



Removal of organic dye compounds in water and wastewater samples based on covalent organic frameworks -titanium dioxide before analysis by UV-VIS spectroscopy

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ABSTRACT

A simple and rapid microwave-assisted combustion method was developed to synthesize homogenous carbon nanostructures (HCNS). This research presents a new and novel nanocomposite structures for removal of methylene red (2-(4-Dimethylaminophenylazo)benzoic acid), methylene orange (4-[4-(Dimethylamino)phenylazo]benzenesulfonic acid sodium salt) and methylene blue (3,7-bis(Dimethylamino)phenazathionium chloride) with semi degradation-adsorption solid phase extraction (SDA-SPE) procedure before determination by UV-VIS spectroscopy. A covalent organic frameworks (COFs) with high purity were synthesized and characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results indicated that the self-assembled carbon nanostructures (COFs) synthesized with the cost-effective method which was used as a novel adsorbent for adsorption of dyes after semi-degradation of methylene red, orange and blue (1-5 mg L⁻¹) as an organic dye by titanium dioxide (TiO₂) nanoparticules in presence of UV radiation. Based on results, the COFs/TiO₂ has good agreement with the Langmuir adsorption isotherm model with favorite coefficient of determination ($R^2= 0.9989$). The recovery of dye removal based on semi-degradation/adsorption of COFs/TiO₂ and adsorption of COFs were obtained 98.7% and 48.3%, respectively (RSD less than 5%). The method was validated by spiking dye to real samples.

1. Introduction

Nanomaterials are particles that are in the size range between 1-100 nm. The importance of nanomaterials in terms of strength is the presence of active sites and their low density. Nanomaterials have a wide range of applications in optical data storage, sensors, light and durable building materials, and wastewater treatment. The gained

importance of the conventional heating methods (CHM) is due to the microwaves interact with the reactants at the molecular level. By CHM, the electromagnetic energy is transferred and converted to heat by rapid kinetics through the motion of the molecules [1-3]. Today, the conservation of water resources has been increasingly considered by various international organizations such as WHO, FDA and EPA. By increasing of population growth as a result of over-exploitation of limited water resources and on the other hand, water pollution due to various biological, agricultural

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and industrial activities caused to water crisis in future years. Methylene organic compounds such as methyl red, methyl orange and methyl blue are the photoactive phenothiazine dyes [4-6]. Paints are one of the main and most important pollutants that are used in various industries to dye related products. Therefore, a significant amount of pollution caused by pigments is produced due to their extensive release into the effluent. The presence of these dyes in water is inappropriate even at very low concentrations and causes widespread environmental pollution by pharmaceutical industries[7]. Recently, many methods based on nanostructure materials was used for removal organic compounds. Hence, a simple and rapid microwave assisted combustion technique was used for synthesis of CdO nanospheres for removal pollution in waters [6]. Microwave assisted reverse microemulsion process as an easy, low cost and fast method can be used for synthesis of nano emulsions [8]. Photocatalytic degradation of compounds using nanoparticles with ultraviolet light is one of the advanced oxidation methods that is expanding in recent decades [9, 10]. Photocatalyst as a catalyst activated in the presence of light is which absorbs light to produce a chemical reaction in the environment [11, 12]. When the UV rays reach to a surface covered with a photocatalyst the electron-cavity can react with molecules on the surface of the particles[13]. Bio photocatalytic materials[14] as a kind of photocatalyst was used in water purification based on degradation and adsorption process[15], during the adsorption process, solute molecules are removed from the solution and adsorbed by the adsorbent. Most of the molecules are adsorbed on the surface of the adsorbent pores and small extent on the outer surface of the particles. The adsorption transfer from the solution to the adsorbent continues until the concentration of the solvent remaining in the solution is in equilibrium with the concentration of the solvent adsorbed by the adsorbent. When equilibrium is established, the adsorption transfer stops. Adsorption equilibrium is established in the dynamic sense when the rate of adsorption of the adsorbed component on the surface is equal to its

rate of absorption [16], self-cleaning glasses and organic molecules degradation[17]. Hydrothermal synthesis method has many advantage such as energy storage[18], simplicity[19], low cost[20], better nuclear control[21], pollution-free (because reaction takes place indoors)[22], better diffusivity[23], high reaction speed and better shape control[24]. In recent years, many nanocomposites used for degradation or adsorption of organic dyes[25-27]. The unique structure of the non-ionic surfactant which their unique structure enables them to encapsulate water-soluble and water-repellent materials [28, 29] and organic building constituent units[30]. One of the new techniques in removing emerging pollutants is the use of environmentally friendly modifiers and reducing the bioavailability of pollutants in the environment[31]. In recent years, bio-charcoal has been gradually approriated which as black gold can be used to solve the problem of sustainable development of agriculture and other aspects by the academic community[32], [33], [34], [35]. In this study, the COFs synthesized and used as a novel adsorbent for removal dyes based on SDA-SPE procedure in water samples after semi-degradation of organic dye by titanium dioxide (TiO_2) nanoparticales in presence of UV radiation. The recovery and absorption capacity of dyes with COFs/ TiO_2 were calculated before determined by UV-VIS spectrometer.

2. Experimental

2.1. Instrumental

Varian UV-VIS spectrophotometer was used for this study (Cary 50, USA). UV-VIS spectrophotometer included dual beam, the monochromator, the wavelength ranges between 190–1100 nm, the spectral bandwidth (1.5 nm), the dual Si diode detectors, the quartz over coated optics based on scan rates of 24000 nm min⁻¹ and computer operating system. The Power Consumption of UV-VIS spectrophotometer has supply of 100 - 240 volts AC and frequency 50 - 60 Hz. The condition of UV-VIS spectrophotometers was shown in Table 1. The unique optical design enables to measure dye samples, also, the large or odd-shaped

Table 1. The condition of UV-VIS spectrophotometers

Parameters	Values
Dimensions	477 mm x 567 mm x 196 mm
Height	196 mm
Light Source	Xenon flash lamp (80 Hz)
Maximum Scanning Speed	24,000 nm min ⁻¹
Photometric System	Double beam
Spectral Bandwidth	1.5 nm

samples to be measured. The highly focused beam also provides superior coupling to fiber optics caused to use the UV-Vis in different matrixes. Powder X-ray diffraction (XRD) was prepared by a PRO X-ray diffractometer. Scanning electron microscopy images were obtained using gun design using a point-source cathode of tungsten (SEM, Philips XL 30 FEG). The transmission electron microscope was used for preparation particle size of COFs (TEM, Philips EM 300).

2.2. Materials and Reagents

Reagents were acquired from Sigma Aldrich and Merck companies, Germany. Methanol (HPLC grade), toluene, acetone, hexane and dichloromethane (HPLC grade) were obtained from Merck Ltd. (Germany). More materials used in this study such as methyl red $[(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{N}-\text{NC}_6\text{H}_4\text{CO}_2\text{H}]$, (2-(4-Dimethylaminophenylazo)benzoic acid, CAS N: 493-52-7], methyl orange $[\text{C}_{14}\text{H}_{14}\text{N}_3\text{NaO}_3\text{S}]$, 4-[4-(Dimethylamino)phenylazo]benzenesulfonic acid sodium salt, CAS N:547-58-0] and methyl blue $[\text{C}_{37}\text{H}_{27}\text{N}_3\text{Na}_2\text{O}_9\text{S}_3]$, 3,7-bis(Dimethylamino)phenazathionium chloride, CAS N:28983-56-4) were purchased from Sigma company(Germany), $\text{C}_3\text{H}_7\text{NO}$ (DMF) was purchased from Merck company in Germany, without further purification. Benzene-1,4-diboronic acid (95.0 %, CAS N: 4612-26-4) and hexahydroxytriphenylene ($\text{C}_{18}\text{H}_6(\text{OH})_6$, CAS N: 4877-80-9, MW 324.3 g mol⁻¹) were purchased Sigma-Aldrich. The B_3O_3 (boroxine, CAS N: 823-96-1)) was prepared From Sigma(Germany). The pH of the water sand wastewater samples were digitally calculated by pH meter of Metrohm (744, Swiss). The pH was

adjusted by favorite buffer solutions (Merck, Germany). The various buffer solutions, the acetate (PH=3.0–6.0), the NaH_2PO_4 / Na_2HPO_4 (pH=6.0–8.0) and $\text{NH}_3/\text{NH}_4\text{Cl}$ (pH=8.0-10) were prepared. After adjusted pH samples, the ultrasonication (Grant, U.K) and the centrifuging (3000-10000 rpm, 3K30 model) was used for extraction and separation nanoparticles from water samples(Sigma, Germany).

2.3. Synthesis of COFs

Covalent organic frameworks (COFs) has two/three dimensional structures(2D,3D) which was generated by reactions between organic precursors. The covalent bonds depended on porous and crystalline form. The COFs is an improvements of organic material based on coordination chemistry. We synthesis COFs was done based on the Yaghi method and COFs framework scaffolds were prepared by the boronate linkages using solvothermal synthetic methods [36-37]. In fact, the synthesis of COFs was obtained by condensation reactions of $\text{C}_6\text{H}_4[\text{B}(\text{OH})_2]_2$ with $\text{C}_{18}\text{H}_6(\text{OH})_6$ and finally the carbon structure of $\text{C}_9\text{H}_4\text{BO}_2$ (COF₅) produced. Moreover, the two nozzles electrospinning was used to fabricate the scaffolds. The electrospinning experimental setup was a nano model (Tehran, Iran) with two nozzles. The voltage applied at the tip of the needle was 18 kV. The mass flow rates were 0.5 ml h⁻¹, and distance between the tip of the needle and the collector was maintained at 15 cm. The speed of the rotary collector was 400 rpm and scanning distance was 10 cm. Experimental conditions for the preparation of self-assembled carbon nanostructures was shown in Table 2.

Table2. Experimental conditions of self-assembled carbon nanostructures.

Sample	DMF: H ₂ O (D.R*)	Time (min)	Temp. (°C)	Morphology
1	2:1	4	180	NPs**+ Agglomerate
2	2:1	8	180	NPs+ Agglomerate
3	2:1	8	200	NPs+ Agglomerate
4	2:1	8	200	NPs+ Agglomerate

*Dilution Ratio, **Nanoparticles

2.4. Removal procedure

For each experiment, a dye solution with a concentration of 5 mg per 1000 mL (5 mg L⁻¹) was prepared and 0.5 g of COFs as catalyst was added to it in presence of TiO₂/UV. Then the pH of the solution was adjusted with buffer solution between 3-9 and irradiated with UV radiation. Then, the all samples, was stirred with a magnetic stirrer for 15 min. By SDA-SPE procedure, the amount of dye (5 mg L⁻¹) removed by COFs/TiO₂/UV. First, the dye semi-degradation was obtained in presence of TiO₂/UV and intermediate forms of dyes created in water samples. The dye and intermediate dye were absorbed on COFs with high recovery up to 98.7%. The nanoparticles of adsorbent separated from water solution by centrifuging. Then the dye concentration in remained solution was directly determined by UV-VIS spectrometry. To prevent the reaction of hydroxyl radicals in the sample, some ethanol was added to the test tubes. Validation of methodology was obtained by spiking of real samples by proposed procedure. The recovery of proposed method based on COFs/TiO₂ was achieved for dyes extraction by the below equation. The C_I is the primary concentrations of dye in sample and C_F is the final concentration of dye by SDA-SPE procedure coupled to UV-VIS (n=5, Eq. 1).

$$\text{Recovery (R\%)} = \frac{(C_I - C_F)}{C_I} \times 100 \quad (\text{EQ.1})$$

3. Results and Discussion

3.1. Structural Analysis

By full width of the half maximum (FWHM) based

on the Debay-Scherer equation, the particle size of COFs nanocomposites was obtained approximately 50-100 nm. **Figure 1** shows the X-ray diffraction analysis (XRD) of self-assembled carbon nanostructures in different conditions. The results show that by increasing of temperature based on solvothermal method from 180°C to 220°C, the crystallized amount of synthesized carbon nanostructures (COFs) gradually increases. The sharper peaks without any noisy peaks was seen. Interestingly, the position (2θ) of the peaks have not changed, and only the intensity of the peaks increased, which indicates an increase in the degree of purity in products.

3.2. Measurement size (DLS)

By increasing of temperature for COFs nanocomposites with solvothermal method, the sintering process and crystallization of COFs was increased and caused to smaller size of nano structures. DLS analysis was displayed in **Figure 2**.

3.3. Morphological and pore characteristics

Microscopic morphology and particle-size distribution (PSD) of the products were visualized by scanning electron microscopy (SEM) images. The **Figures 3** displays the SEM images of carbon nanostructures of COFs. The morphology of COFs nanocomposites under the influence of biochar concentration change into rods with quantum particles-like on its surface. Results show which biochar concentration has a great impact on particle size of final products.

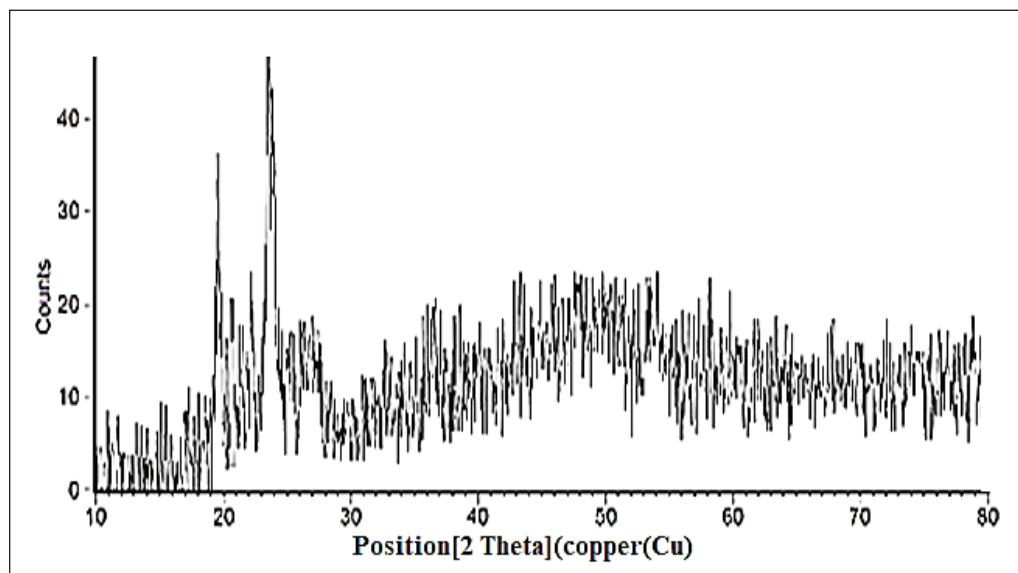


Fig. 1. X-ray diffraction analysis of synthesized self-assembled carbon nanostructures

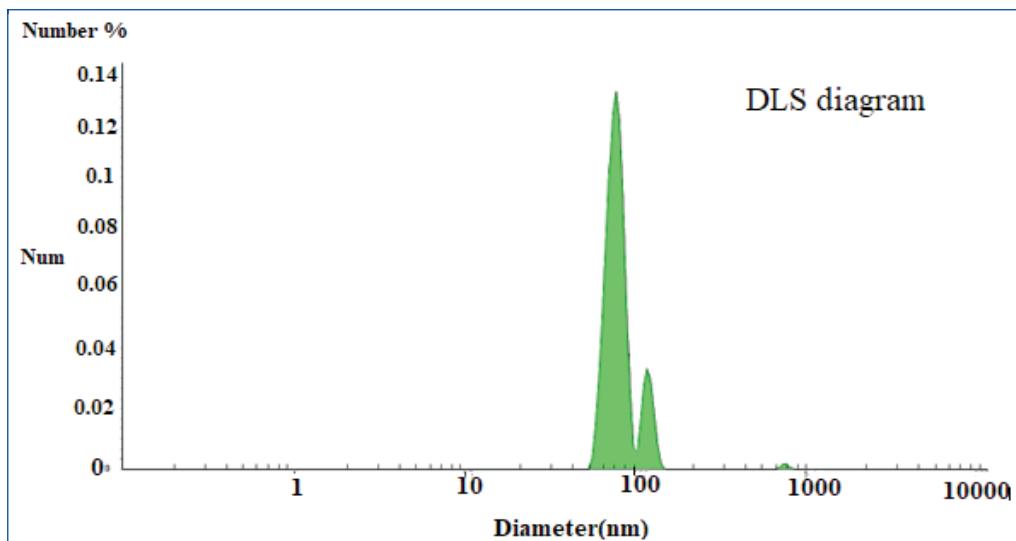


Fig. 2. The DLS diagram related to carbon nanostructures of COFs

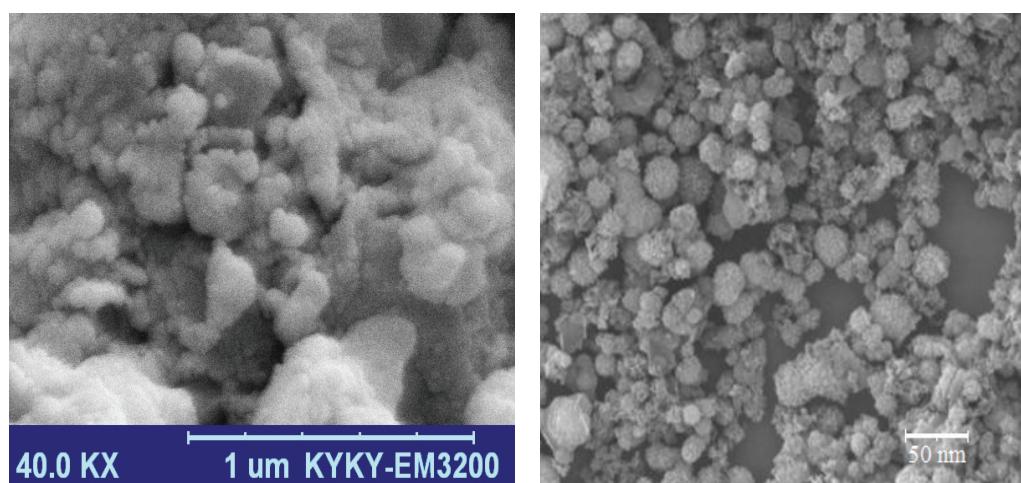


Fig. 3. SEM images of carbon nanostructures of COFs

3.4. Photocatalytic semi-degradation/adsorption and mechanism

The Figure 4 demonstrate the photocatalytic semi-degradation of methylene red, methylene blue and methylene orange organic dyes using COFs/TiO₂ modified with biochar in time cycles (0 min-40 min). The results show that the percent degradation/adsorption of MO is more than 99 % which can be depended on the low steric hindrance of MO structure. Also amount the percent degradation/adsorption of MR is a little more than MB which can also be related to low steric hindrance of MR structure ratio to MB. By reducing of time contact of photocatalyst with organic dyes, the extraction recovery of dyes decreased up to 40-54 % by SDA-SPE procedure. TiO₂ a highly efficient photocatalyst has a small band gap energy and relatively positive valance band edge under UV-light irradiation. TiO₂ caused to photogenerated electron-hole pairs and the transfer of the charge carriers. The charge carriers

transferred to the surface of the TiO₂ and react with O₂, H₂O, or OH groups and generated radicals. The decomposition of Dyes was initiated by the attack of •OH on the methyl group of the benzene ring of dye, leading to make a new compound. On the other hand, the presence of COFs can enhance the adsorption ability of the Dye via π-π stacking interaction between the π-electrons of the benzene rings in dye molecules and π-electron rich region of COFs nanostructure.

The effect of pH on the photocatalytic degradation/adsorption of MB, MR and MO organic dyes were revealed in Figure 5. As results the pH don't effected on extraction dyes on COFs/TiO₂ based on UV radiation by SDA-SPE procedure. By procedure, π-π stacking interaction between the π-electrons of the benzene rings in dye molecules and π-electron rich region of COFs nanostructure caused to efficient adsorption after semi degradation process.

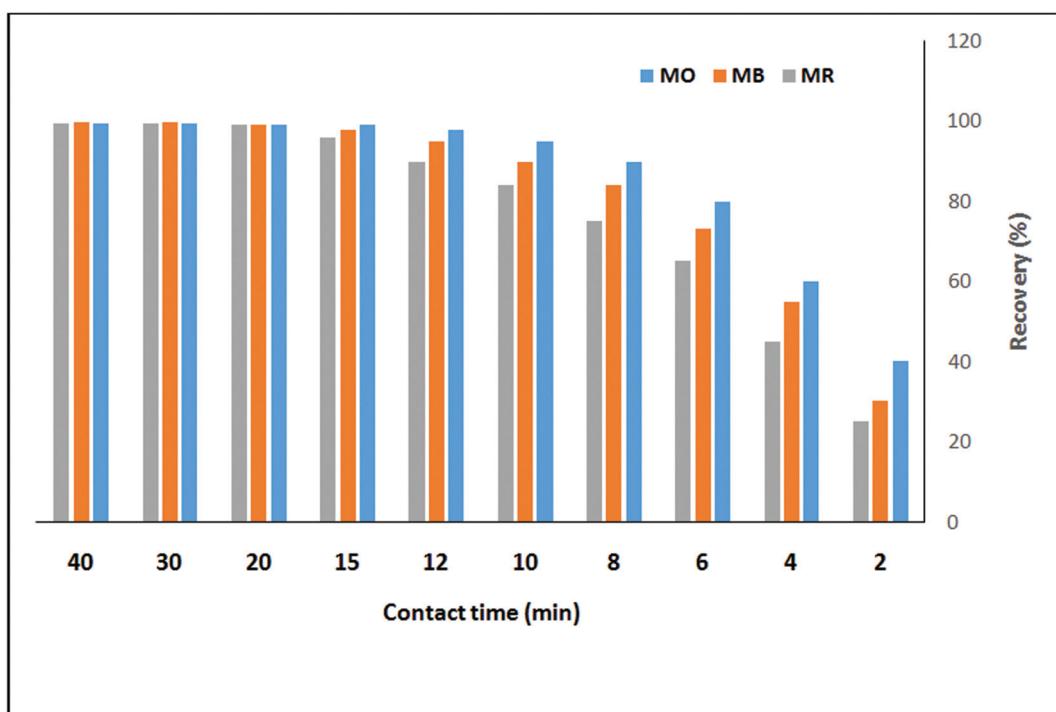


Fig. 4. The effect of time on recovery of adsorption/ photocatalytic degradation of methylene red, methylene blue and methylene orange organic dyes (0 min-40 min)

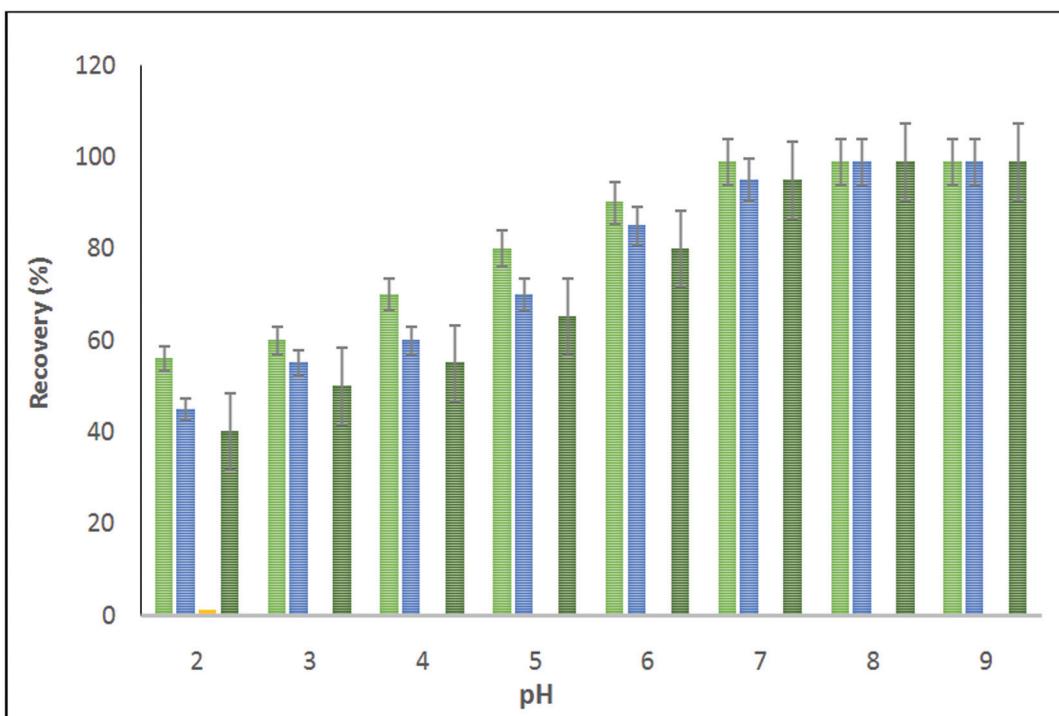


Fig. 5. The effect of pH on the photocatalytic semi-degradation/adsorption of MB(blue), MR(green dark) and MO(green) organic dyes

By increasing of time contact of carbon nanostructures(COFs) with organic dyes for all three dye structures, the degradation/adsorption of dyes initially increased due to high surface area of carbon nanostructures of COFs for photoreaction.

3.5. Kinetic study

Adsorbents in nano sizes of COFs have been shown to have better adsorption performance compared to other materials due to their high specific surface area, small size, and lack of internal penetration resistance. The most widespread models of surface adsorption isotherms for discontinuous systems are the Langmuir and Freundlich models. By the proposed procedure the R^2 for COFs/TiO₂ was achieved about 0.9988 and 0.9575 for the Langmuir and Freundlich models. So, the Langmuir model selected and used for this work. Most nanosorbents follow the Langmuir adsorption isotherm model, which can be evidence of the homogeneity of their surfaces and the fragmentation of the adsorption process. Quasi-first-order and quasi-second-order synthetic models were well used to describe the dye

adsorption process on the surface of nanosorbents. Large amounts of adsorption rate constants in both models can indicate rapid adsorption of dye molecules. After desorption, the nanosorbent can be used for several cycles (23 N).

3.6. Validation of method

The validation of SDA-SPE method based on COFs and COFs/TiO₂ in present of UV irradiation is important to evaluate the correct statistical results for extraction dye from waters. In SDA-SPE method, 5 mg L⁻¹ of dyes was made and used for extraction dyes from water samples and validated by spiking of standard solution to real samples (**Table 3**).

4. Conclusions

In this study, COFs and COFs-TiO₂ as a novel sorbent based on UV radiation was used for dye removal/extraction from water samples by SDA-SPE procedure. Based on results, the applied, fast, sensitive method based on COFs/TiO₂/UV was demonstrated. The semi degradation/adsorption

Table 3. Validation dye extraction based on COFs/TiO₂ and COFs by spiking of real samples

Sample	Added	Dye	Conc. COFs	Conc. COFs/TiO ₂	Recovery (%) COFs	Recovery (%) COFs/TiO ₂
Wastewater	----	MO	1.12 ± 0.07	1.86 ± 0.11	----	----
	1.5	MO	2.59 ± 0.13	3.39 ± 0.17	0.98	102
Wastewater	----	MR	2.64 ± 0.12	3.83 ± 0.19	----	----
	2.5	MR	5.11 ± 0.23	6.26 ± 0.27	98.8	97.2
Wastewater	----	MB	0.95 ± 0.04	1.74 ± 0.08	----	----
	1.0	MB	1.96 ± 0.12	2.70 ± 0.14	101.2	0.96

of dyes based on COFs/TiO₂/UV had efficient extraction in the optimized conditions. According to the evidence of morphological and COFs characterization such as, XRD, SEM and DLs, the dyes were efficiently removed from water samples. The results showed us, the activity and reaction of COFs/TiO₂/UV were more than COFs, primary carbon structure and TiO₂ in optimized conditions. Therefore, the fast, simple and efficient method based on SDA-SPE was used for removal of dye from waters by nanotechnology.

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6. References

- [1] S.A. Khayyat, Photocatalytic oxidation of phenolic pollutants and hydrophobic organic compounds in industrial wastewater using modified nonosize titanium silicate-1 thin film technology, *J. Nanosci. Nanotechnol.*, 14 (2014) 7345-7350.
- [2] C.D. Raman, S. Kanmani, Textile dye degradation using nano zero valent iron: a review, *J. Environ. Manage.*, 177 (2016) 341-355.
- [3] Z.A. Mirian,A. Nezamzadeh-Ejhieh, Removal of phenol content of an industrial wastewater via a heterogeneous photodegradation process using supported FeO onto nanoparticles of Iranian clinoptilolite, *Desalin. Wat. Treat.*, 35 (2016) 16483-16494.
- [4] K. Ordon, Functionalized semiconducting oxides based on bismuth vanadate with anchored organic dye molecules for photoactive applications, *Le Mans*, 2018.
- [5] I.A. Packiavathy, Antibiofilm and quorum sensing inhibitory potential of Cuminum cyminum and its secondary metabolite methyl eugenol against Gram negative bacterial pathogens, *Int. Food Res. J.*, 1 (2012) 85-92.
- [6] R. Saravanan, Visible light degradation of textile effluent using novel catalyst ZnO/γ-Mn₂O₃, *J. Taiwan Ind. Chem. Eng.*, 45 (2014) 1910-1917.
- [7] J. Xu, Magnetic properties and methylene blue adsorptive performance of CoFe2O4/activated carbon nanocomposites, *Mater. Chem. Phys.*, 147 (2014) 915-919.
- [8] Y. Xu, Holey graphene frameworks for highly efficient capacitive energy storage, *Nat. communications*, 5 (2014) 1-8.
- [9] G. Matafonova, V. Batoev, Recent advances in application of UV light-emitting diodes for degrading organic pollutants in water through advanced oxidation processes: A review, *Water Res.*, 132 (2018) 177-189.
- [10] M.Borges, Photocatalysis with solar energy: Sunlight-responsive photocatalyst based on TiO₂ loaded on a natural material for wastewater treatment, *Solar Energy*, 135 (2016) 527-535.

- [11] M. Pelaez, A review on the visible light active titanium dioxide photocatalysts for environmental applications, *Appl. Cat. B: Environ.*, 125 (2012) 331-349.
- [12] T.P. Yoon, M.A. Ischay, J. Du, Visible light photocatalysis as a greener approach to photochemical synthesis, *Nat. Chem.*, 2 (2010) 52-57.
- [13] X. Yu, Controllable preparation, characterization and performance of Cu_2O thin film and photocatalytic degradation of methylene blue using response surface methodology, *Mater. Res. Bull.*, 64 (2015) 410-417.
- [14] J. Cao, In situ preparation of novel p-n junction photocatalyst $\text{BiOI}/(\text{BiO})_2\text{CO}_3$ with enhanced visible light photocatalytic activity, *J. Hazard. Mater.*, 239 (2012) 316-324.
- [15] H. Aziz, Biomaterials supported with titania as photocatalyst in peat water purification, *J. Chem. Pharm.*, 7 (2015) 192-197.
- [16] P.A.F. Rodrigues, M.J. Geraldes, N.J. Belino. Legionella: Bioactive nano-filters for air purification systems. in 1st portuguese biomedical engineering meeting, IEEE, 2011.
- [17] T. Choi, J. S. Kim, J.H. Kim, Transparent nitrogen doped TiO_2/WO_3 composite films for self-cleaning glass applications with improved photodegradation activity, *Adv. Powder Technol.*, 27 (2016) 347-353.
- [18] H. Hayashi, Y. Hakuta, Hydrothermal synthesis of metal oxide nanoparticles in supercritical water, *Mater.*, 3 (2010) 3794-3817.
- [19] J. Wen, High-temperature-mixing hydrothermal synthesis of ZnO nanocrystals with wide growth window, *Curr. Appl. Phys.*, 14 (2014) 359-365.
- [20] C.-Y. Cao, Low-cost synthesis of flowerlike $\alpha\text{-Fe}_2\text{O}_3$ nanostructures for heavy metal ion removal: adsorption property and mechanism, *Langmuir*, 28 (2012) 4573-4579.
- [21] H. Wan, Hydrothermal synthesis of cobalt sulfide nanotubes: The size control and its application in supercapacitors, *J. Power Sour.*, 243 (2013) 396-402.
- [22] X. Xu, Hydrothermal synthesis of cobalt particles with hierarchy structure and physicochemical properties, *Mater. Res. Bull.*, 72 (2015) 7-12.
- [23] J. Chen, S. Wang, M.S. Whittingham, Hydrothermal synthesis of cathode materials, *J. Power Sour.*, 174 (2007) 442-448.
- [24] X. Li, J. Zang, Facile hydrothermal synthesis of sodium tantalate (NaTaO_3) nanocubes and high photocatalytic properties, *J. Phys. Chem. C*, 45 (2009) 19411-19418.
- [25] S. Farhadi, F. Siadatnasab, A. Khataee, Ultrasound-assisted degradation of organic dyes over magnetic $\text{CoFe}_2\text{O}_4@\text{ZnS}$ core-shell nanocomposite, *Ultrasonics Sonochem.*, 37 (2017) 298-309.
- [26] M. Eghbali-Arani, Ultrasound-assisted synthesis of YbVO_4 nanostructure and $\text{YbVO}_4/\text{CuWO}_4$ nanocomposites for enhanced photocatalytic degradation of organic dyes under visible light, *Ultrasonics Sonochem.*, 43 (2018) 120-135.
- [27] E. Costa, P.P. Zamora, A.J. Zarbin, Novel TiO_2/C nanocomposites: synthesis, characterization, and application as a photocatalyst for the degradation of organic pollutants, *J. Colloid Interface Sci.*, 368 (2012) 121-127.
- [28] J. Zhu, Two-dimensional porous polymers: from sandwich-like structure to layered skeleton, *Accounts Chem. Res.*, 51 (2018) 3191-3202.
- [29] Y. Song, A novel ascorbic acid electrochemical sensor based on spherical MOF-5 arrayed on a three-dimensional porous carbon electrode, *Anal. Methods*, 8 (2016) 2290-2296.
- [30] H. Furukawa, The chemistry and applications of metal-organic frameworks, *Sci.*, 341 (2013) 123-146.
- [31] A.U. Czaja, N. Trukhan, U. Müller, Industrial applications of metal-organic frameworks, *Chem. Soc. Rev.*, 38 (2009) 1284-1293.
- [32] M. Larsson, Bio-methane upgrading of pyrolysis gas from charcoal production, *Sustain. Energy Technol. Assess.*, 3 (2013) 66-73.

- [33] B. Shen, Elemental mercury removal by the modified bio-char from medicinal residues, *Chem. Eng. J.*, 272 (2015) 28-37.
- [34] Y.S. Ok, SMART biochar technology: a shifting paradigm towards advanced materials and healthcare research, *Environ. Technol. Innov.*, 4 (2015) 206-209.
- [35] J. Lehmann, J. Gaunt, M. Rondon, Bio-char sequestration in terrestrial ecosystems—a review, *Mitig. Adapt. Strateg. Glob. Chang.*, 11 (2006) 403-427.
- [36] O.M. Yaghi, Reticular Chemistry: Construction, properties, and precision reactions of frameworks, *J. Am. Chem. Soc.*, 138 (2016) 15507–15509.
- [37] O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim, Reticular synthesis and the design of new materials, *Nat.*, 423 (2003) 705-714.