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Efficient and eco-friendly adsorption using low-cost natural sorbents in waste water treatment

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The removal efficiency of BOD_5, COD and turbidity from wastewater using different sorbents to study their adsorption capacity has been studied. An eco-friendly technology in the wastewater treatment field with low cost has been promoted. Experiments have been performed by varying the operating parameters such as adsorbates, *p*H ranges and mixing contact time, the results obtained prove that the *p*H is very important in the retention process and removal efficiency wherein there is a broad variation among the *p*H ranges and that a good correlation coefficient $R^2 = 0.99$ show reliability of pseudo second order in the adsorption kinetics of different parameters onto the different sorbents.

Keywords: BOD_5, COD, Turbidity, Adsorption, Low-cost sorbent, Waste water treatment.

Eutrophication of water body is a major, global environmental problem, its main cause is agriculture runoff or leaching from sludge deposited in landfill fields[1], disposal of nutrients from wastewater plants and organic pollution which contributes to accelerate eutrophication of lakes and rivers, dissolved oxygen depletion and fish toxicity in receiving water, leading thus to a number of health problems involving living species such as humans and animals[2].

In order to avoid this organic pollution, several technologies have been tested, namely biological treatment[3], chemical precipitation[4], supercritical water oxidation[5], steam stripping[6], microwave radiation[7], ion exchange[8] and adsorption[9]. Among these recipes, adsorption technology has received much attention and is considered to be a robust and effective technique used in water and wastewater treatments due to its economic advantages, low energy input and easy operation[10]. Amongst those products, activated carbon is the most known of them because of its abundance and cost effectiveness[11], however, it’s use is limited to wastes with low organic concentrations[12].

Recently, in the field of pollution control, bentonite has known a vast scope for either the degradation of organic compounds, pollutants or their transformation into less dangerous forms[13]. The use of bentonite as adsorbent of organic pollutants and minerals has attracted the attention of many researchers[14].

On the other hand, chitosan is known as an ideal natural support for enzyme immobilization because of its special characteristics such as hydrophilicity, biocompatibility, biodegradability, non-toxicity, adsorption properties[15] obtained from chitin deacetylation using alkaline medium, and has acquired a remarkable importance as an adsorbent in downstream processes involving bioproducts. Chitin and chitosan are the main components of crustacean shells and are thus widely distributed in nature[16].

Experimental Section

Characterization of the adsorbent

Bentonite used in our study is extracted from the deposit at Hammam-Boughrara Maghnia (Tlemcen). It has been provided as a finely divides powder (about 54% of the grains have a diameter less than 2 µm) by (ENOF) bentonites Maghnia (Tlemcen). The specific surface area measured by nitrogen adsorption at 77 K for bentonite is 23 m^2/g. From an examination of the results of the chemical composition of bentonite has a high content of SiO_2 trend aluminium[17]. Chitin and chitosan have been provided by the laboratory of Inorganic Chemistry and Environment, Department of Chemistry, Faculty of Sciences, University of Tlemcen, Algeria.

Batch adsorption studies

Batch adsorption studies were carried out by shaking 500 mL stoppered conical flasks containing a concentration of bentonite of 750 mg/L in 250 mL of sewage water of desired concentration and *p*H at 200 rpm and 25°C for 5 min. Then a concentration of 2 mg of chitosan powder or chitin was added to the initial solution and stirred for 3 min (coagulation), the stirring speed was reduced to 40 rpm for 20 min (flocculation)[18]. In this study, all the adsorption experiments were conducted in triplicate. For the study on the optimum *p*H, the initial *p*H values of the solutions were varied from 4 to 8 by drop-wise addition of 0.1 N HCl or NaOH solutions with the initial concentration fixed at 500 mg L^{-1}. At the end of the adsorption period of 180 min, the supernatant solution was filtered and settled for 30 min. The supernatant solution was again filtered using a Watmann Paper filter. The amount of the pollutant in the solutions before and after adsorption was analysed by spectrophotometry and turbidimetry. In this study, all the adsorption experiments were conducted in triplicate.

The removal efficiency was calculated based on the following formula:

$$\eta = [(C_0 - C_e) / C_0] \times 100\% \quad \ldots (1)$$

where C_0 and C_e are the initial and final concentrations, respectively.

Through the study, the contact time was varied from 10 to 180 min and the *p*H of the solution from 4 to 8.

Results and Discussion

These systems (adsorbents/adsorbates) were applied to fix the organic matter present in the waste water collected from the treatment plant. The samples of waste water were taken on a daily basis from the influent of the plant at 10:00AM. Table 1 is summarizing the average influent parameters measured during the experimentation.

The removal efficiency is calculated at each time interval and is plotted versus time.

The adsorption of organic matter was followed by spectrophotometry and turbidimetry under various conditions of adsorbents, contact time, *p*H and stable ambient temperature and stirring speed.

Table 1—Average influent parameters at the treatment plant at *p*H 7

Parameters	Turbidity	BOD_5	COD
mgL	88.9 NTU	197	390

Effect of the contact time *vs* adsorbents

Turbidity removal

The results obtained showed an important and fast adsorption capacity of turbidity on Chitin for the first 30 min (87.22%), then it dropped continuously after 60 min.

Bentonite associated with chitin reached 84.41% of its removal efficiency despite its slow reactivity.

According to other researchers[19,20] by mixing bentonite and chitin or chitosan to the coagulation/flocculation process, in some cases coagulant adds positively affected on pollutant removal, which was the case in our study, wherein the adsorption capacity of bentonite increased from 76.59% for bentonite alone to 84.41% for bentonite+ chitin. However, turbidity removal efficiency acted reversely and decreased slightly from 76.59% for bentonite alone to 69.50% for bentonite+ chitosan.

Biochemical Oxygen Demand removal

The results proved that bentonite is the most efficient adsorbent used for the removal of BOD_5. Indeed, the adsorbance capacity of BOD_5 on bentonite alone is excellent with 90.35%, followed by bentonite associated with chitin (87.30%) followed by bentonite associated with chitosan (85.27%).

BOD_5 removal on chitosan and chitin represent 73% and 68.52% respectively at residual concentration of 197 mg/L.

Chemical Oxygen Demand removal

The necessary time to obtain the adsorption equilibrium is about 60 min with maximum removal efficiency of COD of 78.56% on chitin, 77% on bentonite after 180 min, 67.43% for chitosan after 120 min and 74.82% for bentonite+ chitosan at residual value of 390 mg L^{-1}

Results from other experiments[21] showed that sorption equilibrium of COD was reached in 30 min.

Effect of *p*H *vs.* adsorbents

Generally, *p*H value is one of the most important parameters controlling the adsorption process. In order to determine the effects of *p*H values on the removal efficiency, experiments were carried out using various *p*H levels in the range of 4.0-8.0, as shown in Figs 1, 2 and 3. It appears that the adsorption capacity of the different adsorbents is fluctuating.

Effect of pH on turbidity removal

The turbidity removal efficiencies of the individual coagulants are depicted in Fig. 1. The maximum

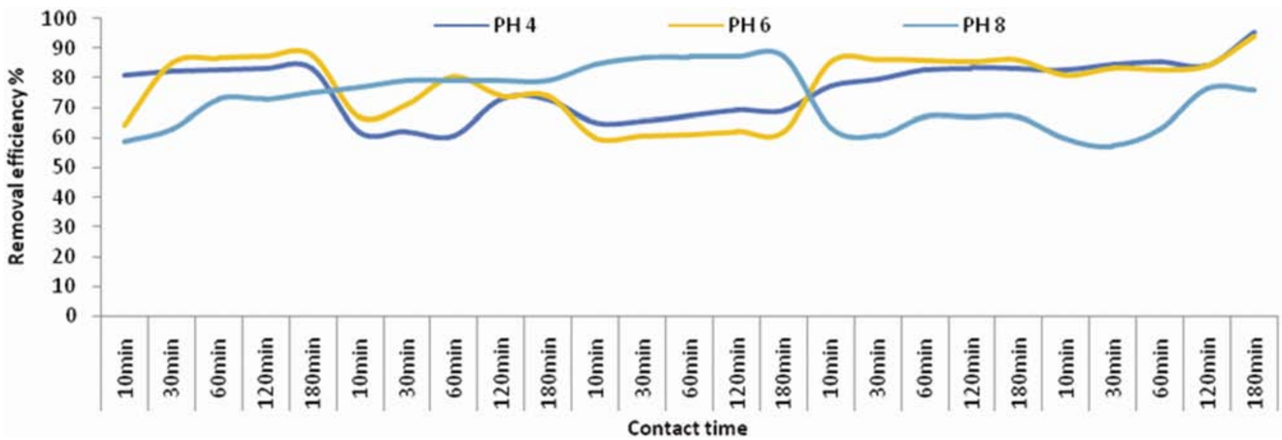

Fig. 1—Effect of *p*H on turbidity adsorption on different sorbents (adsorbent description is on the horizontal axis).

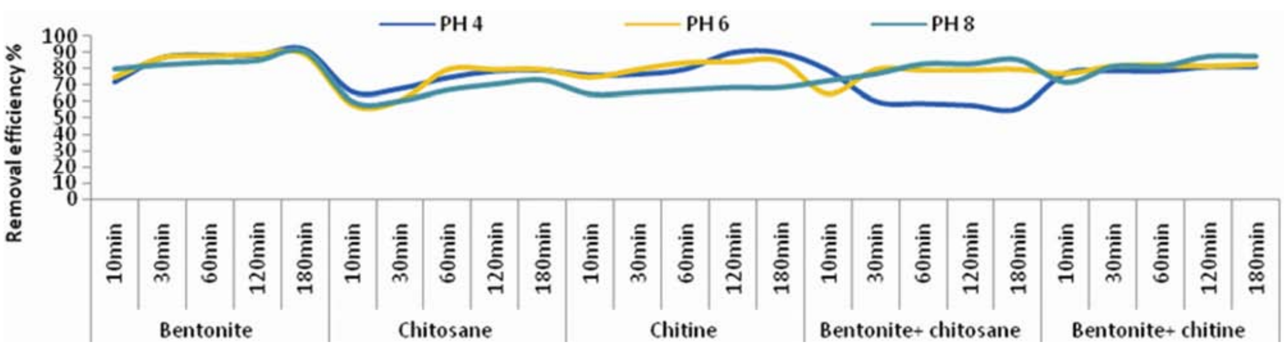

Fig. 2—Effect of *p*H on BOD_5 adsorption on different sorbents (adsorbent description is on the horizontal axis).

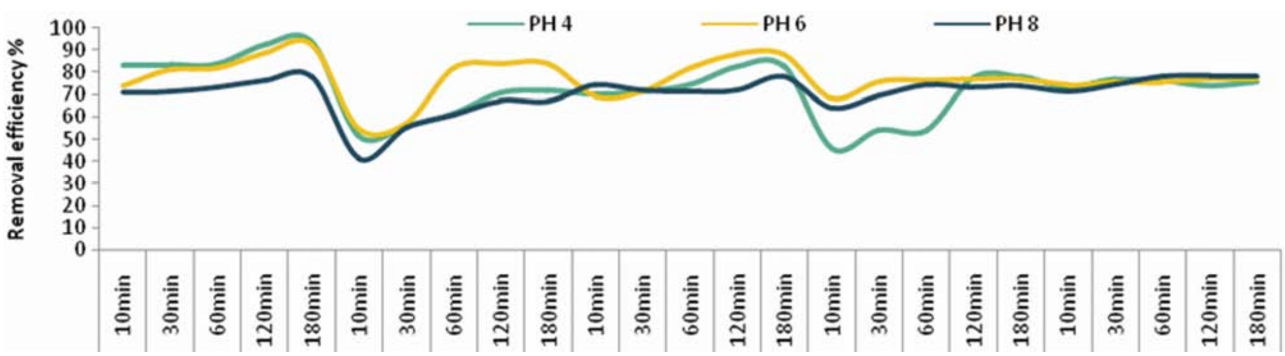

Fig. 3—Effect of *p*H on COD adsorption on different sorbents (adsorbent description is on the horizontal axis).

reduction was observed with 88% of chitin at *p*H 8, followed by bentonite associated with chitosan with 86.86% at *p*H 6 followed by bentonite with 86% at the same *p*H, followed by 84% of removal efficiency for bentonite associated to chitosan at *p*H 6. The tracking for the least efficiency showed chitin at *p*H 4 with 60.78%.

Effect of pH on BOD_5 and COD removal

In Figs 2 and 3, it is seen that the *p*H range had a different impact on BOD_5 and COD Indeed, at *p*H 4, the removal capacity of chitosan on COD has achieved 84%, and on BOD_5, 79.69% . At *p*H 6, COD percentage uptake on chitin was 88.22% and 84.77% on BOD_5.

At *p*H 8, on bentonite modified by chitin. The maximum adsorbance has reached 87.30% for BOD_5 and 78.56% for COD.

At *p*H 4 on bentonite, BOD_5 and COD removal maximum efficiency adsorbance has raised 91.87% and 92.66% respectively.

On bentonite modified by chitosan COD uptake had been achieved with 78.56% vs. 55.83% for $BOD_{5.}$ other researchers[21] proved that the solubility of chitosan decreases as the *p*H varies towards the basic condition. Chitosan dissolves in aqueous solution at *p*H less than 6.0. Over *p*H 6.0, it becomes insoluble in solution and exists as solid particles.

Chitosan at alkaline *p*H showed very low efficiency and required high concentration of chitosan to achieve the required treatment levels[22,23]. This confirmed that, at least partial, protonation of chitosan amino group was required to achieve efficient coagulation of these organic suspensions. So we can deduce that the adsorbance capacity is more effective at a *p*H range between 4 and 6.

Adsorption kinetics

In order to identify the adsorption kinetics of the different parameters onto the different sorbents, first-order and pseudo second- order and second order kinetic models were applied to the experimental data.

For the first order adsorption rate constant k_v is given by the relationship:

$$\log\frac{q_e - q_t}{q_e} \qquad \text{… (2)}$$

For the pseudo second order rate constant K' is given by the following equation:

$$\frac{t}{q_t} = \frac{1}{2k'} \qquad \text{… (3)}$$

For the second order rate constant k is given by the following equation:

$$\frac{1}{q_e - q_t} \qquad \text{… (4)}$$

q_e = amount of adsorbate at equilibrium per gram of adsorbent (mg/g), t = contact time (min), k_v, K and k constants of adsorption rate respectively for the first order (min^{-1}), the pseudo second order ($min^{-1}.g/mg$) and the second order ($min^{-1}.g/mg$).

Turbidity kinetics

The rate constants of adsorption of turbidity onto the different sorbents for the first, pseudo second order and second order were determined graphically, however, only the one of pseudo-second order has been reported as shown in by (Fig. 4).

The results thus obtained for the determination of K' by calculating t/qt versus time for the pseudo second order are presented in Table 2.

The results with a good correlation coefficient (R^2 = 0.99) detailed on Table 2 showed that the pseudo second order model is the most reliable way to determine order of adsorption kinetics of turbidity onto the different sorbents. Similarly, and from the values of qe shown in Table 5, we note that the values calculated by the pseudo second order model are the most close to those determined experimentally.

Chemical Oxygen Demand kinetics

The rate constants of adsorption of COD onto the different sorbents for the first, pseudo second order and second order were determined graphically, however, only the one of pseudo-second order has been reported as shown in by (Fig. 5).

t/qt versus time for the determination of K' for the pseudo second order obtained are presented in **Table** 3.

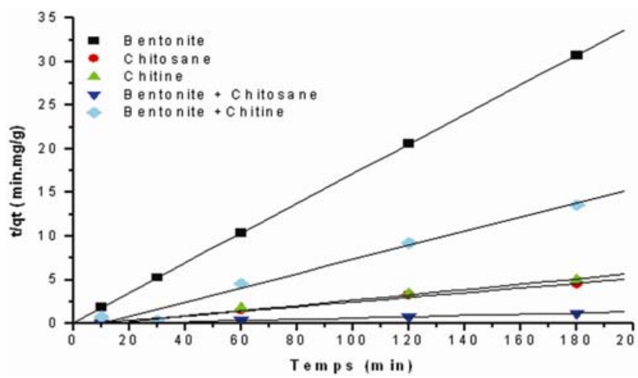

Fig. 4—Pseudo-second order kinetic plot for turbidity adsorption

Table 2—Constant of pseudo second order rates for turbidity

Sorbent	q_e (mg/g)	K'(min^{-1}.g/mg)	R^2
Bentonite	5.877	9.03×10^{-3}	1
Chitosane	37.65	2.684×10^{-4}	0.99
Chitine	32.62	6.301×10^{-4}	0.99
Bentonite + Chitosane	140.05	6.730×10^{-6}	0.98
Bentonite + Chitine	12.406	8.455×10^{-3}	0.99

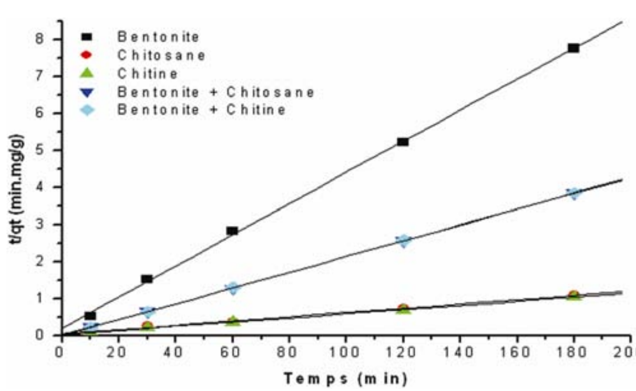

Fig. 5—Pseudo second order kinetic plot for COD adsorption

Table 3—Constant of pseudo second order rates for COD

Sorbent	q_e (mg/g)	K'(min^{-1}.g/mg)	R^2
Bentonite	23.79	7.514×10^{-4}	0.99
Chitosane	173.61	3.456×10^{-6}	0.99
Chitine	177.93	1.983×10^{-6}	0.99
Bentonite + Chitosane	47.014	1.476×10^{-5}	0.99
Bentonite + Chitine	46.860	1.215×10^{-5}	0.99

Table 4—Constant of pseudo-second order rates for BOD_5

Sorbent	q_e (mg/g)	K'(min^{-1}.g/mg)	R^2
Bentonite	88.41	4.1470×10^{-6}	0.99
Chitosane	72.93	4.0025×10^{-5}	0.99
Chitine	67.98	4.981×10^{-6}	0.99
Bentonite + Chitosane	26.00	8.128×10^{-4}	0.99
Bentonite + Chitine	25.13	1.472×10^{-4}	0.99

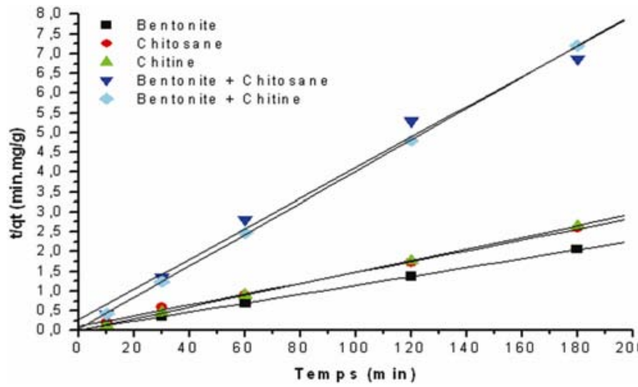

Fig. 6—Pseudo second order kinetic plot for BOD_5 adsorption

Table 5—Theoretical and experimental comparison of the adsorption the different pollutants on different supports

Sorbent	Experimental pseudo-second order Qe			Theoretical pseudo-second order Qe			First order Qe		
	Turbidity	DCO	DBO_5	Turbidity	DCO	DBO_5	Turbidity	DCO	DBO_5
Bentonite	5.85	23.176	87.6	5.877	23.79	88.41	4.014	26.04	60.45
Chitosane	36.70	163.75	69.5	37.65	173.61	72.93	23.99	210.52	39.682
Chitine	35.85	172.2	67.5	32.62	177.93	67.98	16.31	91.743	118.76
Bentonite + Chitosane	149.90	46.768	26.20	140.05	47.014	26.00	22.11	8.776	30.487
Bentonite + Chitine	13.24	46.78	24.96	12.406	46.860	25.13	31.21	43.327	113.12

The results with a good correlation coefficient (R^2 = 0.99) detailed on Table 3, show that the pseudo second order model is the most reliable way to determine order of adsorption kinetics of turbidity onto the different sorbents. Similarly, and from the values of qe shown in Table 5, we note that the values calculated by the pseudo second order model are the most close to those determined experimentally.

Biochemical Oxygen Demand kinetics

According to Table 4, we noticed that the pseudo second order model is the most likely model to determine the kinetics adsorption of BOD_5 on the different sorbents with (R^2=0.99).

On the other hand, according to Table 5, representing qe constants, the pseudo second order is closer to the experimental study which proved that the kinetics of all the studied pollutants belongs to the pseudo-second order model.

The rate constants of adsorption of BOD_5 onto the different sorbents for the first, pseudo second order and second order were determined graphically, however, only the one of pseudo-second order has been reported as shown in by (Fig. 6).

Conclusion

This study was mainly devoted to the study of adsorption capacity of turbidity, BOD_5 and COD on bentonite, chitin, chitosan and associated bentonite by a low cost process to reduce water pollution discharges. The experiments have shown that the pollutants can be adsorbed on the different adsorbents at different levels of removal efficiency at different time of equilibrium.

The kinetics of adsorption of organic pollutants on different sorbents are fast and similar (pseudo second order).

The adsorption capacities of the pollutants in equilibrium with all kind of the studied sorbents are influenced by the *p*H.

Chitin showed good coagulating properties, Chitosan coagulation had also been considered as a good coagulant, both sorbents are sustainable and cheap solution for smaller waterworks, if the supply of chitin can be guaranteed. Complementary tests should however be carried out in order to determine the impact of other parameters in raw water on treatment efficiency.

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