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BiOCl/SrHA nanoparticle for photocatalytic degradation of a malachite green dye

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ABSTRACT

In this research, we discuss the removal of malachite green dye by strontium hydroxyapatite supported BiOCl. A modified hydrolysis model, one can synthesise BiOCl/SrHA. BiOCl/SrHA was characterized using Fourier transform-infrared spectroscopy (FTIR), UV-visible (UV-vis) analysis, X-ray diffraction (XRD), energy diffraction X-ray (EDX), and scanning electron microscopy (SEM). SEM outcome confirmed the dispersion of BiOCl onto strontium hydroxyapatite. The shape of the BiOCl catalytic samples overlapped with each other to form 3D hierarchical flower-like structures. The UV-visible was used as a radiation source during photocatalysis. BiOCl/SrHA had an effect on malachite green dye degradation. The oxidative removal occurred through hydroxyl radical formation. UV-visible (UV-vis) /BiOCl/SrHA showed perfect photocatalytic property for the decay of malachite green (MG) from an aqueous solution. According to kinetics analysis, the dye degradation rates could be in a pseudo-first-order model.

1. INTRODUCTION

Pollutants can be elements, molecules, or particles that have a great impact on living organisms and cause damage to the environment[(1)]. Plants and trees cannot grow in the absence of clean water. That is, there is no source of food, and this, in turn, can affect the economic conditions of humans, and here we must admit that

people are the main source of environmental pollution[2]. One of the most important water pollutants is included insecticides and herbicides, nutrition processing waste, pollutants from cattle operations, volatile organic compounds, heavy metals, chemical waste, and others[3,4]. Many of these factors that are important, especially for the production and distribution of healthy drinking water, Furthermore, several water factors are of fateful importance to the optimal process of Advanced Oxidation Processes (AOPs), such as the alkalinity, the pH, the transmittance, or absorbance, and temperature of the water, play a great role in photochemical water purification processes. Recently, the world has paid a lot of attention to the photocatalytic process. In, this field researchers and scientists have conducted many types of experimental research. Heterogeneous photocatalysis is a promising new alternative method for the removal of organic pollutants from water. The photocatalytic mechanism is based on the advanced oxidation process(AOP), which has shown a high ability to decompose and mineralize harmful organic and inorganic compounds in the environment. One of the most important compounds that were used in the photocatalytic process is TiO2 and ZnO, The importance of these two compounds is there non-toxicity and for their strong oxidizing power. The incorporation of bismuth into a given material yields an additional filled Bi 6s state, which appears to be more than O 2p. The transition to the s/d states of a transition metal from Bi 6s (or hybrid Bi 6s–O 2p states) becomes possible, which decreases the bandgap. Compounds of the bismuth oxyhalide (BiOX) group exhibit some semiconducting and optical properties. In 1935, the scientist Bannister discovered the BiOX crystal structure and found that it possessed layers linked by covalent bonds of the three elements that it made up [X-Bi-O-Bi- X, and X= halogens Cl, Br, I respectively][5,6]. The form geometric of BiOCl/SrHA is tetragonal, so an electric field can be generated work that activates photocatalytic thus preventing recombination between electron and Holes formation[7]. Zhang et al. (2006) investigated the photocatalytic properties of

bismuth oxychloride (BiOCl) as the first BiOX compound[8]. In recent years, there have been many medical, domestic, and industrial pollution problems. So As a result, efforts have been made to address this serious issue through practical research [9]. In this field, nanoparticles have been used extensively to reduce this dangerous phenomenon[10] Many nanomaterials have been used, including bismuth oxyhalide BiOX, and these compounds are distinguished by the fact that they have unusual properties that make them distinguished compounds in this field. The formed Bi nanoparticles on the BiOCl surface accelerate the transfer of photo-induced electrons from BiOCl to Bi, and the surface oxygen vacancies on the BiOCl photocatalyst result in its bandgap narrowing to the visible light range[11]. Many experiments have been carried out in the process of replacing the element strontium (Sr+2) to replace the element calcium (Ca+2) in the compound hydroxyapatite, particularly in biological experiments, specifically in bones, where experiments have proven that the element strontium (Sr+2) is non-toxic and stable when bound to hydroxyapatite[12-16]. The use of more than one in pH of the liquid mixture(solution) has a significant influence on the process of adsorption of the solution, because of its action on both the solvent and solvent surfaces. In the situation of surfaces that include polarized or charged positions, the amount of adsorption increases if the surface obtains a charge that skips the charged minute charge through the action of the acidic function. On the contrary, the amount of adsorption is low if the surface and the absorbed minutes obtain a similar charge[17]. One of the parameters that are considered an important factor and play a major role in the absorption process is the temperature. The reaction takes one of two paths either it is an exothermic or endothermic process.

2. EXPERIMENTAL

2.1. Preparation of SrHA

The Synthesis of SrHA in the following method: [18-19]. A solution of H3PO4 0.3 mol. L-1 was vigorously mixed with a solution of Sr(NO3)2 0.5 mol. L-1 (Merck, 99.67%) (molar ratio Sr/P =1.67. By adding NH4OH (Merck, 30%), the pH of the solution was adjusted to 9.0. A white precipitate was formed, and the suspension was stirred for 2 h. Thereafter, the precipitate was washed with distilled water and vacuum filtered.

The preparation reaction occurs according to equation (1).

$$10\ Sr(NO_3)_{2(aq)} + 6\ H_3PO_{4(aq)} + 2\ NH_4OH_{(aq)} \rightarrow Sr_{10}(PO)_6(OH)_{2(s)} + 18\ HNO_{3(aq)} + 2NH_4NO_{3(aq)} \quad \text{----------(1)}$$

2.2. Preparation of BiOCl/SrHA

BiOCl/SrHA nanoparticles were synthesized by a modification hydrolysis method using bismuth oxide, HCl, and SrHA as precursors. In perfect synthesis Bi_2O_3 (1.5g) was dissolved in excessive concentrated hydrochloric acid (10 mol/L, 10 mL) to obtain a transparent BiO_3-HCl aqueous solution. To this solution, 1.2 g of SrHA was added with simultaneous stirring. The obtained mixture was sonicated for 15 min. The pH of the solution was adjusted between 2 and 3 using ammonia. The mixture was heated at 90 ^oC for half an hour to obtain white precipitates. The precipitates were washed several times with water and ethanol and then dried at 75 ^oC for 10 h. The acquired product is calcined in an electric furnace for 3 h at 550 ^oC. to obtain BiOCl/SrHA nanoparticles.

3. Photocatalytic dyes degradation and reactor

Experiments were carried out in a mode photoreactor. The sample was irradiated with UV light using (λ=254nm, 30V). The photocatalytic dye's degeneration tests were operated by mixing different amounts of BiOl/SrHA nanoparticle in a photoreactor containing 1000 mL of each dye solution (20 mg/L) at room temperature (25^{o}c). The solution patterns were withdrawn from the reaction medium at systematic time intervals. We separate BiOCl/SrHA from the solution and note the change in the catalyst adsorption process for these dyes at the maximum wavelength (λ_{max}) 615 nm for Malachite green (MG) by UV–vis spectrophotometer (Perkin-Elmer Lambda 25). The effect of BiOCl/SrHA nanoparticles concentration on photocatalytic dyes degeneration was investigated by contacting 1000 mL of dyes solution 10 mg/L for Malachite green (MG) at room temperature (25^{o}C) for 5 h. Various amounts of BiOCl/SrHA nanoparticles were used. The effect of initial dye concentration on photocatalytic dye degeneration was calculated. The BiOCl/SrHA nanoparticles (0.05 g) Malachite green (MG) were added to 1000 mL of different dye concentrations (10, 20, 30 and 40 mg/l) of Malachite green (MG).

4. RESULTS AND DISCUSSION

4.1. Characterization of specimens

Figure 1 shows the FT-IR spectra of BiOCl/SrHA, the range of (3483-3448) cm−1 may refer to the stretching vibrations of −OH that existed in the adsorbed water molecule. Furthermore, the distinct peaks at range (1627) cm-1 refer to the O-H bending vibrations-for pure BiOCl, 509 cm−1 corresponds to valence symmetrical

A2u-type vibrations of the Bi-O bond, a reference that the compounds of BiOCl are obtained. The broadband at 3483 cm-1 is refer to O–H vibration of H2O absorbed in the specimen.

1410 cm-1 peak is refer to the carbon-related pollution and a small amount of $(CO_3)^{2-}$ caused by the CO_2 in an aqueous solution or air during the synthesis. (1627) cm-1 peak is refer to carbon-related pollution. The bands at 1031 cm-1 are a marker of asymmetric stretching. The two groups of bands in the low wavenumber ranging from 603-563 cm-1 are attributed to the bending vibrations of O–P–O in $(PO_4)^{3-}$ groups. confirmed the formation of BiOCl/SrHA.

Figure 2 was sample BiOCl/SrHA overlapped with each other. The morphology of BiOCl/SrHAp diagnosed by scanning electron microscopy (SEM) is fixed in SEM visual data which shows a quite different morphology. Notably, the surface structure of BiOCl/SrHA changes to marked rise with some holes that look like bunches of grapes that were not present before being installed when modified, This explains the presence of a large surface area, which increased the adsorption process of the dye Malachite green (MG). The widely used dyes, were chosen as the test pollutant to evaluate the photocatalytic activity of synthesized BiOCl/SrHA. The phase structures of the as-synthesis BiOCl/SrHA specimens were examined by XRD.

As displayed in Figure 3 In the case of the following figure(3c), we notice the appearance of peaks that differ from the peaks that appeared in the figures(3a, and 3b). Peaks from BiOCl/SrHA sample appear at 15.1, 22.1, 31.4, 33.4, 38.6, 40.7, 44.95, 50.5, 55.7, 65.1, 69.8, 74.1, and 78.35 2θ values with corresponding hkl values of (002), (102), (211), (300), (202), (003), (112), (200), (213), (321), (004), (104) and (212) planes.respectively[20].d escribe the EDX pattern of BiOCl and BiOCl/SrHA. in Figure 4, The presence of elements O, P, Cl, Sr, and Bi in BiOCl/SrHA. confirmed the formation of BiOCl/SrHA.

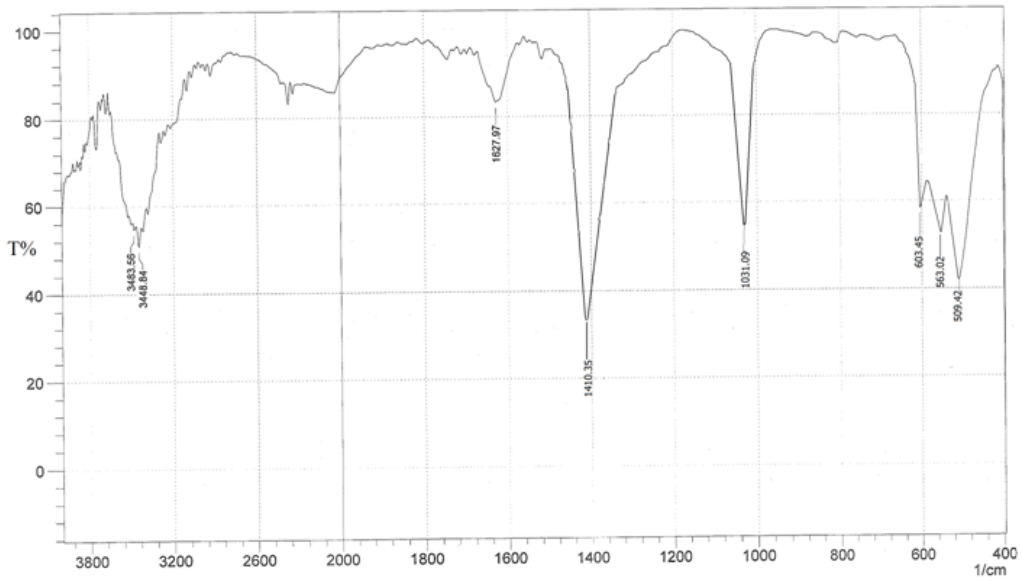
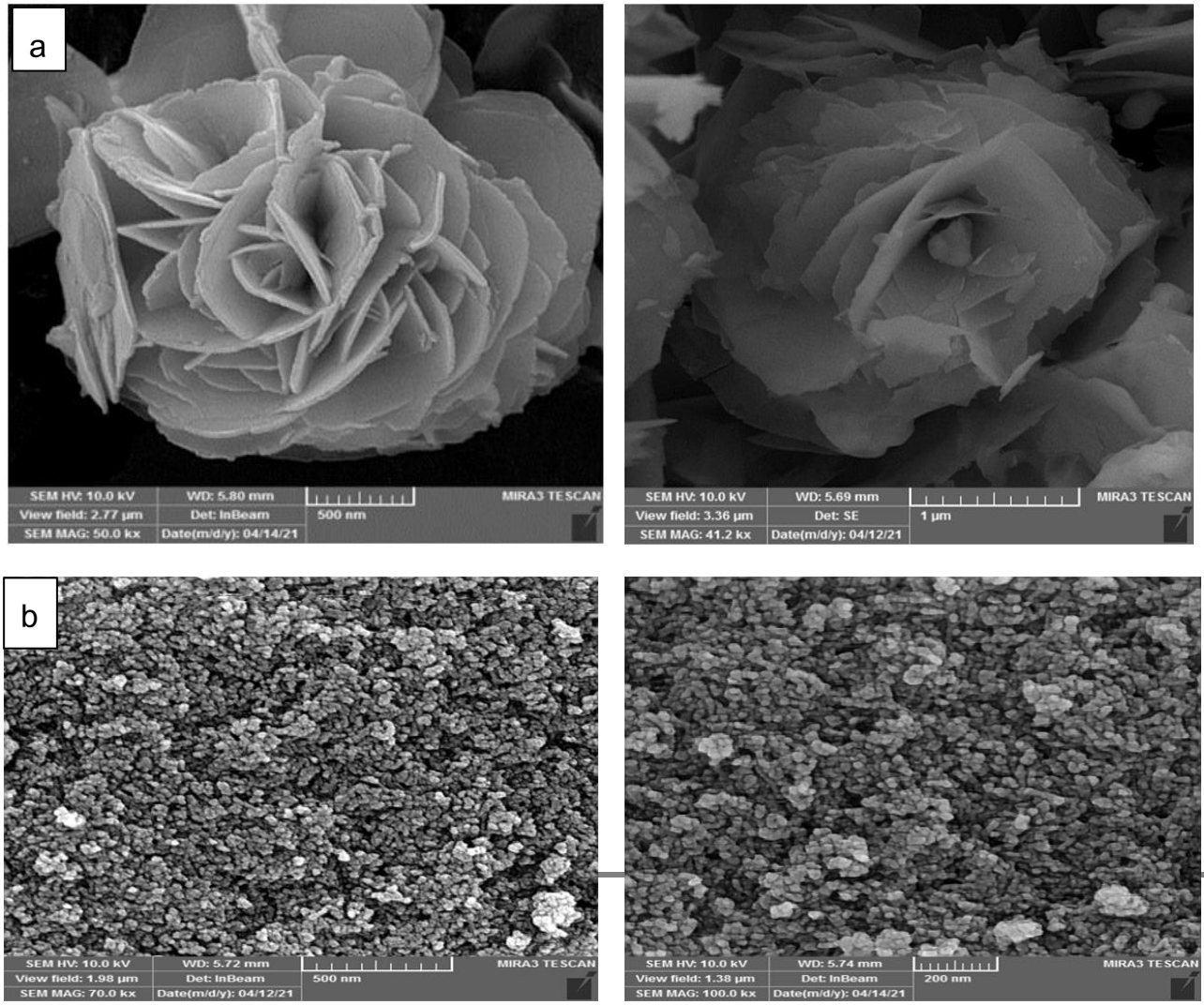


Fig.1: FTIR spectrum of BiOCl/SrHA



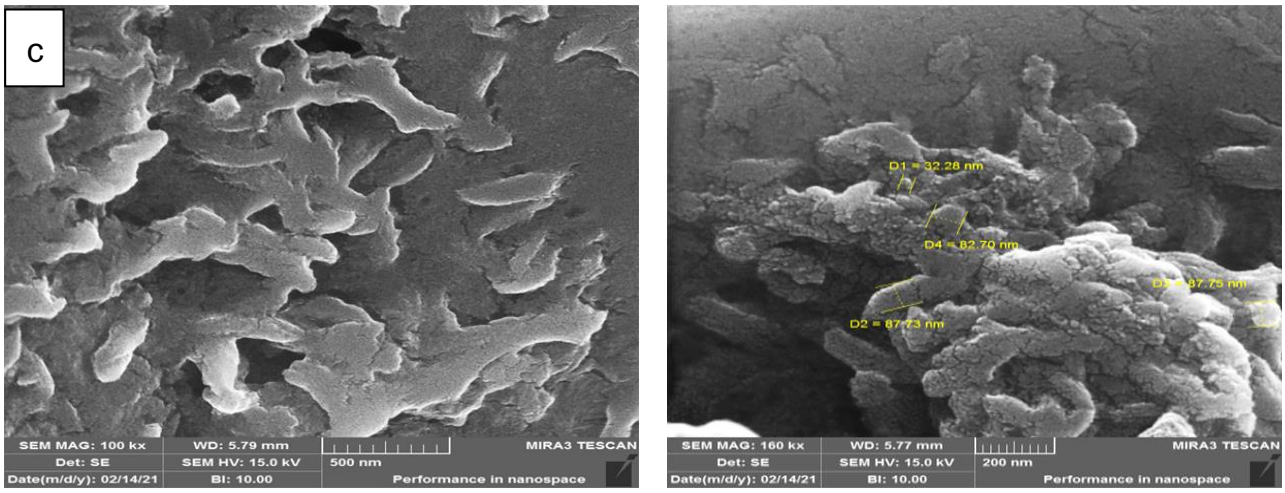
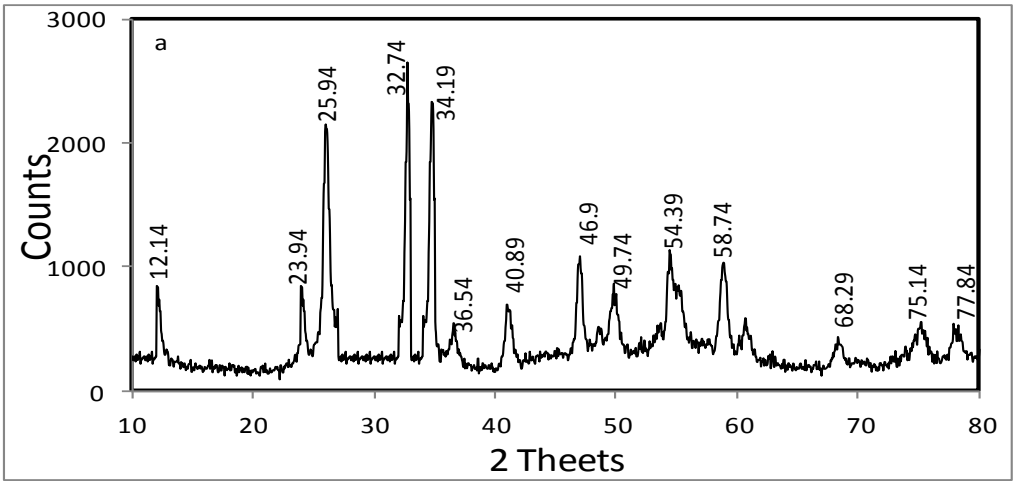
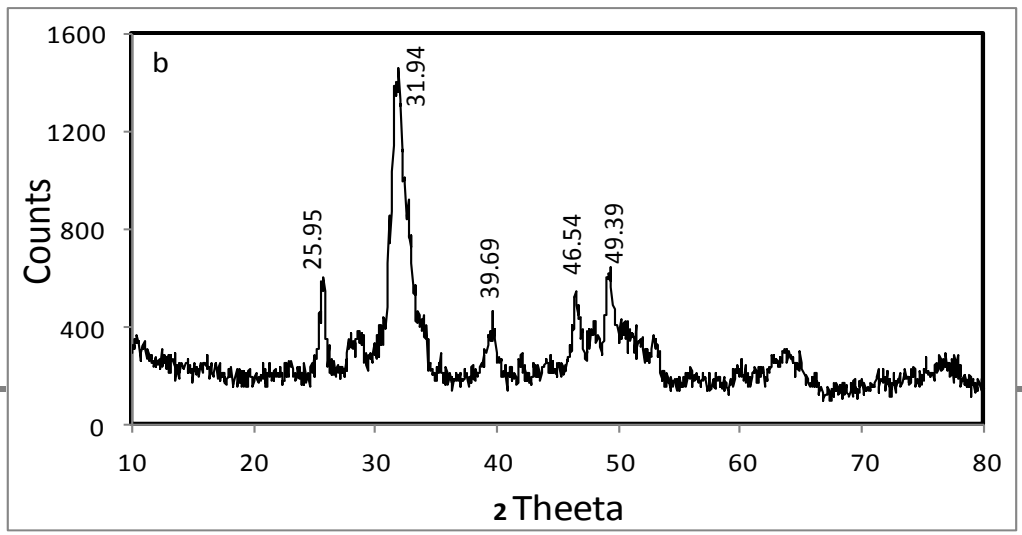


Fig. 2: SEM of (A) BiOCl, (B) SrHA and (C) BiOCl/SrHA





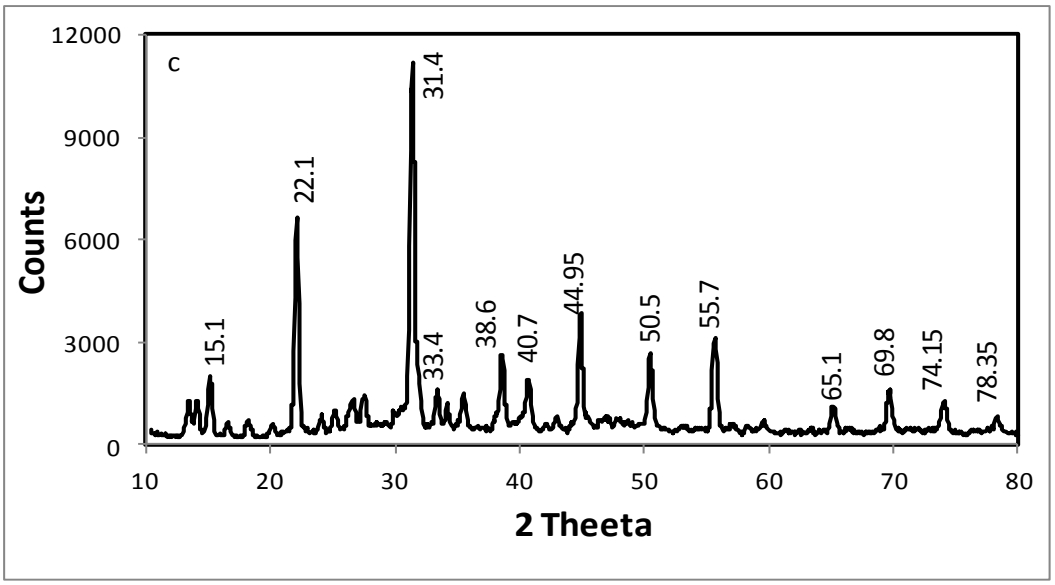


Fig.3 : (A) X-rays diffraction patterns of BiOCl, (B) X-rays diffraction patterns of SrHA (C) X-rays diffraction patterns of BiOCl/SrHA

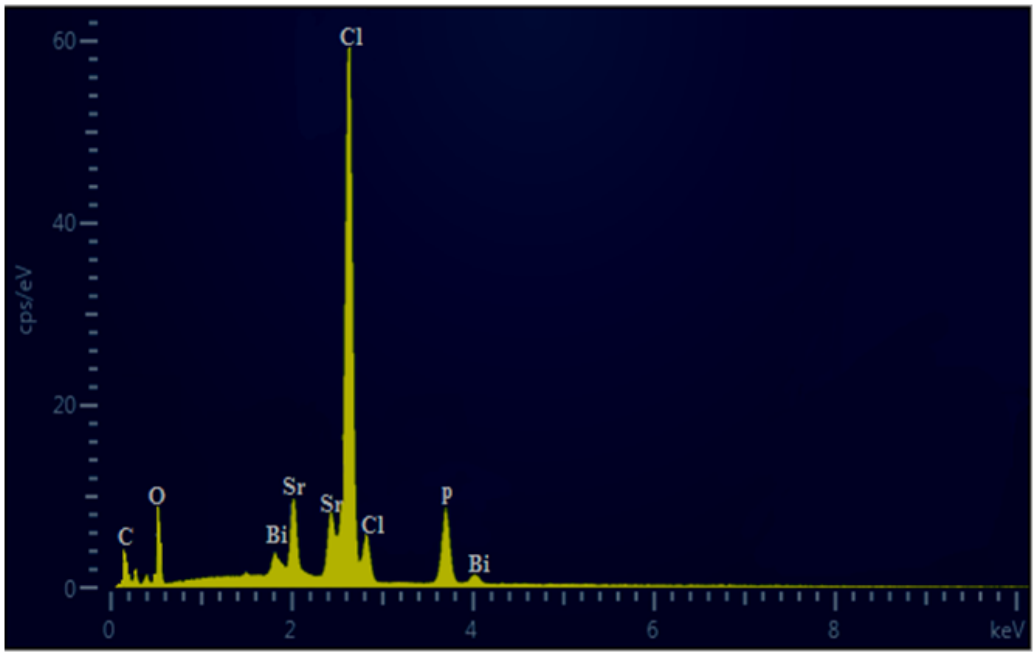


Fig.4 : EDX pattern of BiOCl/SrHA

5. Impact of some parameters on dyes degradation

5.1. BiOCl/SrHA dosage

Figure 5 display the impact of BiOCl/SrHA concentration on photocatalytic dyes decay. believe that the UV alone is not sufficient to oxidize dyes in the colored wastewater specimens The use of BiOCl/SrHA as a photocatalyst with UV led to a lot more dye decay than when UV was used alone [20]. The nanoparticles BiOCl on SrHA as support is an experimentally efficient photocatalyst that uses light energy to form the e-/h+ pair on its surface. Where this pair works e-/h+ on dye decomposition via the formation of active oxygen species superoxide radical anions (O2.-) and hydroxyl radicals (HO.). Which is the main factor in the decay of pollutants. The zero-order (eq. 1), first-order (eq. 2), and second-order (eq. 3) kinetics of photocatalytic dye degeneration by the photocatalyst BiOI/ SrHA were studied[21] .

$C_o - C = k_o t$ ----------(1)

$\ln (C_o/C) = k_1 t$ ----------(2)

$1/C = k_2 t + 1/C_o$ ----------(3)

where C_o and C are the initial dye absorbance and dye absorbance at time t, respectively. The k_o, k_1, and k_2 are the zero-order, first-order, and second-order rate constants, respectively. To insert the applicability of the zero-order, first-order, and second-order kinetics models for photocatalytic dye degradation by the nanoparticle of BiOCl/SrHA at different catalyst dosages, linear plots of C_o - C against different

irradiation time (t), ln (C_o/C) against different irradiation time (t), and 1/A against different irradiation time (t) are plotted. The values of k_o, k_1, and k_2, R_2 (correlation coefficient values) are displayed in Table 1. The results showed that the kinetics of photocatalytic dye degeneration via BiOCl/SrHA at various catalyst dosages followed the first-order kinetic.

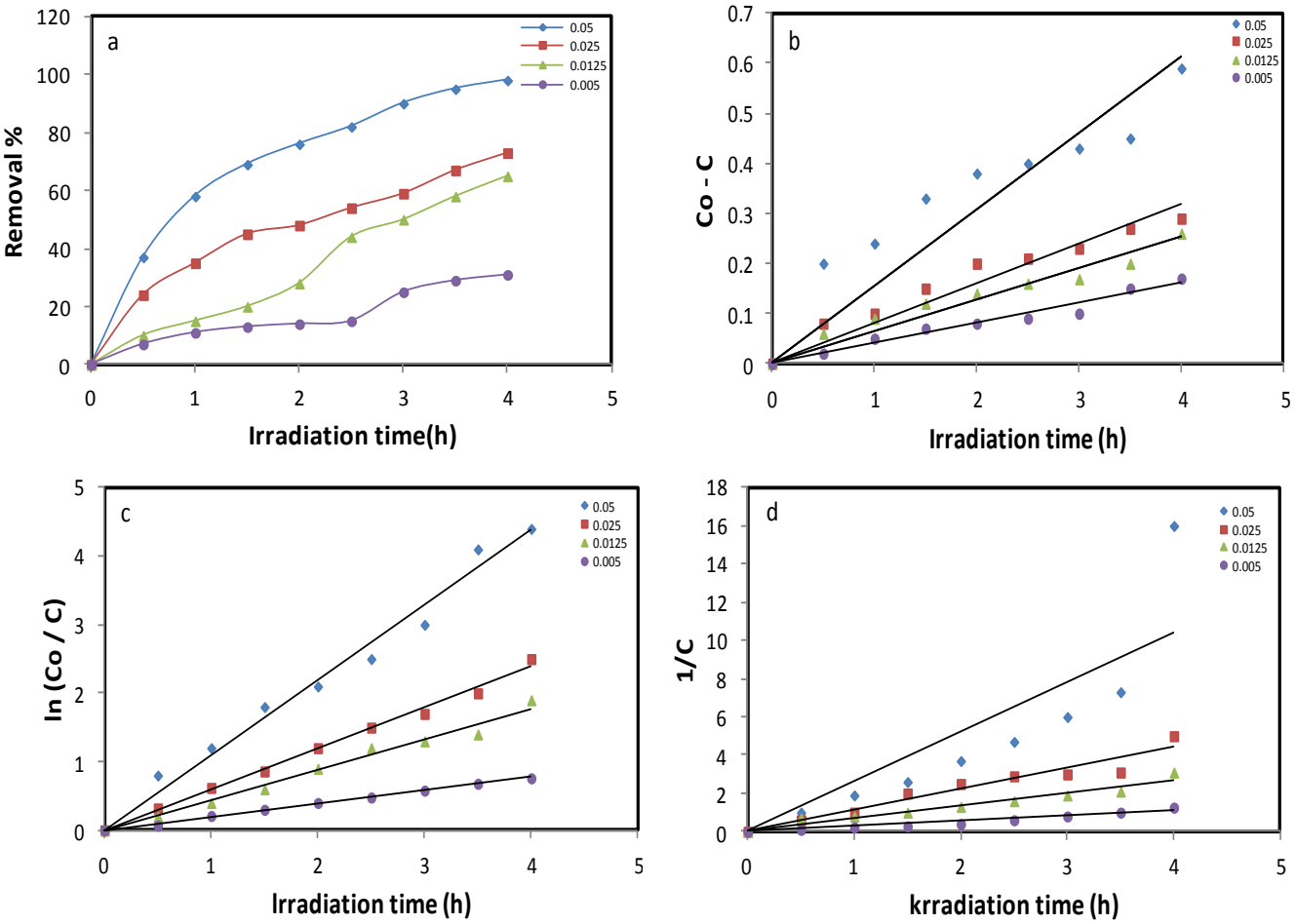


Fig.5 :(a)BiOCl/ SrHAp dosage effect on degradation of dye (MG) using UV/BiOCl/ SrHA (b) The zero-order (c) The first-order (d) The second-order kinetic of photocatalytic dye degradation by BiOCl/SrHA at different catalyst dosages

BiOCl/SrHA (g)	zero-order kinetic		first-order kinetic		second-order kinetic	
	Ko	R^2	K1	R^2	K2	R^2
MG						
0.05	0.1245	0.8463	0.1768	0.9991	0.4327	0.658
0.025	0.0776	0.8057	0.1559	0.9955	0.0229	0.9419

Table 1: The kinetics constants of photocatalytic Malachite green (MG) dye degradation by BiOCl/SrHA at various catalyst dosages

5.2. Initial dye concentration

Figure 6 displays the impact of initial dye concentration on photocatalytic dye decay at various time intervals. The results show that dye degradation decreases as the initial dye concentration increase. The potential reason for the increase in the dye concentration, is the intervention of intermediates composed upon the decay of the parental dye molecules. Such repression would be more obvious in the presence of a high level of degradation intermediates composed upon an increased initial dye concentration[22]. To insert the application of the zero-order, first-order, and second-order kinetics types for photocatalytic dye degradation by the nanoparticles at various initial dye concentrations, linear plots of C_o - C versus irradiation time (t) for zero-order model, ln (C_o/C) versus irradiation time (t) for first-order order model, and 1/C against irradiation time (t) for second-order types are plotted. The values of k_o, k_1, and k_2, R^2 (correlation coefficient values) are shown in Table 3 and 4. The outcome showed that the kinetics of photocatalytic dye degeneration by BiOCl/SrHA at various initial dye concentrations followed the first-order kinetic type.

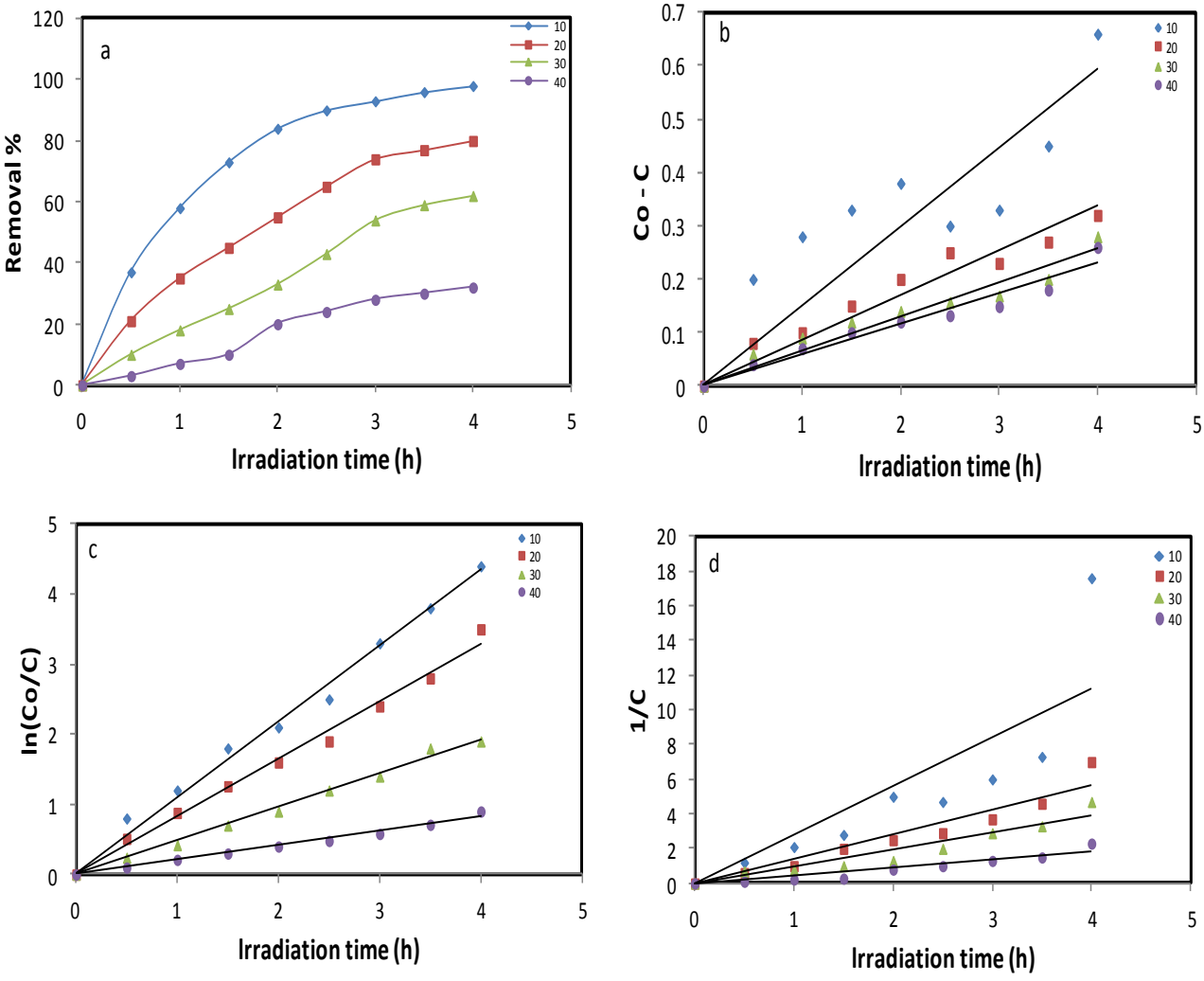

a
Removal %
Irradiation time (h)
10
20
30
40
b
Co - C
Irradiation time (h)
c
ln(Co/C)
Irradiation time (h)
d
1/C
Irradiation time (h)

Fig.6 :(a) Dye concentration effect on the degradation of dyes using UV/BiOCl/ SrHA, (b) The zero-order (c) The first-order (d) The second-order kinetic of photocatalytic dye degradation by BiOCl/SrHA at different dye concentrations

day (mg/l)	zero-order kinetic		first-order kinetic		second-order kinetic	
	K_o	R^2	K_1	R^2	K_2	R^2
MG						
10	0.3197	0.6892	0.1225	0.9902	3.0987	0.719
20	0.0931	0.9271	0.3215	0.9906	0.0554	0.9235
30	0.0558	0.9275	0.1244	0.9934	0.0732	0.9148
40	0.2231	0.9496	0.1567	0.9871	0.1154	0.894

Table 2: The kinetics constants of photocatalytic dye degradation by BiOCl/SrHA at various dye concentrations

6. Conclusions

In this work, BiOCl/SrHA was prepared and characterized. The photocatalytic dye degradation capacity of BiOCl/SrHA from colored wastewater was studied. Active dyes were used as efficient compounds. The influence of BiOCl/SrHA dosage and initial dye concentration on photocatalytic dye decay was estimated. The photodegradation with UV in the absence of BiOCl/SrHA presents a low efficiency for dye decay from solutions (≤5). The cooperation impact of BiOCl/SrHA and UV was observed because of the catalytic efficiency of BiOCl/SrHA for the production of hydroxyl radicals. It can be Concluded that the BiOCl/SrHA could be used as a photocatalyst to degrade dyes in wastewater.

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