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Batch mode treatment of wastewater from the Maroua artisanal tannery using silica extracted from rice husks and silica/sand mixture

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ABSTRACT. Tanning activity consumes high volumes of water resulting in large volumes of highly colored polluted wastewater being discharged to the environment. In this study, the discoloration of the wastewater of the local artisanal tannery using SiO_2 synthesized from rice husks and silica/sand mixture at different process conditions was investigated. The results revealed that the discoloration process is favorable for both adsorbents at 35°C with maximum of 61% for sand/SiO_2 mixture system and 64% for SiO_2 system. The presence of NaCl electrolyte enhanced the discoloration for both adsorbents increasing from 44% for sand/SiO_2 mixture at 0 NaCl to 72% at 0.5M NaCl and from 49% for SiO_2 system at 0 NaCl to 63 % at 0.5M NaCl. Increasing the amount of sand from 0.2 to 1 g at fixed SiO_2 of 0.1 g in sand/SiO_2 mixture showed discoloration from 40-41 % while increasing SiO_2 in SiO_2 alone system from 0.05 to 0.5 g had a discoloration of 45-71%. Results of this study shows that sand a very abundant local and worldwide material can be complemented with silica in a very low cost tannery wastewater discoloration process.

1. INTRODUCTION

Tanning is amongst main human activities contributing to the pollution. About 40-45 L water/kg of raw-hide is used by tanneries for processing finished leathers. It is estimated that about 690,000 tons of raw-hide are processed worldwide annually [1]**.** This implies about 30 billion liters of water is required for the tannery industry annually worldwide. Much of the water containing large amounts of chemicals such as lime, sodium sulfide, ammonium sulfate, sodium chloride, bactericides, vegetable tannins, dyes and chrome salts are discharged to the environment. Other pollution contributors include phosphate discharges from agricultural and domestic activities. A global estimate of about 1.5 millionTons/year phosphates is discharged in to freshwater systems from both diffuse and point sources annually with the domestic sector contributing 54%, followed by agriculture (38%) and industry (8%) [2]. Slaughter house activity also significantly pollutes water sources as 29% of the total freshwater used in the agricultural sector worldwide are consumed by the meat processing industry alone [3]. Tanning involves the transformation of animal hides into leather that can be used to make handbags, shoes, belts, etc [4]. Tannery effluents are highly polluted due to the presence of highly colored compounds, chlorides, phosphates and sulfates, various organic substances, metallic compounds and different types of biologically oxidizable materials [5]. However, due to the difficulties related to the transformation of animal skin into leather, tanning is a water-consuming activity [6]. This huge consumption of water induces the discharge of a significant amount of pollutants into the soil, runoff and even into the groundwater through the phenomenon of diffusion. This environmental pollution can thus cause various health problems to the riparian population [6]. The implementation of an efficient tannery wastewater treatment technique presents a double challenge: on the one hand, the reduction of the pollutant loads of tannery wastewater before its discharge into nature and, on the other hand, the recycling of wastewater for a possible reuse in the same leather production chain in order to create water saving system.

Previous study by Abba et al. [4] on artisanal tannery wastewater of Maroua focusing on the characterization and its treatment by flocculation technique revealed that it was highly colored with the presence of numerous organic and inorganic pollutants. Unfortunately the flocculation had very minimal reduction in the organic and inorganic load. Therefore, an alternative method is urgently needed in order to improve the treatment of this wastewater. Many methods for wastewater treatment have been reported in the literature including advanced oxidation processes, membrane separation and adsorption processes [5]. Among them, the adsorption technique is

the most suitable one for removing pollutants from wastewater because it's cheap, easy, not generate secondary sludge and the efficiency could be enhanced by modifying the properties of the adsorbent [2,8-9].

The common adsorbents used are clay, activated carbon, biochar, sand and silica [9-11]. The valorization of solid agricultural wastes as precursors for adsorbents synthesis is of high interest because it's low cost and in the same time represents a good way to solve the problem of their disposal in the environment. It has been reported in the literature that silica prepared from rice husk ash exhibit good efficiency for dye removal [12, 13]. Therefore, its combination with sand may be an interesting option to improve the adsorption process performance. Sand is a natural adsorbent with many advantages such as recyclability, free and largely available in Maroua, hence could be valorize as adsorbent for the environmental protection [8, 14].

In this work therefore, we evaluated the discoloration of real wastewater derived from Maroua artisanal tannery using two systems; i) SiO_2 prepared from rice husk in one system and ii) sand/ SiO_2 mixture in the second system where the quantity of SiO_2 was fixed at 0.1g while that of sand was fixed at 0.3 g for all tested parameters except for the effects of adsorbent. The effects of experimental parameters on the efficiency of the discoloration were investigated. The experimental data were fitted with kinetic models (pseudo-first, pseudo-second, intraparticle and Elovich models). The colour removal efficiency parameters were determined by fitting experimental data to the Langmiur, Freundlich, Temkin, Dubinin-Radushkevich and Elovich isotherms models.

2. MATERIALS AND METHODS

2.1 Chemicals and instrumentation

All chemicals used in this work were analytical grade and distilled water was used for the preparation of solutions. NaCl and HCl were purchased from a Scharlab S. L. Spain. The calcination was performed in a muffle furnace (Nabertherm GmbH 30–3000°C, L3/12/C450). The absorbance of the samples and pH of the media were measured by using UV spectrophotometer 23RS, labo med.inc (USA) and Mettler Toledo Education line pH meter, respectively.

2.2 Preparation of the adsorbents

The sand used was collected in a river near the Maroua artisanal tannery. It was washed thoroughly with water to remove impurities and dried under sun light for 10 h (35°C). To obtain the fine particles needed, the sample was sieved (Ø < 1 mm) and kept for further experiments.

The silica used in this work was synthesized by [13]. The rice husk collected from the rice processing unit of SEMRY (Cameroon) was used as a raw material for the preparation of the silica. Accordingly, the rice husk was washed several times with distilled water, dried at ambient temperature for 15 days. 1 kg of dried rice husk was burnt in open air to ash point. The silica was then extracted from rice husk ash according to following procedure. 5 g of rice husk ash was dispersed in a 100 mL solution of HCl (1M) to remove the metals and maintained under stirring at 80°C for 2 h. The mixture was kept overnight for decantation. After that, the suspension was filtered through whatman filter paper N° 1and the solid phase was washed with distilled water until neutral condition (pH = 7). The acidified rice husk ash was subsequently dried at 110°C in an oven for 24 h. Finally, 4.82 g (96.40% yield) of a white silica sample (SiO_2) was obtained after thermal treatment at 700°C for 2 h.

The chemical composition obtained by X-ray fluorescence analysis of the obtained silica is given in Table 1. Also, the surface charged of SiO_2 was determined to be - 15 mV and the FTIR analysis showed the presence of the Si–O and Si–O–Si groups [13]. Results reported in [13], showed that the small surface charged value enhanced rhodamine dye removal from wastewater. This study also showed that this SiO_2 can easily be regenerated as 91.65% rhodamine B was regenerated in the third cycle from an initial 91.98% adsorbed.

Table 1: Chemical composition of rice husk silica [13].

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	P_2O_5	LOI
89.84	0.41	0.09	0.31	0.04	0.75	0.2	0.59	0.04	3.94

2.3. Sampling and Preliminary Treatment of Tannery Wastewater

The tanning industry in Maroua is still very traditional. The sampling site was previously described by [4]. The sampling was carried out on all the five processes of the tanning activities with different colors as shown in the images in Figure 1. The five samples were mixed in equal proportions to form unique representative sample for the whole site. The collected wastewater sample, stored in polyethylene bottle was kept in the laboratory for 24 h to allow decantation and was filtered through Whatman filter paper Nº. 1 to remove coarse particles before discoloration studies.

Figure 1. Overview of the staining of different tannery wastewater samples from Maroua.

2.4 Discoloration experiments

These experiments were done in batch mode using 20 mL essay tubes without stirring (Figure 2). For every parameter studied wastewater volume of 20 mL was used. The contact time was studied at 0, 1, 24, 48 and 72 h. For silica only, the dose was varied from 0.05 to 0.5 g while in the case of sand/silica, the quantity of silica was maintained at 0.1 g while the sand was varied from 0.2 to 1g. Trials with sand alone showed a discoloration efficiency of less than 20% in 72 hours, so that's why it was not used on its own. The effect of tannery wastewater (denoted TW) initial concentration (represented by absorbance) was studied with TM absorbances of 0.097, 0.217, 0.330, 0.387 and 0.427 on Sand/SiO_2. Pre-trial experiments saw SiO_2 having exactly the same results as those with Sand/SiO_2 for the effect of initial concentration, thus only results of Sand/SiO_2 are reported. The ionic effect was studied by mixing the TW with sodium chloride (NaCl) solutions at various concentrations of 0.05, 0.1, 0.25 and 0.5 mol/L. Finally, the study of the temperature effect consisted of performing the experiments under working temperatures of 25, 35, 45, and 60°C. In all experiments, after each treatment time and decantation, 5 mL was taken and analyzed by UV-visible spectrophotometer (Spectron 23RS) to determine residual concentrations at 432 nm. This maximum absorption wavelength was obtained after a preliminary scanning of the TW solution. The adsorbed quantities (A_e) and percentage of discoloration (R_e) were calculated according to equation (1) and (2), respectively:

$$A_e = \frac{(A_0 - A_e)V}{m} \quad (1)$$

$$R_e = \frac{(A_0 - A_e)}{A_0} x\ 100 \quad (2)$$

Where A_e is the quantity discolored at a time t (ABS/g), A_0 is the initial absorbance, A_e is the residual absorbance at a time t, m is the quantity of adsorbent (g) and V is the volume of the solution (L).

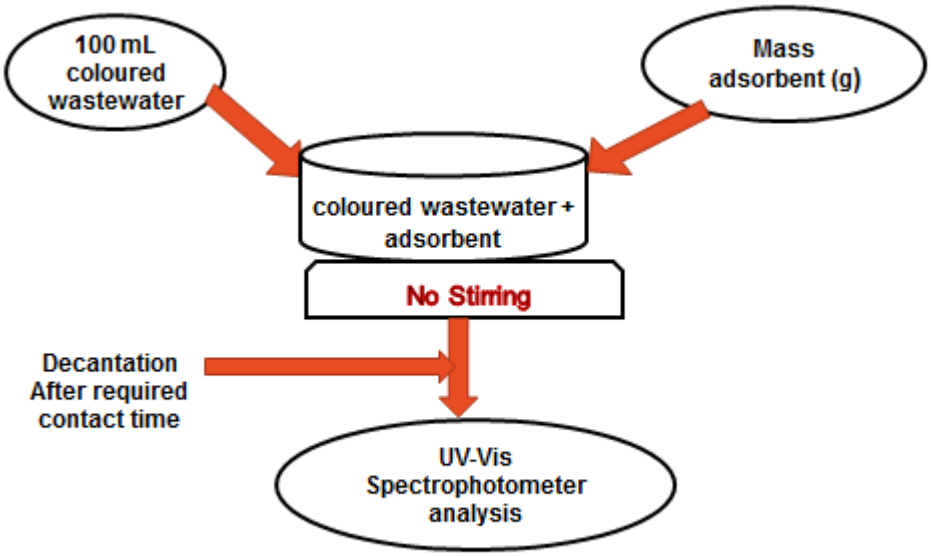

Figure 2: Adsorption process used in this work

2-5. Modeling of adsorption kinetics

Adsorption kinetics describes the rate at which solutes are adsorbed and this rate controls the residence time of the adsorbate attached to the solid-fluid interface. We studied the kinetics of the adsorption process by the pseudo-first order (equation 3), pseudo-second order (equation 4), the intra-particle diffusion (equation 5) and Elovich (equation 6) kinetic models.

$$log(q_e - q_t) = log\, q_e - \frac{K_1}{2{,}303}t \quad (3)$$

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

$$q_t = k_{id} t^{1/2} \quad (5)$$

$$q_t = \frac{1}{\beta} ln(\alpha\beta) + \frac{1}{\beta} lnt \quad (6)$$

2.6. Modeling of adsorption isotherms

Langmuir isotherm: This model is very useful to describe the monolayer adsorption of a solute on the surface of an adsorbent and also applies in the case of chemisorption and physisorption [15]. The linear form of this equation is given in Eq (7):

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \quad (7)$$

q_e = quantity adsorbed per unit mass of the adsorbent (mg/g); C_e = concentration of the adsorbate at equilibrium (mg/L); q_m = maximum quantity adsorbed per unit mass of the adsorbent (mg/g); b : Langmuir constant. The knowledge of the value of the separation constant R_L allows to predict if the adsorption is favorable or not: For favorable adsorption, $0 < R_L < 1$; $R_L > 1$, $R_L = 1$ and $R_L = 0$, respectively, describe unfavorable, linear and irreversible adsorption

$$R_L = \frac{1}{1 + bC_0} \quad (8)$$

Freundlich isotherm: This model is also used when the adsorbent has a heterogeneous adsorption surface i.e. the adsorption sites are energetically different [15]. Its linear form of the Freundlich equation is as follows (Equation 9):

$$lnq_e = lnK_f + \frac{1}{n} lnC_e \quad (9)$$

q_e: quantity adsorbed per gram of solid at equilibrium (mg/g) ; C_e: adsorbate concentration at adsorption equilibrium (mg/L) ; K_f and 1/n: Freundlich constants characteristic of the efficiency of an adsorbent. By plotting ln q_e vs ln C_e, we obtain a straight line with slope 1/n and intercept ln K_f.

Rubinin-Radushkevich (D-R) isotherm: Langmuir and Freundlich isotherms have been shown to be insufficient to explain the physical and chemical characteristics of adsorption. D-R is most often used to describe sorption isotherms in single solute systems [15]. Its linear form is expressed in Eq (10):

$$lnq_e = lnq_m - \beta \mathcal{E}^2 \quad (10)$$

With q_m is the maximum amount to fill a monolayer (mg/g); q_e = equilibrium adsorbed amount in the solid phase (mg/g); R = perfect gas constant ($J.K^{-1}.mol^{-1}$). Ɛ is the Polanyi potential which can be calculated as follows (Eq11):

$$\mathcal{E} = RTln(1 + \frac{1}{C_e}) \quad (11)$$

β is obtained by plotting $lnq_e = f(\mathcal{E}^2)$ and the average adsorption energy E (in $kJ.mol^{-1}$) can be obtained by the following relation (Eq 12):

$$E = (2\beta)^{-1/2} \quad (with\ \beta = K_{D\text{-}R}) \quad (12)$$

Temkin isotherm: This model assumes that the heat of adsorption is due to the interactions between the adsorbent and the adsorbate [16]. Linearization of the relationship gives the equation (13):

$$q_e = BlnA + BlnC_e \quad (13)$$

With q_e: B=RT/b_T is a constant related to the adsorption energy; b_T is the adsorption potential (J/mol).

Elovich Isotherm: The equation that defines this model based on a kinetic principle which assumes that adsorption sites increase exponentially with adsorption; this implies a multilayer adsorption [16]. The equation was first developed to describe the kinetics of chemisorption of gas onto solids. The linear forms of the Elovich model are expressed as follows:

$$ln\frac{q_e}{C_e} = lnk_e\, q_m - \frac{q_e}{q_m} \quad (14)$$

Elovich maximum adsorption capacity and Elovich constant can be calculated from the slope and intercept of the plot of ln (q_e/C_e) vs q_e.

2-7- Modeling of thermodynamic parameters

Thermodynamic parameters such as Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) are essential for any evaluation of any adsorption process [2]. The thermodynamic properties were calculated using the following equations:

$$\Delta G = -RTlnK \quad \text{with} \quad lnK = \left(\frac{\Delta S}{R}\right) - \left(\frac{\Delta H}{RT}\right) \quad (15)$$

Where R is the perfect gas constant ($kJ.mol^{-1}.K^{-1}$) and T is the temperature (K). The enthalpy change (ΔH) and entropy change (S) are calculated from the plot of lnK vs 1/T. K is calculated from the relation:

$$K = C_{ads}/C_e \text{ with } C_{ads} = C_o - C_e \quad (16)$$

Where K is the equilibrium constant, C_e is the equilibrium concentration (mg/L) at temperature T, C_0 is the initial concentration of (mg/L), C_{ads} is the concentration in the adsorbent at equilibrium (mg/L) at temperature T.

3. RESULTS AND DISCUSSION

3.1 Adsorption on silica and sand-silica in batch mode

3.1.1 Influence of contact time

The adsorbent/adsorbate contact time is a determining factor in the study of the depollution process. It is a parameter that allows evaluating the kinetics of the adsorption process. Results of the effect of contact time on

the discoloration of tannery wastewater using SiO_2 only and SiO_2/sand mixture are shown in Figure 3. It can be observed from this Figure 3 that the discoloration of tannery wastewater on both adsorbents increases rapidly up to 1 hour. Equilibrium is attained in 48 h for both adsorbents with discoloration of about 41 % for sand sand/SiO_2 mixture and about 60 % SiO_2 sample alone. However, increasing the contact time to 72 h, increase discoloration to nearly 100 % on SiO_2 material as against about 40 % on sand/SiO_2 mixture. Hence, tannery wastewater is easily decolorized by using only SiO_2 silica alone as compared to sand/SiO_2 mixture. The superior adsorption capacity of SiO_2 could be justified by the fact that silica alone has a large specific surface [13], having available binding sites for organic and inorganic pollutants contained in this wastewater. Contrarily, the low discoloration capacity of the sand/silica combination could be due to the particle agglomeration resulting from mixing of the two materials thus limiting surface area or number of sites available for discoloration.

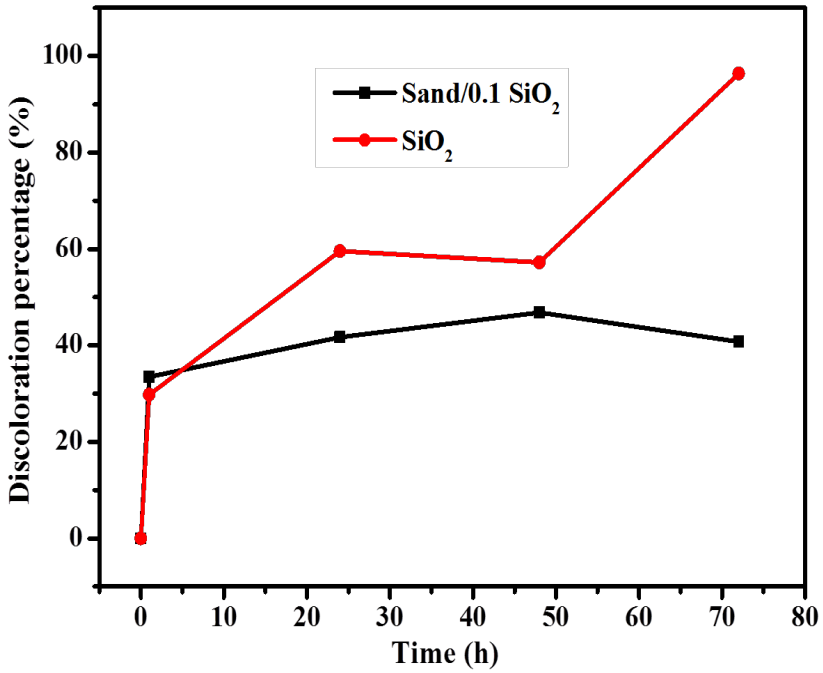

Figure 3: Influence of contact time.

3.1.2 Influence of adsorbent mass

The mass of the adsorbent is an important factor for the economic point of view since the main goal of the wastewater treatment processes is to achieve good performance at low cost. The influence of adsorbent mass on TW discoloration is depicted in Figure 4 where it is clearly shows that the discoloration of tannery wastewater remains constant around a removal rate of 40% irrespective of the quantity of sand/SiO_2 mixture used. Meanwhile, it can be seen that the discoloration rate increases from 45 to 73% when the SiO_2 mass increases from 0.05 to 0.5g. This increasing in discoloration percentage with increasing SiO_2 mass is due to the availability of the increasing number of active sites leading to better discoloration performance [17]. By contrast, the result shows that the adsorption capacity of Sand/SiO_2 remains unchanged for all sand mass variation for TW treatment. This is probably caused by agglomeration of sites from sand and SiO_2, hence causing only few sites to be available for discoloration. Equally, it may also be due to the fact that firstly sand alone is probably not efficient in discoloration and secondly the fact that discoloration was performed without stirring did not allow pollutant molecules to get to surfaces of sand and silica in the mixture.

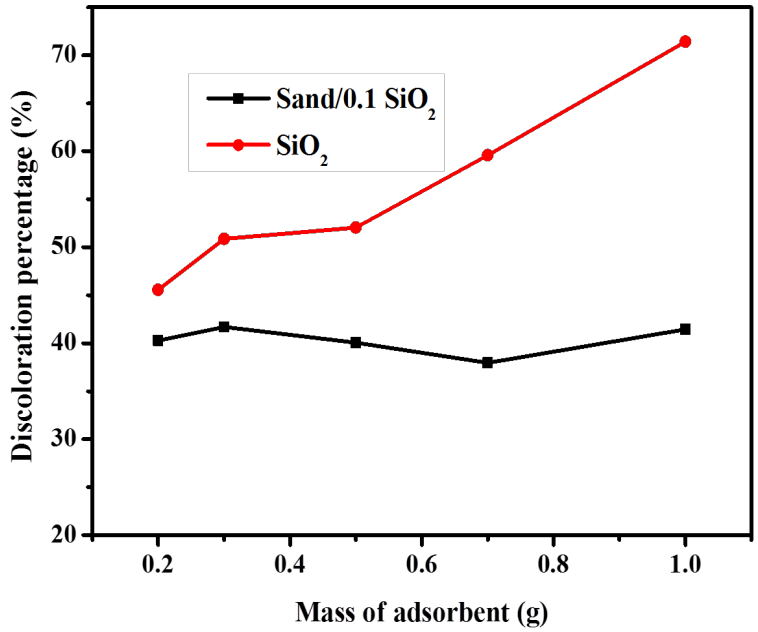

Figure 4: Influence of Adsorbent dose on the discoloration process.

3.1.3 Effect of initial concentration

Results of the influence of tannery wastewater initial concentration measured as absorbance on the discoloration efficiency is presented in Figure 5. Only results from sand/SiO_2 mixture are presented because almost the same values were obtained with SiO_2 alone. It can be seen that the percentage of discoloration decreases as the concentration increases. This result is explained by the limitation of the active sites with the increase in the initial concentration of the tannery wastewater [17]. In other words, when the solution is highly polluted, the pollutants contained in the solution are likely to bind to the active sites and consequently quickly saturate them, thus, leading to poor efficiency of the treatment especially with increasing initial concentration.

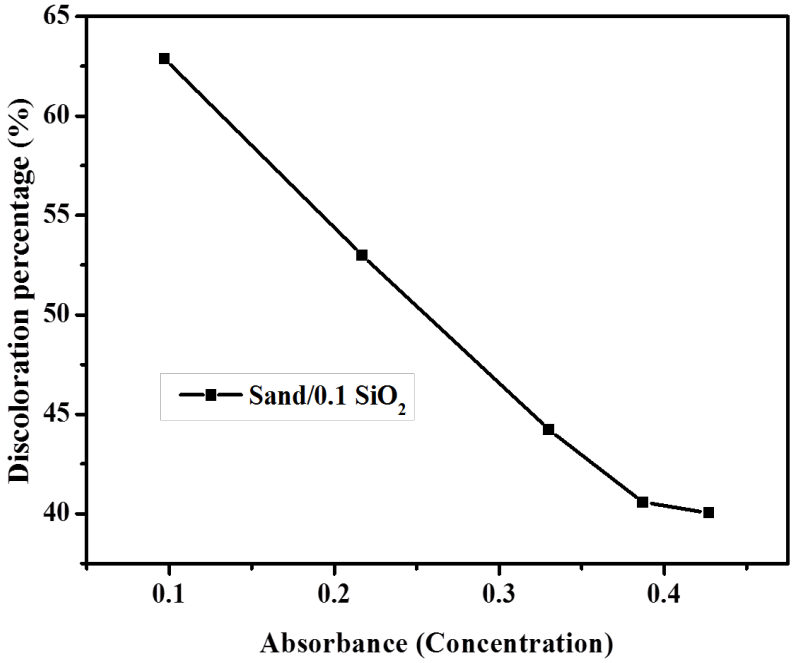

Figure 5: Influence of initial concentration on the discoloration process.

3.1.4 Ionic strength effect

Figure 6 shows the variation in TW discoloration efficiency as a function of the NaCl concentration. The results show that regardless of the nature of the adsorbent used, the percentage of discoloration increases as the concentration of the NaCl solution increases. This observation could be firstly focused on ionic species contained in TW since they are affected by the electrolyte (NaCl) in the solution [18]. The increase of the ionic strength increased mobility of the ions, and consequently more chance for the ions to be combined with the active sites on the adsorbents [8]. Also, increase of NaCl concentration can favor the reduction of solubility of some organic pollutants in the medium which benefit their mass transfer from the aqueous phase to the solid phase of SiO_2 and sand/SiO_2 and increase the discoloration quantity [19, 20]. Probably this phenomenon explained the reason why sand/SiO_2 showed better discoloration performance than SiO_2 because more sites were now available from the two materials in the mixture. Since the NaCl is added in small amounts and low concentrations to modify the conditions of the treatment, the reduction of its effects such as increase in treatment cost from possible corrosion can be handled by addition of biomass adsorbent in to the water. This can significantly reduce the NaCl concentration. Nikolay Agudelo [21] used Fique fibers obtained from the leaves of *Furcraea* spp to eliminate NaCl from water. The fibres exhibited high simultaneous removal of chloride and sodium ions up to four times higher than exchange capacities commonly observed for most commercial ion exchange resins. The second option is using filtration through activated carbon cloth (ACC) placed just before the filtration design. Hisham [22] used this method and observed that the rate of adsorption on ACC cloth was linearly proportional to NaCl initial concentration and that the adsorption capacity increased with increasing concentration. They also observed that the cumulative adsorption efficiency increased with an increase in the number of treatment cycles (three cycles) and most of the salts (initial concentration: 1000–3600 mg/L) were captured in the first cycle. This uses no energy. All the adsorbents are highly available locally at very low or no cost, hence very little increase in cost of treatment.

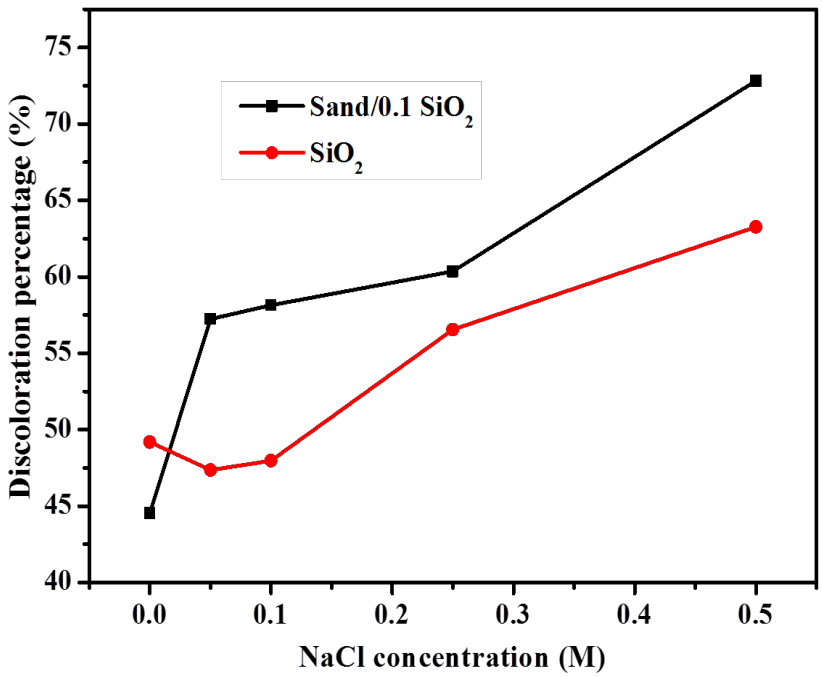

Figure 6: Influence of ionic strength on the discoloration process.

3.1.5 Effect of temperature

It appears from Figure 7 that irrespective of the nature of the adsorbents used, the discoloration efficiency increases rapidly up to maximum value at 35°C; 61 % for sand/SiO_2 mixture and 64 % for SiO_2 alone. These results are explained by the fact that slight increase in temperature leads creation of new active sites as adsorbents undergo a rearrangement in structure with heating. However, with further increase in temperature, firstly, the fixation of the pollutant on the surfaces of the adsorbents (SiO_2 and sand/SiO_2) is not favorable due to destruction of the active sites when the temperature of the medium is high. Secondly, the decreasing of adsorbed quantity could also be justified by the enhancement of solubility of pollutants leading to less interaction with solid adsorbent. This was probably the case with SiO_2 system. However increase in temperature showed slight positive trend in TM

discoloration on sand/SiO_2 mixture, probably due to liberation of agglomerated sites, hence creating more sites for discoloration.

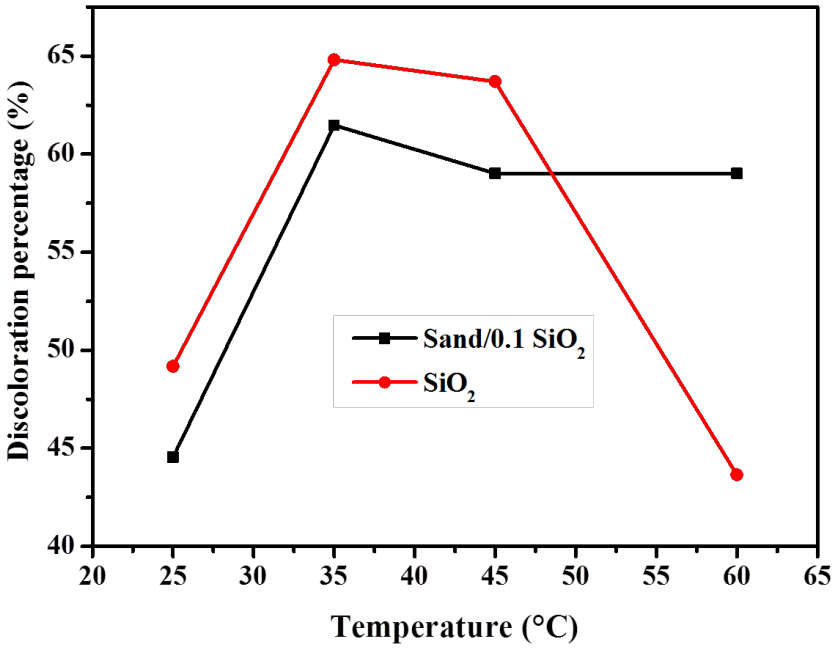

Figure 7: Influence of temperature on the discoloration process.

3.2. Adsorption kinetics modeling

To investigate the kinetic parameter of different adsorbents on the discoloration process of Maroua tannery water, four kinetic laws were employed for the TW pollutant removal process: the pseudo-first order, pseudo-second order, intra-particle diffusion and Elovich models. The calculated kinetic parameters are presented in Table 2. From the data reported in Table 2, it is clear that the correlation factors of the adsorbents used (SiO_2 and sand-SiO_2) represented are not reasonable ($R^2 \leq 0.95$) for the pseudo-first-order, intra-particle diffusion and Elovich models. However, it can be seen that pseudo-second order model describes the adsorption of TW pollutants on SiO_2 and sand-SiO_2 with the R^2 values of 0.999 and 0.990 respectively. This is also supported by closeness between q_e, exp' and q_e, cal for both systems (Table 2).

Table 2: The parameters of the adsorption kinetics of the TW discoloration process.

Model	Parameters	SiO_2	Sand/SiO_2
Pseudo-fisrt order	k_1(min^{-1})	0.007	0.010
	q_e, exp'(Abs/g)	1.126	0.100
	q_e, cal (Abs/g)	0.735	0.029
	R^2	0.598	0.277
Pseudo-second order	k_2 (g/Abs/min)	0.703	0.089
	q_e, exp' (Abs/g)	1.126	0.100
	q_e, cal (Abs/g)	1.011	0.835
	R^2	0.999	0.990
	k_{id} (Abs/g/min$^{1/2}$)	0.047	0.003
Intra-particle diffusion	C (Abs/g)	0.353	0.072
	R^2	0.793	0.583
Elovich	α (Abs/g.min)	5.966	7316.773
	β (g/Abs)	11.737	196.078
	R^2	0.938	0.722

Abs : Absorbance ; $q_{e,\,cal}$ and $q_{e,\,exp}$, are, respectively, calculated and experimental equilibrium amounts adsorbed.

The values of the kinetic constants K_2 show a rather fast retention rate for SiO_2 (K_2 = 0.703) compared to the sand-SiO_2 combination (K_2 = 0.089). This result means that the adsorption process between adsorbents and pollutants occurs in two steps in accordance with some authors [9, 20]. The first is the diffusion of the pollutants

from the TW to the surface of the adsorbents, and the second step is the fixation of pollutants on the active sites in the adsorbents.

3.3. Modeling of adsorption isotherms

In this work, five adsorption equilibrium models were studied: Langmuir, Freundlich, Temkin, Dubin-Radushkevich and Elovich. The values of the different adsorption parameters are calculated from the linearized equations of each model. The obtained values are reported in Table 3.

The different adsorption equilibrium constants clearly show that on the five models studied for SiO_2 adsorbent, only the Elovich model ($R^2 = 0.963$) is able to explain the adsorption equilibrium phenomenon taking place during the discoloration process. On the other hand, the results for the sand-SiO_2 combination indicate that almost all the models applied in this study are consistent with the TW discoloration process, except the Dubinin-Radushkevich model ($R^2 = 0.028$).

It can therefore be said that the Langmuir, Freundlich, Temkin and Elovich models with regression coefficients of 0.996; 0.995; 0.998 and 0.984, respectively; are appropriate for the description of the tanning water discoloration phenomenon in Maroua when using the sand/SiO_2 mixture. This implies that the adsorption process can take place both in monolayer (single layer) with energetically homogeneous adsorption surface and in multilayer with energetically heterogeneous adsorption surfaces [23, 24].

Temkin equilibrium constant (A_T (L/Abs)) were very high for the two systems; 0.989 for sand/SiO_2 mixture and 2.441for SiO_2 indicating the favorable reaction from left to right, hence the ease of discoloration of TM by these systems. Negative Temkin adsorption energy (b_T (kJ/mol)) of -19.416 and -16.969 was obtained for sand/SiO_2 mixture and SiO_2 system respectively (Table 3), showing that the discoloration process occurred by physical adsorption.

Table 3: Parameters of the adsorption isotherms of the TW discoloration.

Model	Parameter	SiO_2	Sand-SiO_2
Langmuir	q_m (Abs/g)	0.035	0.091
	K_L (L/Abs)	15.999	8.815
	R_L	1.119	0.238
	R^2	0.858	0.996
Freundlich	K_F (Abs/g)(L/Abs)$^{1/n}$	0.001	0.056
	n_F	-0.332	-1.281
	R^2	0.329	0.995
Dubinin- Radushkevich	q_m (Abs/g)	0.468	0.535
	K_{D-R} (mol^2/kJ^2)	0.010	0.008
	E (kJ/mol)	7.142	7.905
	R^2	0.648	0.028
Temkin	B	-0.146	-0.127
	A_T (L/Abs)	2.441	0.989
	b_T (kJ/mol)	-16.969	-19.416
	R^2	0.177	0.998
Elovich	q_m (Abs/g)	0.184	0.056
	K_E (L/Abs)	0.501	26.825
	R^2	0.963	0.984

3-4 Thermodynamic study

The calculated thermodynamic parameters are summarized in Table 4. The Gibbs energies are positive for SiO_2 and negative for the sand/SiO_2 adsorbent with exception at 25°C. The negative values of $\Delta G°$ were obtained at different temperatures for the sand/SiO_2 except for discoloration at 25°C, explaining the spontaneous and favorable character of the adsorption process of the pollutants of the tanning water of Maroua on the sand/SiO_2. On the other hand, the positive values for the SiO_2 case only indicate that the discoloration process is not spontaneous with increasing temperature [13]. The positive value of entropy $\Delta S°$ shows that there is an increase in disorder during the adsorption process of pollutants contained in Maroua tanning wastewater. The positive value

of enthalpy ΔH^o in both cases means that the TW discoloration process is an endothermic process. Thus, an increase in temperature would decrease the efficiency of discoloration.

Table 4: Thermodynamic parameters of TW discoloration.

Parameters	T(K)	Kc	ΔG° (kJ/mol)	ΔH° (KJ/mol)	ΔS° (kJ/mol/K)
SiO_2	298	0.095	5.829	116.487	0.372
	308	0.903	0.263		
	318	0.796	0.594		
	333	20.381	8.346		
$Sand/SiO_2$	298	0.803	0.543	11.319	0.038
	308	1.595	-1.157		
	318	1.440	-0.904		
	333	1.440	-0.904		

4. CONCLUSION

In this study, the discoloration efficiency of silica alone and sand/silica mixture were tested for discoloration of wastewater from tannery processing units of Maroua (Cameroon). For both absorbents, the results showed that increase in contact time, adsorbent mass and ionic strength have a positive effect on discoloration efficiency. The best discoloration efficiency was obtained at 35°C for both systems. However, increase in temperature has a negative effect on SiO_2 system and little effect on $Sand/SiO_2$ system. 41% discoloration was obtained with $sand/SiO_2$ mixture system in 48 hours equilibrium time against 60% for SiO_2 system. While all the tested isotherm models fitted discoloration on $sand/SiO_2$ mixture system, only Elovich isotherm model described discoloration on SiO_2 system. However, the pseudo-second order kinetic model fitted discoloration on the two systems. Adsorption energy calculated from Temkin isotherm model was negative indicating physical discoloration process. Though discoloration was more efficient on SiO_2 under most tested conditions, negative Gibb's enthalpy values obtained for $sand/SiO_2$ system shows that discoloration was more spontaneous using this mixture. The presence of an electrolyte strongly enhances the efficiency of $sand/SiO_2$ system in discoloring TM. This is very important for the economy of the process since sand is locally available at almost zero cost. The synthesized silica alone and its combination with sand are very effective for the treatment of complex wastewater containing both organic and inorganic pollutants.

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CONFLICT OF INTEREST

The author declares that there is no conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancies have been completely observed by the authors.

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