•XXV Galyna Puchkovska International School-Seminar “Spectroscopy of Molecules and Crystals” (XXV ISSSMC) September 21-24, 2021 Kyiv, Ukraine

Magnetic nanoparticles interactions with wastewater pollutants

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AIM OF THE STUDY

Synthesis of magnetic nanoparticles (MNP) for the study of their interactions with wastewater models. Comparison between MNP effect in Rhodamine B solution and phenolic solution. Studying the influence of UV exposure and hydrogen peroxide supply.

I. INTRODUCTION

The most used kind of nanoparticles are magnetic nanoparticles, MNPs, that easily interact with other biological molecules being able to cover them if it is wanted (Esterlrich, et al. 2015). The magnetic nanoparticles, which are also part of ferromagnetic materials category, are easy to control in the presence of external magnetic fields, that is an important feature in their use in various applications (Conroy, Lee and Zhang 2008). From the total volume of 1400 billion km^3 of water on Earth, just 0.01% is drinking water.

Therefore, the management of this water is a critical factor for the maintenance and development of human life on Earth. In the textile industry, as we know, enormous amounts of water and dyes are used for dyeing and finishing materials (Garcia - Montano, et al. 2008).

These wastewaters that are then released into the environment are a powerful source of pollution and destabilization of aquatic life (Garcia - Montano, et al. 2008).

One of the colorants that is of interest at present time is *Rhodamine B* while Phenol is quite frequent toxic compound with low degradability .

Phenolic compounds present in cork wastewater are known for their high antioxidant activity (Benitez et al., 2003), and their recovery could be not only a method of water purification but also a potential way to capitalize on the content of these waters. waste studies have focused on water polluted with phenol, one of the most toxic and widespread recalcitrant products in the environment.

II. THEORETICAL MODELING

Density Functional B3LYP 6-31G* method implemented in Spartan 18 software was applied to model the optimized molecules of Rhodamine B and phenol with some structural and energetic parameters.

III. EXPERIMENTAL

Materials: MNP synthesis

1.332 g ferrous chloride ($FeCl_2 \times 4H_2O$) , 3.622 g ferric chloride ($FeCl_3 \times 6H_2O$) , 100 mL distilled water, 1.7 M hot NaOH

The tested concentrations of MNP powder in the wastewater samples were 4 and 8 g/L. The estimation of the pollutant removal efficiency was carried out spectrophotometrically based on the intensity of light absorption in the maximum of the representative electronic absorption band for each pollutant.

Fig. 1 Reaction vessel, on heating plate before hot NaOH adding (left) and after that when black MNP in suspension (right).

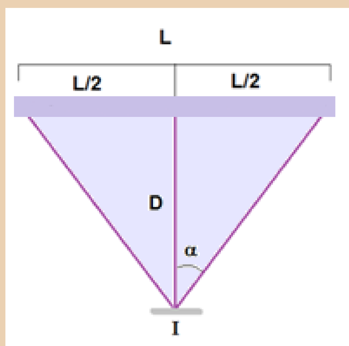

Fig 2. UV tube lamp exposure

L (tube length L=0.87 m), **D** (distance to sample D=0.20 m), the irradiance **I** (W/m^2), under the angle **α** (about π/3 rad), **P** (emission power = 12 W emission in UV-C range), **I** (irradiance- according to (1) was of 0.88 W/m^2, in the center of the exposed sample. Total energy on the sample **W** (W= Ixt, t-the exposure time). The diameter (0.03 m), of the vessel with the sample, is much smaller than L and D. Such energy ranged between 558 and 2232 J. Such results are reliable with ±5% accuracy - in good agreement with goniometric measurements (Lawal et al., 2017).

$$I = P\frac{2\alpha + \sin 2\alpha}{(2\pi^2 DL)} \quad (2)$$

The efficiency of the photo-Fenton process occurring under UV exposure has been attributed to the reactivity of the HO radical, which can react with various chemical species present in the liquid phase. Under radiation impact (hν) the water and oxygen radicals production is also intensified; the addition of the instable hydrogen peroxide (H_2O_2) is another source of free hydroxyl reactive radicals that can attack pollutant molecules.

Wastewater models

10 µM Rhodamine B (Rh B) solution, 5 µM Phenol solution, Hydrogen peroxide 30% reagent (10mM and 20 mM)

Devices:

Semi-analytic weighting device, 10^{-4} g accuracy

Magnetic stirrer Cole-Parmer type

Shimadzu PharmaSpec 1700 UV-Vis spectrophotometer

A-light absorbance at 554 nm for Rh B and 270 nm for phenol

UV tube lamp (30 W total emission power, 12 W emission in UV-C range)

TEM – Transmission Electron Microscopy (device model Hitachi High-Tech HT7700).

Photo-Fenton reactions: $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO$ (3)

$Fe^{3+} + H_2O\ (h\nu) \rightarrow Fe^{2+} + H^+ + HO$ (4) $HO + RH \rightarrow H_2O + R$ (5)

where R is a molecular radical - for example RH - phenol.

IV. RESULTS AND DISCUSSION

Computational modeling results

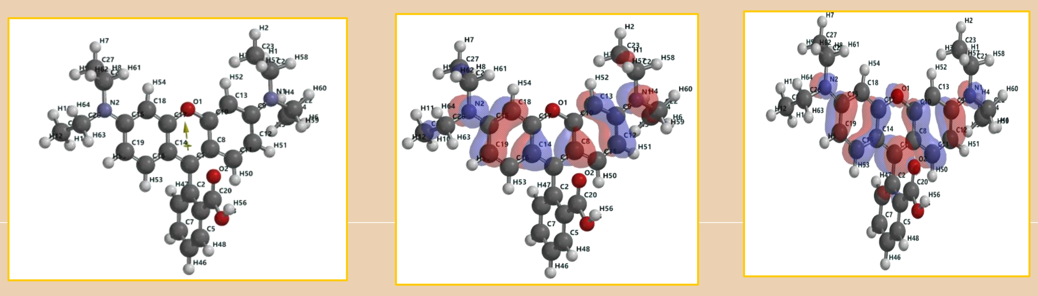

Fig. 3. Rhodamine B optimized structure (a) with dipole moment; the frontier orbitals: (b) HOMO (Highest Occupied Molecular Orbital) and (c) LUMO (Lowest Unoccupied Molecular Orbital)

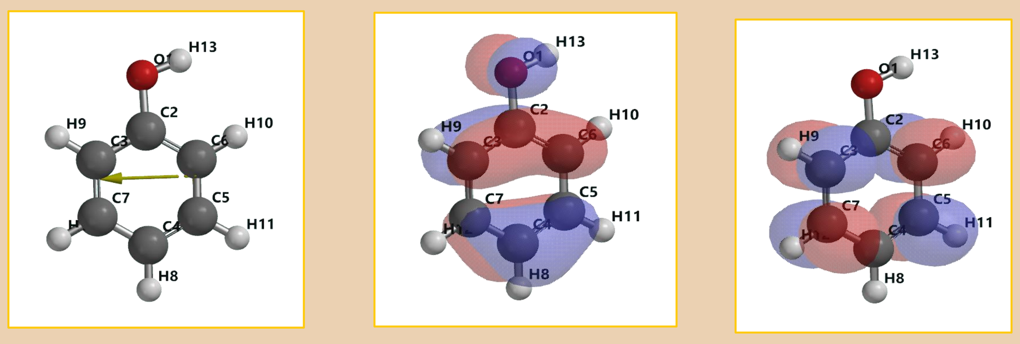

Fig. 4. Phenol optimized structure (a) with dipole moment; the frontier orbitals: (b) HOMO (Highest Occupied Molecular Orbital) and (c) LUMO (Lowest Unoccupied Molecular Orbital)

Both molecules are rather symmetrical with small dipole moment (Table 1), relatively stable structures - high IP (ionizing potential, IP=-E_{HOMO}). Electron Affinity of Rhodamine B (EA=-E_{LUMO}) is higher than for phenol, denoting higher reactivity, i.e. interaction with surrounding molecules or free radicals like those generated by the iron catalytic action on the water.

Table 1

RHODAMINE B	
E_{HOMO} (eV)	-7.97
E_{LUMO} (eV)	-5.27
Log P	1.17
Polarizability (Å^3)	79.34
Dipole Moment (D)	0.3
PHENOL	
E_{HOMO} (eV)	-5.96
E_{LUMO} (eV)	0.04
Log P	0.46
Polarizability (Å^3)	48.59
Dipole Moment (D)	1.35

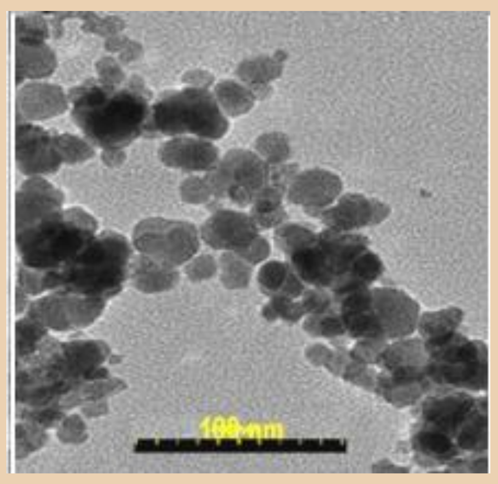

Fig. 5. TEM method for the imaging of MNP used in pollutant degrading

We presented the quasi-spherical and cubical particles with mean size (of 10 nm) of synthesized MNP since it the determining factor of efficiency of MNP interactions with Rhodamine B and phenol from wastewater models.

We presented the morphological characteristics (quasi-spherical and cubical particles) and mean size (of 10 nm) of synthesized MNP since it the determining factor of efficiency of MNP interactions with Rhodamine B and phenol from wastewater models. It is expected that:

(i) Pollutant molecules are attached by physical interactions at the MNP surface (Rh B was found to bind by hydrogen bonds (Zhang et al., 2021)

(ii) Surface iron ions of MNP trigger Fenton-type catalysis reactions of water and dissolved oxygen, generating reactive free radicals that can modify pollutant molecules turning them into degradation compounds.

(iii) Both phenomena occur.

Experimental results -selection

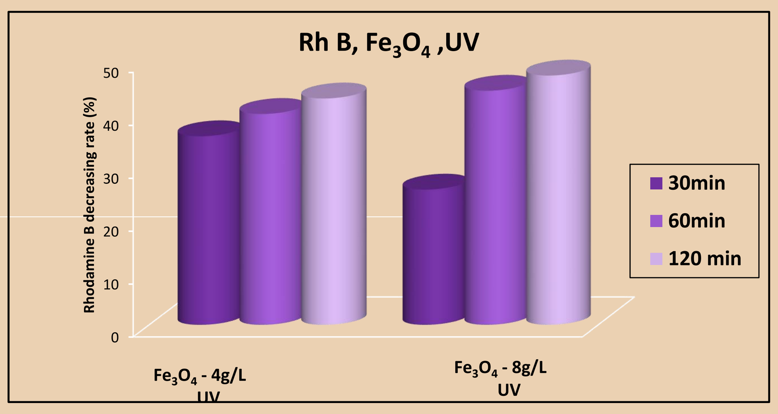

Fig. 6. Rhodamine B decreasing rate – UV exposure

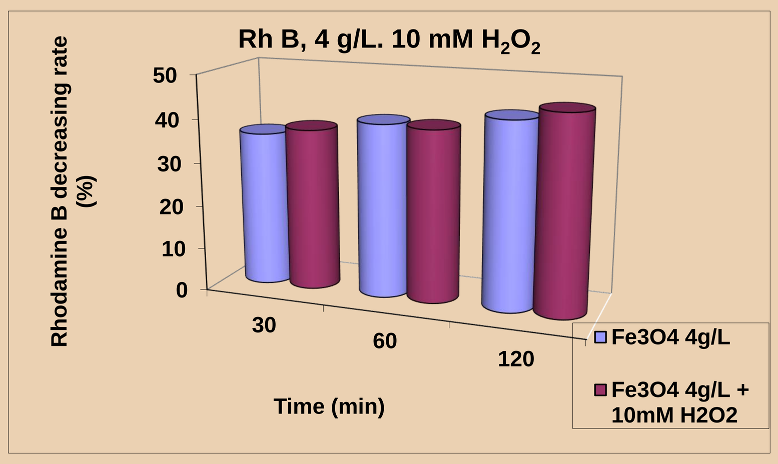

Fig. 7. Rhodamine B decreasing rate – with 10 mM hydrogen peroxide

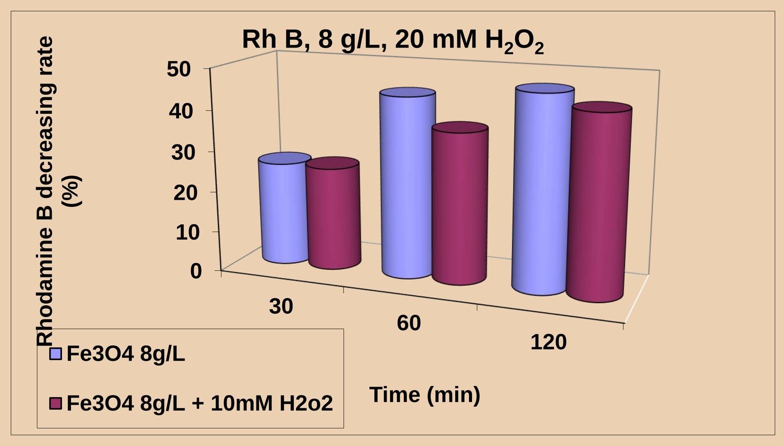

Fig. 8. Rhodamine B decreasing rate – with 20 mM hydrogen peroxide

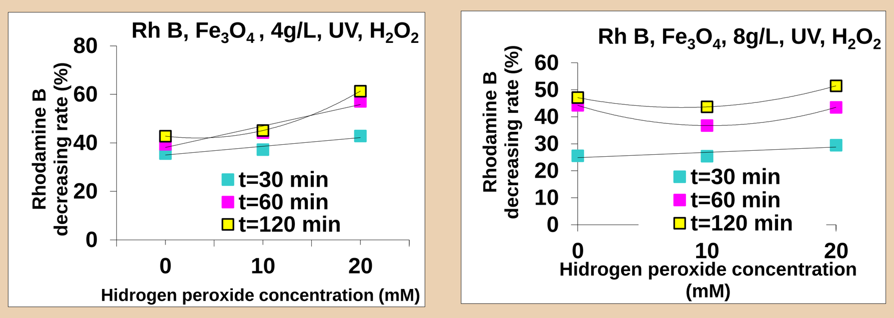

Fig. 9. Rh B removal under UV exposure and hydrogen peroxide supply

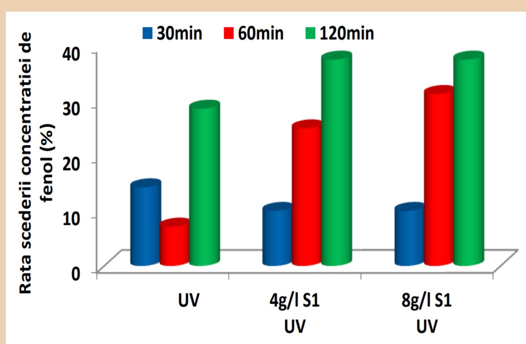

Fig. 10. Phenol removal under UV exposure

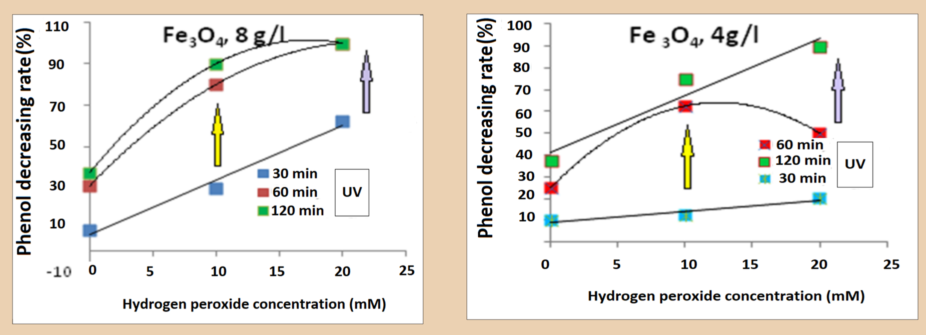

Fig. 11. Phenol decreasing rate under UV exposure and hydrogen peroxide supply

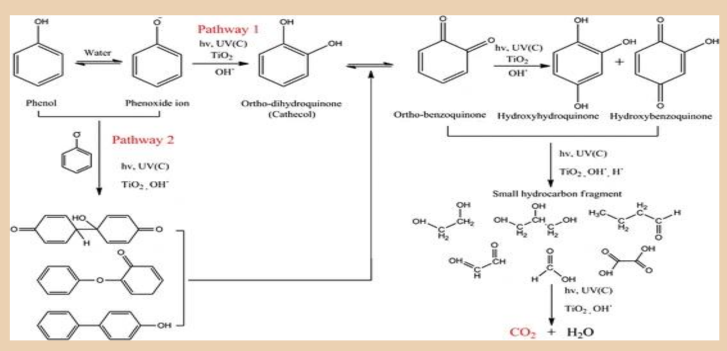

Fig. 12 Phenol photo-degrading hypothesis (Dang et al., 2016)

V. CONCLUSIONS. Magnetite nanoparticles succeeded in removing Rhodamine B with maximum rate of about 60% for 180 min exposure to UV and 4 g/L MNP in the presence of 20 mM hydrogen peroxide ; the main interaction seems to be the adsorption through hydrogen bonds developed between Rhodamine B molecule and MNP surface. In the case of phenol model wastewater the decreasing rate reached 100% for 8 g/L MNP, 120 min exposure to UV radiation and 20 mM hydrogen peroxide.; the main phenomenon seems to be the gradually decomposing of phenol up to small fragments that can easily attach to MNP to be removed from the wastewater. Further research will be focused on the optimization of reaction factors involved in the experiment with Rh B aiming to increase its removal rate as well as on the testing of other water pollutants with magnetic nanoparticles.

ACKNOWLEDGMENTS: The results of this research was partially supported by Dubna-JINR-Ro projects 2019

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