Oran Mohamed Boudiaf, 2015.

[33] H. Poormand, M. Leili, M. Khazaei, *Water Sci. Technol.*, 75.2 (2017).

[34] M. Lotfi, L. Belkhirib, J. C. Bollingerc, A. Bouzazad, A. Assadid, A. Tirrib, F. Dahmounee, K. Madanie, H. Remini, *Appl. Clay Sci.* 153 (2018) 38–45.

[35] V. K. Gupta, A. Mittal, V. Gajbe, *J. Colloid. Interf. Sci.*, 284(1) (2005) 89-98.

[36] A. B. Karim, B. Mounir, M. Hachkar, M. Bakasse, A. Yaacoubi, *Journal of Water Science*, 23(4) (2010) 375-388.

[37] N. Tazerouti, M. Amrani, *Journal of Water Science*, 233 (2010) 233-245.

[38] C. Zaharia, D. Suteu, *Environ Sci Pollut Res*, 20(2013) 2226–2235.

[39]M.Bennaja,Traitement des rejets industriels liquide par électrocoagulation/électroflotation en réacteur airlift, Thèse de doctorat, Institut National Polytechnique De Toulouse, France, (2008)

[40] C.H. Weng, Y.J. Chen, *Environ. Eng. Manag J.*, 10 (2015) 2383-2391.

[41]A. Gannouni, A. Bellagi, *J. Soc. Chim. Tunisie*, 4 (2001) 1357.

[42] G.J. Ross, *Can. Mineral*, 9 (1968) 522.

[43] A. Numan, E. W. Charles, *Clays Clay Miner*., 17(1969) 169.

[44] D. R. Taylor, D. B. Jenkins, *Transactions*, 1901(1988) 282.

[45] E. L. Tavani, C. Volzone, *Ceramica*, 45(295) (1999) 133-136

[46] Préservation de la qualité des ressources en eau et lutte contre la pollution (Valeurs Limites de Rejet à respecter par les déversements (Normes de pollution)), Juin 2014 www.water.gov.ma/wp-content/uploads/2016/01/4.3.3.Valeurs-Limites-de-Rejet