

Assessment of coastal water quality in BouIsmaïl Bay: Contribution to pollution reduction through sorption on local natural materials

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Abstract

The Bay of Bou-Ismaïl is subject to various forms of anthropogenic pressure, including untreated domestic and industrial discharges, macro-waste accumulation, agricultural pollution, and the impacts of fishing, aquaculture, and maritime transport. In this context, assessing the chemical and ecological status of the marine environment influenced by these factors is essential. This study has two main objectives (i) to assess the quality of the coastal waters in Bou-Ismaïl Bay and (ii) to conduct sorption tests on Magenta Red (MR), a dye present in effluents from the paper and packaging industry located in Bou-Ismaïl. In addition to the physicochemical analysis, a noticeable decrease in water transparency was observed, attributed to the presence of dyes and inks in both industrial discharges and mixed waters. This visible alteration serves as an initial indicator of the degradation of marine water quality. The results of the physicochemical characterization showed that both industrial effluents and seawater contain high concentrations of organic and mineral matter, particularly ammonium (NH_4^+) and phosphate (PO_4^{3-}) ions: i1: Mean concentrations of NH_4^+ were (1.25 ± 1.11) mg/L in the discharges and (0.72 ± 1.08) mg/L in the mixed waters; i2: PO_4^{3-} concentrations reached (2.00 ± 1.59) mg/L in the discharges and (1.14 ± 1.55) mg/L in the mixed waters; i3: Salinity values were (2.05 ± 1.04) for the discharges and (28.95 ± 9.30) for the mixed waters, reflecting a strong contrast between continental inputs and marine waters. The MR dye was subsequently subjected to physicochemical sorption treatment using three different sorbent materials: a geomaterial (GEOM), a calcite-rich attapulgite clay (CAL), and granulated activated carbon (GAC). This selection aimed to evaluate the sorption capacities of these three materials toward MR. Corresponding experimental results showed removal efficiencies of 72% for GAC, 98% for CAL, and 99% for GEOM, with respective contact times of 4, 5, and 6 hours.

Keywords: Industrial pollution, marine ecosystem, Magenta Red, sorption.

Résumé

La baie de Bou-Ismaïl est soumise à diverses formes de pressions anthropiques, notamment les rejets domestiques et industriels non traités, l'accumulation de macrodéchets, la pollution agricole, ainsi que les impacts de la pêche, de l'aquaculture et du transport maritime. Dans ce contexte, l'évaluation de l'état chimique et écologique du milieu marin soumis à ces influences s'avère plus qu'essentielle. Cette étude, articulée en deux volets, vise (i) à évaluer la qualité des eaux côtières de la baie de Bou-Ismaïl et (ii) à réaliser des tests de sorption du Magenta Red (MR), un colorant présent dans les effluents issus de l'industrie du papier et de l'emballage implantée à Bou-Ismaïl. En complément de l'analyse physico-chimique, une diminution notable de la transparence de l'eau a été observée, attribuée à la présence de colorants et d'encre dans les rejets industriels et les eaux de mélange. Cette altération visuelle constitue un premier indicateur de la dégradation de la qualité du milieu marin. Les résultats de la caractérisation physico-chimique ont montré que les effluents industriels et l'eau de mer contiennent des concentrations élevées de matières organiques et minérales, notamment en ions ammonium (NH_4^+) et phosphate (PO_4^{3-}). Les teneurs moyennes en NH_4^+ sont de ($1,25 \pm 1,11$) mg/L pour les rejets et de ($0,72 \pm 1,08$) mg/L pour les eaux de mélange, tandis que celles en PO_4^{3-} atteignent ($2,00 \pm 1,59$) mg/L pour les rejets et ($1,14 \pm 1,55$) mg/L pour les eaux de mélange. La salinité, quant à elle, est de ($2,05 \pm 1,04$) pour les rejets et de ($28,95 \pm 9,30$) pour les eaux de mélange, traduisant un fort contraste entre les apports continentaux et les eaux marines. Le colorant

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MR a été soumis à une série de tests de sorption physico-chimique sur trois matériaux adsorbants : un géomatériau (GEOM), une argile ²d'attapulgite riche en calcite (CAL) et un charbon envers ce polluant. Les résultats expérimentaux ont montré des efficacités de l'ordre de 72 % pour le CAG, 98 % pour le CAL et 99 % pour le GEOM, pour des temps de contact respectifs de 4, 5 et 6 heures.

Mots clés : Pollution industrielle, écosystème marin, rouge magenta, sorption.

1. Introduction

Covering an area of 350 km², Bou-Ismaïl Bay harbors invaluable fish and shellfish resources, as well as significant aquaculture activity, the quality of which requires monitoring and better control of production conditions. The variety of pollution sources in the Bou-Ismaïl area (urban, industrial, and agricultural) poses a huge threat to the marine environment, due to the introduction of biodegradable and/or non-biodegradable pollutants (Houma, 2009; Belhouche et al., 2024). This is why a complete and in-depth study of the Bou-Ismaïl area is necessary and indispensable in order to assess the ecotoxicological risks and thus avoid the dangers that could arise.

The Bay of Bou-Ismaïl, located along the central Algerian coast, is subject to increasing anthropogenic pressure due to the rapid expansion of urban and industrial activities. These activities result in the direct discharge of untreated domestic and industrial effluents into the marine environment, significantly impacting water quality and threatening marine ecosystems. Among the main pollutants are nutrients, suspended solids, heavy metals, and synthetic dyes, which alter the physico-chemical balance of the coastal waters and contribute to eutrophication and habitat degradation. This study aims to assess and monitor the level of pollution in the coastal waters of BouIsmaïl area, focusing

specifically on the impact of untreated wastewater discharges. It also seeks to contribute to environmental protection by testing and proposing a mitigation process based on the use of low-cost sorbent materials for the upstream removal of pollutants. The study explores the potential of local clay, geomaterial and activated carbon as a sustainable solution to reduce pollutant loads before they reach the marine environment.

2. Materials and methods

The objective of this study is twofold:

- Monitoring of the state of pollution in the studied area,
- Propose an adequate treatment by eliminating RM by sorption as a real model dye on some effective solid supports.

2.1 Sampling

At each sampling site, two distinct water samples were collected in order to assess the impact of discharges on coastal water quality. The first sample was taken directly at the discharge point before any mixing with seawater, allowing for the analysis of the raw effluent's physico-chemical characteristics. The second sample was collected from the sea, in close proximity to the discharge area, after the mixing of the effluent with seawater. This comparative

approach aims to evaluate the dilution effect and the dispersion of pollutants in the marine environment. Inspect the studied site as shown in Fig.1 and Table 1 below. The samples of seawater and discharges were

carried out according to the protocols recommended previously by (Aminot and Chaussepied, 1983; Schiavone and Coquery, 2011).

Table 1. Sampling plan and frequencies.

Sampling operation	Effluent	Effluent with sea water	Date	Geographic Coordinates
1	DW1	SW1	18/02/2013	N : 36° 39' 3.53'' E : 2° 41' 43.02''
2	DW2	SW2	18/03/2013	
3	DW3	SW3	08/04/2013	
4	DW4	SW4	26/05/2013	



Figure 1. (A-C) Photographs taken during the samples (between February and May 2013), (B): Location of the study area via Google-Earth.

2.2 Sorption tests on local materials

In this section, we carried out a batch sorption study of (MR) as a basic ink used in cardboard and paper printing by the TONIC industry based in BouIsmaïlon three different sorbents (calcite-rich attapulgite clay (CAL), geomaterial prepared from clay and activated carbon

And cement (GEOM) and finally a local granulated activated carbon (CAG) made from olive stones.

This dye was chosen because of its frequency in wastewater from the paper industry (Tonic packaging), a major source of water pollution in the study area.

Table 2. Link solutions composition used in printing (Recipe used by the Tonic-Packaging industry)

Products	Constituents (% weight)
Dye	20
Diluent	75
Water	05

In this section, we studied the physico-chemical treatment of liquid effluents from the paper packaging industry. The determination of the maximum wavelength of Magenta Red (MR) and its concentrations was carried out using a JASCO V-630 UV-Visible spectrophotometer.

The wavelength corresponding to maximum absorbance was identified as $\lambda_{\max} = 568 \text{ nm}$ (Fig. 2). The depollution tests were divided into three main parts:

- A kinetic study of contact time.
- A study of the influence of sorbent mass on MR retention. A study of the influence of solution pH
- A study of the influence of (MR) concentration on the purification capacity of the studied sorbents.

2.2.1 Sorption Tests

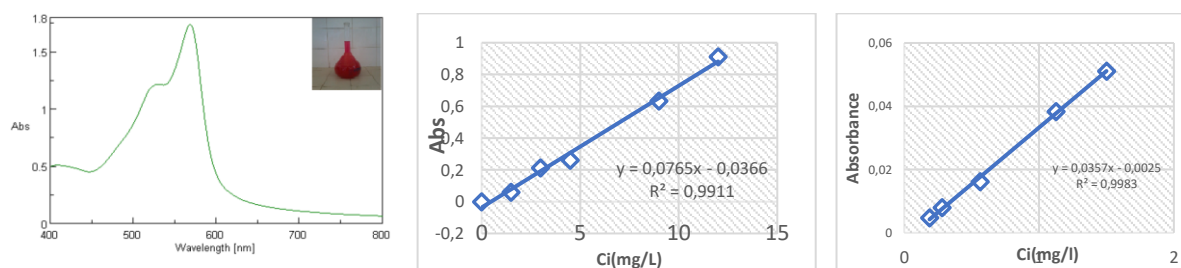


Figure 2. (a) Magenta Red (MR) absorption spectrum in the visible range; C (MR) = 24 mg/l, pH=7.9. (b) Calibration curve of Magenta Red at $\lambda_{\max} = 568 \text{ nm}$.

a) Sorption Kinetics

MR sorption onto the studied materials was carried out in batch reactors. Kinetic study aims to determine the optimal contact time (or pseudo-equilibrium time) required to maximize the sorption of a dye (MR) on an adsorbent material. The experiment consists of introducing a constant mass of adsorbent (0.2 g) into vials containing 50 mL of (MR) solution, which is then stirred at 170 rpm at room temperature. Samples are taken at intervals ranging from 0 to 24 hours, filtered (whatman filter, $0.45 \mu\text{m}$), and then analyzed by UV-Visible spectrophotometry at 568 nm. The data are represented as $q_t = f(t)$ curves, and dye removal efficiencies are calculated using this formula:

$$q_t = \frac{V(C_0 - C_t)}{m} \quad (1)$$

Where the following parameters represent:

q_t : Sorption capacity at time t (mg/g).

C_0 : Initial MR solution concentration (mg/L).

C : RM concentration in solution at time t (mg/L).

V : Volume of solution (L).

m : Mass of sorbent (g).

b) Effect of weight sorbent

MR sorption onto various sorbents (CAL, GEOM and GAC) was conducted in batch mode. Sorbent masses ranging from 100 to 1000 mg were mixed with 50 mL of MR solution (initial concentration $C_0 = 24$ mg/L) and agitated at 170 rpm for 4 hours, a duration assumed sufficient to reach sorption equilibrium. After vacuum filtration, the residual concentrations were analyzed using UV-Vis spectroscopy at 568 nm. Sorption isotherms ($q = f(C_e)$) were established at ambient temperature (25 °C) with identical contact time for all samples.

c) Effect of pH

The influence of pH on MR sorption was investigated over a wide pH range (1–12). For each test, 200 mg of adsorbent was added to 50 mL of MR solution (24 mg/L), and the pH was adjusted using H_2SO_4 for acidic conditions or NaOH for alkaline conditions. The aim was to evaluate the sorption performance under different protonation states of the dye and surface charges of the materials.

d) Effect of MR Concentration

To assess the impact of initial dye concentration, 200 mg of each sorbent material was mixed with 50 mL of MR solution at varying concentrations: 6, 12, 24, and 48 mg/L. The experimental conditions (contact time, temperature, agitation) were kept constant to isolate the effect of concentration on sorption capacity.

2.2.2 Sorption kinetics

The kinetic data for the sorption of MR onto CAG, CAL and GEOM were analyzed using the pseudo-first-order and pseudo-second-order (Wu et al., 2020, Ho et al., 2004).

Pseudo-first-order model

The pseudo first order equation is explained as follows (Ho et al., 2004)

$$q_t = q_e (e^{-k_1 t}) \quad (2)$$

The linearized form is:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

Where k_1 is the pseudo-first-order rate constant (min^{-1}), Q_e is the sorption capacity at equilibrium (mg/g), and Q_t is the sorption capacity (mg/g) at time t (min)

Pseudo-second-order model

The pseudo second order equation is explained as follows (Ho et al., 2004)

$$q_t = k_2 q_e^2 t / (1 + k_2 q_e t) \quad (4)$$

The linearized form is:

$$t/q_t = t/q_e + 1/k_2 * q_e^2 \quad (5)$$

Where k_2 (g/mg min) shows the pseudo-second-order rate constant.

3. Results

At each sampling, a pronounced chemical coloration was observed *in situ* in both the discharged effluents and the mixed waters, leading to a marked reduction in the transparency of the receiving coastal waters (Fig.1(A-C1-C2). BouIsmaïl Bay, which hosts *Posidonia oceanica* constitutes a sensitive marine ecosystem that is highly vulnerable to such physico-chemical disturbances. Elevated turbidity levels can significantly reduce light penetration in the water column, thereby impairing the photosynthetic activity of submerged vegetation and potentially disrupting the ecological balance of these habitats over the long term (Kirk, 1994).

3.1 Physicochemical parameters

Fig.3 shows the variation in physico-chemical parameters and nutrient salts in both the discharge water (DW_i) and the mixed seawater (MW_i).

a) Temperature

Water temperature is a key factor influencing the solubility of gases, particularly dissolved oxygen, which is essential for aquatic life. Rapid temperature changes of more than 3 °C can have adverse effects on ecosystems (Smith et al., 1999). The temperatures measured in industrial discharges (between 17 and 25 °C) remain below the regulatory limit of 30 °C according to Executive Decree No. 06-141 of April 19, 2006. Similarly, the temperatures of seawater samples (14.2 to 17.5 °C) are considered compliant, as they reflect seasonal temperatures.

b) Salinity

Salinity is a key environmental parameter for the distribution and physiological functioning of marine organisms (Kültz, 2015). Salinity values range on average from (2.05 ± 1.04) in discharge waters to (28.95 ± 9.3) PSU in mixed waters. The decrease in salinity in mixed waters is directly attributed to substantial freshwater inflows from industrial and domestic discharges near the sampling sites. This dilution of salinity may disrupt the ecological balance of the marine environment and impact local biodiversity.

c) pH

The pH, an indicator of water acidity, influences metal toxicity and ammonia concentration, which has an impact on aquatic life. The average pH values

measured in discharges are (7.88 ± 0.88), while those measured in seawater are (7.91 ± 0.86). The results for discharges are in line with generally accepted Algerian standards (Executive Decree No. 06-141 of April 19, 2006), which considers a pH between 6.5 and 8.5 to be compatible with the protection of aquatic ecosystems. For seawater, pH was found to be influenced by untreated discharges. Persistent values below 7 may cause stress to marine organisms (Weerathunga, 2018).

d) Dissolved Oxygen

The concentration of dissolved oxygen is critical for the survival of sensitive aquatic species, with a threshold value generally accepted to be around 4 to 5 mg/L (Aminot and Chaussepied, 1983, Rodier, 2005). The average dissolved oxygen concentration recorded in industrial discharges is (1.83 ± 1.67) mg/L, which is below this threshold, while the average concentration in mixed waters is (5.12 ± 1.89) mg/L, generally complying with environmental standards. The decrease in dissolved oxygen in mixed waters is attributed to its consumption during the oxidation of organic and mineral wastes in the aquatic environment, which can lead to hypoxic conditions harmful to aquatic life (Wang et al. 2018).

e) Nutrients variation

Nutrients are key indicators in assessing the quality of surface waters, particularly in marine environments. The results show that industrial discharges are highly enriched in nutrients (Fig. 3). Among them, phosphorus exhibits the highest average concentration, with values of (2.00 ± 1.59) mg/L in discharges and (1.14 ± 1.55) mg/L in mixed waters. This nutrient enrichment is primarily attributed to the discharge of

urban and industrial effluents, particularly due to the widespread use of phosphate-based detergents and the breakdown of organic matter (Smith et al., 1999). Elevated levels of phosphorus, along with nitrogen compounds, can accelerate eutrophication in marine and coastal environments. This phenomenon often results in algal blooms that limit light penetration into deeper waters, thereby disrupting aquatic ecosystems (Howarth and Marino, 2006; Baudrier et al., 2015). Although algae produce oxygen during daylight via photosynthesis, they consume it at night through respiration. Moreover, the microbial decomposition of dead algal biomass increases the biochemical oxygen demand (BOD), which can lead to hypoxic or even anoxic conditions, posing a serious threat to aquatic life (Diaz and Rosenberg, 2008). Additionally, oxygen depletion promotes the accumulation of toxic compounds such as ammonia (NH_3) and nitrites (NO_2^-), further degrading water quality and endangering marine biodiversity (Oschlies et al., 2018).

3.2 Sorption tests

In industrial settings, particularly in paper manufacturing, effluents are often heavily laden with organic pollutants such as dyes and inks, posing a significant threat to aquatic ecosystems if not properly treated. In order to evaluate alternative, sustainable, and economical solutions for pollution control, laboratory tests were conducted on two naturally occurring clay materials, as well as activated carbon made from olive pits. The aim of this test is to examine the ability of these materials to sorb colored compounds present in industrial wastewater. These potential sorbents have

the advantage of being abundant, inexpensive, and environmentally friendly, paving the way for their use as treatment media in paper mill effluent decontamination systems.

3.2.1 Sorption Kinetics

In this part of our study, we focused on the physico-chemical treatment of liquid effluents from the TONIC packaging industry. Three sorbent materials were used: GEOM, a geomaterial sorbent made from montmorillonite, activated carbon, cement, and small amounts of polymer and silica. CAL, a clayey material (palygorskite) rich in natural calcite; and CAG, activated carbon. The physicochemical characteristics of the sorbents were reported in our subsequent study. GEOM features a mesoporous, hydrophilic surface, a moderate specific surface area ($176.78 \text{ m}^2/\text{g}$), a total pore volume of $0.111 \text{ cm}^3/\text{g}$, and a micropore volume of $0.078 \text{ cm}^3/\text{g}$ properties, particularly the specific surface area and porosity, that are crucial for sorption. In comparison, the CAL sorbent exhibits a lower specific surface area ($26.82 \text{ m}^2/\text{g}$) and a total pore volume of $0.065 \text{ cm}^3/\text{g}$. (Belhouchet et al., 2019; Belhouchet et al., 2024). The results relating to MR sorption processes on the three materials lead to the following conclusions:

Sorption equilibrium times are respectively of the order of 4 for CAL; 5 for GEOM and 6 h for CAG (Fig.4). The contact time helps to find the optimum time at which equilibrium is reached, which can then be applied in wastewater treatment plants depending on the design of the purification process and the nature of the wastewater being treated (Ngulube et al., 2017).

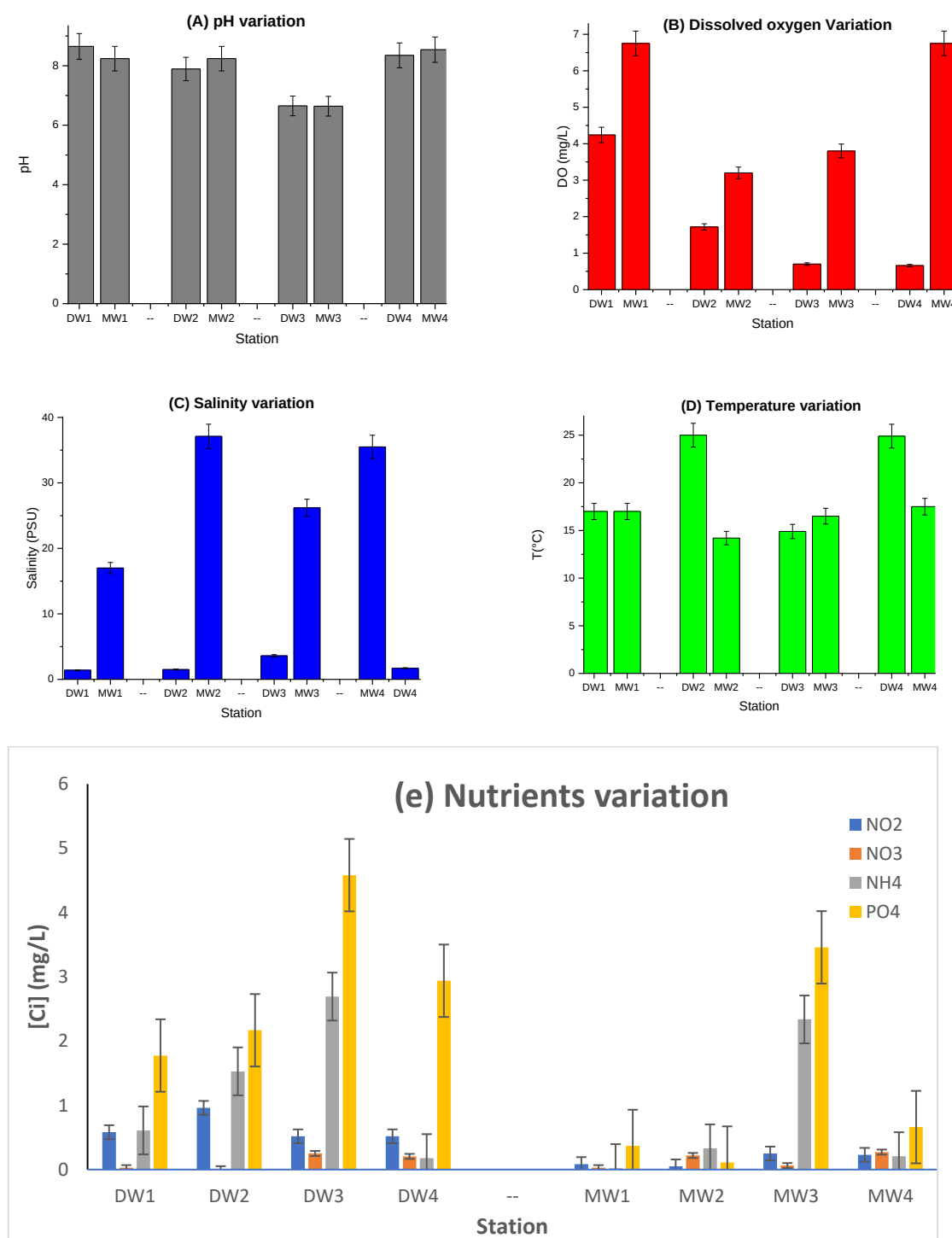


Figure 3. Physicochemical parameters and nutrients variation in BouIsmaïl area.

As shown in Fig. 5, increasing sorbent addition leads to a corresponding increase in MR dye sorption. This behavior may be

due to the increase in the number of active sorption sites provided by the sorbent support (Ngulube et al., 2017). For masses

ranging from 100 to 1000 mg, they increase in the order of 4.11 to 5.53 mg/g for CAL and 4.2 to 5.34 mg/g for GEOM, whereas they vary only from 2.5 to 4.5 mg/g for CAG. The results also indicate that the optimal mass for each sorbent is approximately 200, 300, and 700 mg for CAL, GEOM, and CAG, respectively, beyond which a saturation plateau is observed. For this parameter, we can therefore propose the following preferred sequence: $CAG < CAL < GEOM$. These results indicate that dye sorption is also influenced by the amount of sorbent present in the solution. Increasing the sorbent mass enhances the removal efficiency of MR. The experimental data showed removal efficiencies of 72% for CAG, 97% for CAL, and 98% for GEOM, with corresponding contact times of 4, 5, and 6 hours, respectively.

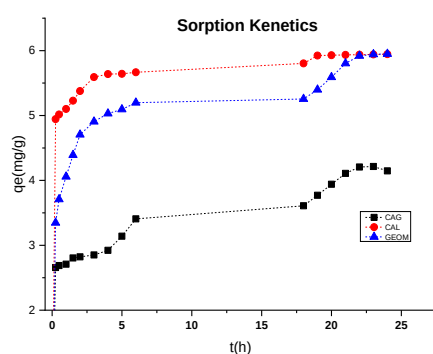


Figure 4. MR sorption kinetics on the three studied materials ($C_0 = 24$ mg/L; $M = 200$ mg; $pH = 7.9$).

Regarding the influence of initial MR concentration on the purification efficiency of the tested materials, we observed that the amount adsorbed increased with increasing initial MR concentration (Fig.6).

The results regarding the influence of pH on MR retention by the three sorbents are presented in Fig. 7,8. Results show that the acidic pH range provides optimal conditions for dye removal. The decrease in the amount of MR adsorbed at basic pH can be explained by the pH_{pzc} of the sorbents. Indeed, the pH_{pzc} values of CAL and GEOM are higher than 7 (12.45 for CAL and 7.8 for GEOM), while that of CAG is around 6.45 (Belhouchet et al., 2019; Belhouchet et al., 2024). This greatly enhances MR retention by the sorbents, as Magenta Red is a basic dye. Overall, pH affects dye sorption by modifying both the surface characteristics of the sorbents and the chemical behavior of the dye molecules.

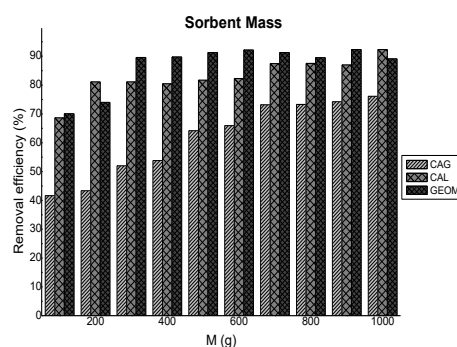


Figure 5. Effects of sorbent mass on MR elimination ($t = 4$ h; $C_0 = 24$ mg/L; $pH = 7.9$).

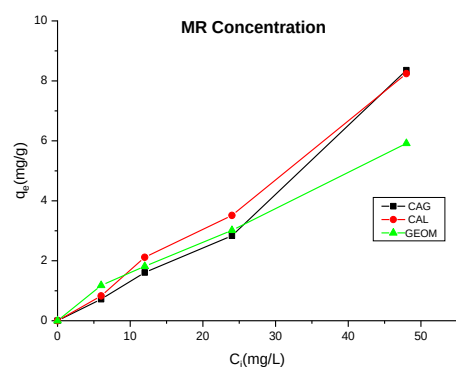


Figure 6. Effect of initial MR concentration on its elimination of different sorbents ($t = 4\text{h}$; $M = 0.2\text{ g}$).

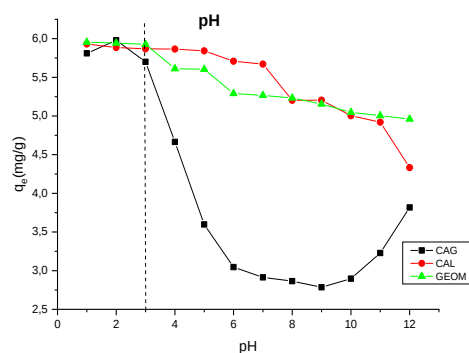


Figure 7. Evolution of the quantity of MR sorbed on the three sorbents studied as a function of pH ($C_0 = 24\text{ mg/L}$, $M = 200\text{ mg}$, $t = 4\text{ h}$)



Figure 8. Photographs showing the different samples obtained after pH variation, ($t = 4\text{h}$)
a) CAL; b) GEOM; c) CAG.

3.2.2. Sorption kinetics analysis

The sorption kinetics were analyzed using the pseudo-first-order and the pseudo-second-order. The fitting results are presented in Fig. 9, and the corresponding kinetic parameters are summarized in Table

3. Overall, the results indicate that the pseudo-second-order model provides a more accurate description of the sorption kinetics compared to the pseudo-first-order model.

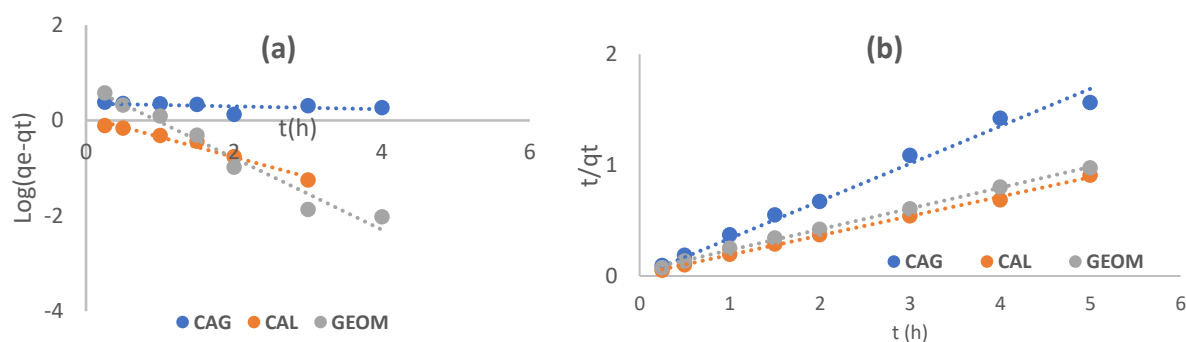


Figure 9. Graphical representation of (a) pseudo-first-order and (b) pseudo-second-order sorption kinetics of MR sorption onto CAG, CAL, and GEOM.

Table 3. Kinetic data for MR sorption by CAG, CAL and GEOM

Sorbent	Pseudo-first order			Pseudo-second order			q _{exp}
	K ₁	q _e	R ²	K ₂	q _e	R ²	
CAG	0.029	1.42	0.2293	0.33	2.96	0.9863	4.12
CAL	0.418	1.07	0.9723	0.17	5.72	0.9976	5.84
GEOM	0.753	2.05	0.9623	0.18	5.33	0.9987	5.16

Conclusion

The objective of this study was to assess anthropogenic pollution in the coastal waters of BouIsmaïl Bay. The results clearly highlight the impact of untreated urban and industrial effluents on the marine environment, particularly through the discharge of dyes and nutrients, which alter water transparency, promote eutrophication, and modify key physicochemical parameters such as salinity.

Simultaneously, the study of Magenta Red sorption using two Algerian materials and granulated activated carbon confirmed their potential as low-cost sorbents, with equilibrium times ranging from four to six hours and significant retention capacities under acidic conditions

Overall, this study emphasizes both the environmental pressures affecting BouIsmaïl Bay and the feasibility of developing locally sourced sorption materials for pollutant removal. Based on these findings, future research should include comprehensive analyses of water and sediments (PAHs, COD, BOD₅, TOC, Kjeldahl nitrogen, trace metals, etc.), extended sorption experiments targeting other organic and metallic contaminants, as well as the scale-up of sorption processes through granulation and column testing. Furthermore, upstream industrial pre-treatment measures, such as sedimentation,

coagulation–flocculation, and integrated wastewater recycling systems, remain essential to reduce pollutant loads prior to discharge.

It is also worth noting the significant progress made in recent years with the commissioning of the BouIsmaïl wastewater treatment plant in 2020, which has contributed to reducing direct discharges and improving the overall quality of coastal waters. Continued efforts in monitoring, treatment optimization, and the development of cost-effective remediation technologies will be crucial for ensuring the long-term environmental protection of BouIsmaïl Bay.

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