

Adsorption of antibiotics and dyes with individual and simultaneous mechanisms onto halloysite nanoclay and regeneration by cold plasma bubbling technology of saturated adsorbent

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Abstract: Methylene blue (MB) dye and the antibiotic enrofloxacin (ENRO) were individually and simultaneously removed from aqueous solutions while halloysite nanoclay (HNC) was also regenerated using cold atmospheric plasma (CAP) bubbling. In contrast to Fenton oxidation, the CAP-bubbling method efficiently regenerated the saturated HNC, while in parallel enhanced adsorption capacity of the CAP-regenerated HNC (compared to raw HNC) was noticed after reuse in new adsorption cycles which indicates the activation of the adsorbent during the regeneration process. This study proposes a safe, long-lasting, and highly efficient method for contaminated water remediation in which pharmaceuticals and dyes co-exist.

Keywords: nanoclays; adsorption; cold atmospheric plasma; regeneration; halloysite

1. Introduction

Antibiotics and dyes, which are frequently found in aquatic systems, have a negative impact on the environment and human health. [1]. Drugs and dyes, which are frequently found in aquatic systems, have a negative impact on the environment and human health. Particularly, the degradation-resistant characteristics of antibiotics cause important public health problems, such as some forms of cancer, skin conditions, allergies, and other grave health issues [2]. Hence, before disposing of wastewater, both groups of pollutants must be removed [3]. In the present study, the individual but also simultaneous adsorption of the dye methylene blue (MB) and the antibiotic enrofloxacin (ENRO) was carefully explored. CAP bubbling was investigated for the regeneration of the saturated HNC adsorbent, while the performance of the CAP-regenerated adsorbent was compared with raw HNC used for a number of adsorption cycles.

2. Methods

2.1. Batch Adsorption Experiments

For the simultaneous removal of pollutants, a variety of treatment techniques have been suggested, including ion

exchange, reverse osmosis, liquid membrane separation, adsorption, ozonation, photo-catalysis, coagulation, etc. [4-6]. The most efficient, user-friendly, and cost-effective of these is adsorption. According to the literature, numerous adsorbents (such as clay minerals, biosorbents, polymers, etc.) have already been studied for the removal of dyes and antibiotics [7-13]. For the adsorption studies the solution was placed in a tightly closed glass bottle. The impact of the initial pH (i.e., 2.0-11.0), adsorbent dosages (i.e., 0.5, 1, 2, and 3 g/L), contact time, and initial pollutant concentration (i.e., 10 to 150 mg/L) was examined. Concerning the binary system, one pollutant was added at various concentrations, keeping the other constant at 40 mg/L.

Samples were centrifuged at 12,000 rpm for 1 min and analyzed by a UV-Vis spectrophotometer (Shimadzu, UV-1900, Kyoto, Japan), based on the adsorption bands 663 and 272.5 nm for MB and ENRO respectively.

2.2. Saturated HNC Regeneration and New Adsorption Cycles

Using the Fenton oxidation, CAP bubbling, and air bubbling procedures, the regeneration of saturated HNC was examined. For CAP bubbling-based regeneration procedure, 50 mL of 3D water and 30 mg of saturated raw HNC were added to a plasma reactor. The CAP-regeneration system was composed of a discharge characterization system and a plasma microbubble reactor with a custom design that was powered by an NPG-18/3500 nanosecond pulse generator. The power source was able to generate positive, high-voltage nanospikes with rinsing time 4ns. Figure 1 presents the experimental setup together with a schematic representation of the plasma microbubble reactor. Adsorbent regeneration by plasma took place for 30 minutes at a constant pulse voltage and frequency of 28 kV (200 Hz) and air flow rate at 3 L/min.

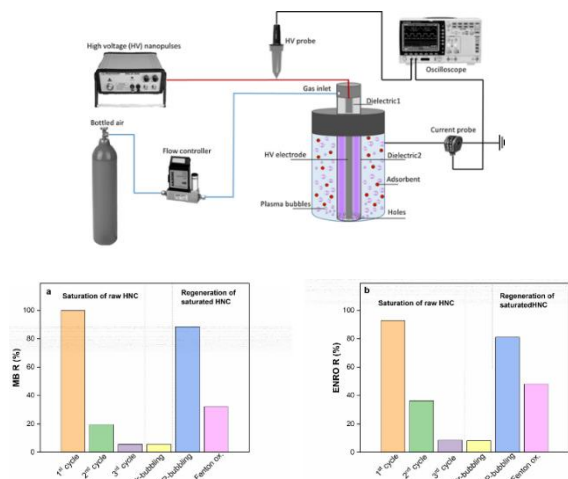


Figure 1. The experimental setup used for HNC adsorbent regeneration by cold atmospheric plasma (CAP) bubbling.

Finally, after its saturation, HNC was treated with air bubbling (without plasma ignition).

The best regeneration technique was selected, and the first regenerated HNC underwent adsorption cycles until it reached saturation. A new regeneration process was applied after the first regenerated HNC had reached saturation, producing the second regenerated HNC, and new adsorption cycles were continued until saturation. Every experiment was carried out twice.

3. Results and Discussion

3.1. Removal of MB and ENRO individually or in mixture

According to the results obtained, for the treatment of individual samples, quick adsorption of both pollutants was achieved. It is important to note that maximum removal efficiency was accomplished close to neutral pH for both ENRO and MB. The HNC adsorption capacity at equilibrium, q_e (mg/g) versus C_e at equilibrium (mg/L) is presented in Figure 2.

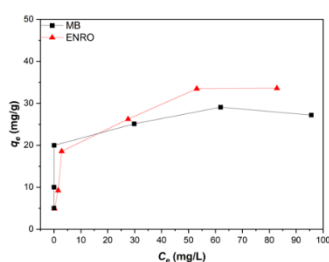


Figure 2. Adsorption isotherm (single system) for MB and ENRO ($\text{pH} = 6.2$, $C_{\text{HNC}} = 2 \text{ g/L}$, $T = 28 \text{ }^\circ\text{C}$).

A rapid increase of q_e value was noticed within the first 5 min being maximized after ~ 30 min for both pollutants (27.18 mg/g and 33.57 for MB and ENRO, respectively). As for the simultaneous adsorption of pollutants, it seems that the presence of MB acts antagonistically at ENRO's adsorption onto HNC, while on the other hand, the presence of ENRO does not affect the MB's adsorption.

3.2. Improve Process Sustainability Via Adsorbent Regeneration

Two of the biggest problems of the adsorption-treatment process are the recovery and long-term management of

spent adsorbents. Due to its high efficiency at regeneration and low energy requirement, cold atmospheric plasma (CAP) has become a fascinating substitute for traditional regeneration techniques. In the current investigation, saturated raw HNC was subjected to CAP bubbling, Fenton oxidation, and air bubbling and tested for new adsorption cycles for MB (Figure 3a) and ENRO (Figure 3b). The removal efficiency of both contaminants was almost entirely restored when CAP bubbling was used for the regeneration of the saturated HNC, reaching up to 88.5% and 81% for MB and ENRO respectively. The removal efficiency of regenerated HNC through Fenton oxidation was much lower, up to 47% and 32% for ENRO and MB respectively. The use of air bubbling (without CAP) revealed that there was no desorption of the contaminants.

Figure 3. The performance of HNC after three adsorption cycles for (a) MB and (b) ENRO after HNC regeneration with different methods ($C_{\text{ENRO}} = 40 \text{ mg/L}$, $C_{\text{MB}} = 40 \text{ mg/L}$, $\text{pH} = 6.2$, $C_{\text{HNC}} = 2 \text{ g/L}$, $T = 28 \text{ }^\circ\text{C}$).

After the first regeneration of HNC with CAP (1st CAP-regenerated HNC), new adsorption cycles were performed up to saturation. After that new regeneration was followed (2nd CAP-regenerated HNC) and new adsorption cycles. It is noticeable to mention that the 1st CAP-regenerated HNC and 2nd CAP-regenerated HNC exhibited much higher efficiency compared to the raw HNC.

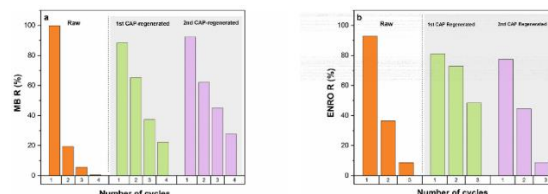


Figure 4. Adsorption cycles for (a) MB and (b) ENRO using raw, 1st CAP-regenerated and 2nd CAP-regenerated HNC, ($C_{\text{ENRO}} = 40 \text{ mg/L}$, $C_{\text{MB}} = 40 \text{ mg/L}$, $\text{pH} = 6.2$, $C_{\text{HNC}} = 2 \text{ g/L}$, $T = 28 \text{ }^\circ\text{C}$).

It is noteworthy that as the number of cycles increases (3rd and 4th cycle) the efficiency of the 2nd CAP-regenerated HNC was higher in the case of MB compared to that of the 1st CAP-regenerated HNC (Figure 4a). The increased removal efficiency achieved for the CAP-regenerated HNC in comparison with the raw HNC could be due to the active role of the plasma-generated species, e.g., $^1\text{O}_2$, $\cdot\text{OH}$, O , $\cdot\text{O}_2^-$, O_3 , H_2O_2 , etc., which may modify the adsorbent in an effective way.

4. Conclusions

In this study, the efficiency of HNC adsorbent used for the individual (single) and simultaneous (binary) removal of the antibiotic ENRO and the cationic dye MB was investigated. In the single system, a very quickly (10–20 min) removal was noticed for both pollutants adsorbed onto HNC, while an analogous trend was also observed for both pollutants in the binary system reaching equilibrium after ~ 20 –30 min. The presence of MB in the binary system acted antagonistically for ENRO adsorption onto HNC, while no effect of MB's

removal was noticed due to the presence of ENRO. The CAP-bubbling regeneration of the saturated HNC revealed significant results, firstly by effectively regenerating the adsorbent with a relatively low energy cost (16.67 Wh/g-adsorbent) and secondly the fact that high removal efficiencies were noticed for both pollutants using the regenerated HNC compared to the raw HNC.

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