Zeolitic Imidazolate/Fe₃O₄ Nanocomposite for Removal of Polystyrene and 4-tert-butylphenol via Adsorption

DELİA TERESA SPONZA^{*}, RUKİYE ÖZTEKİN Department of Environmental Engineering, Dokuz Eylül University, Tınaztepe Campus, 35160 Buca/Izmir, TURKEY

*Corresponding Author

Abstract: - Simultaneous removal of microplastics and endocrine disruptors was performed with high yields using Zeolitic imidazolate/Fe₃O₄ nanocomposite. Polystyrene and 4-tert-butylphenol were used to indicate the microplastic and endocrine disruptors. Under optimal conditions for maximum yields, the matrix was as follows: 1.5 mg/l Zeolitic imidazolate/Fe₃O₄ nanocomposite, 30 min adsorption time at a Zeolitic imidazolate to Fe_3O_4 ratio of 1/1, and 6 mg/l individual polystyrene 4-tert-butylphenol concentrations. Under these conditions, 99% and 98% removals were detected for polystyrene and 4-tert-butylphenol, respectively via adsorption. An excellent reproducibility was found for Zeolitic imidazolate/Fe₃O₄ nanocomposite under steadystate operational conditions. The FESEM analyses showed that Zeolitic imidazolate/Fe₃O₄ nanocomposite diameter was around 30 nm at a Zeolitic imidazolate to Fe₃O₄ nanocomposite ratio of 1/1 while some larger dodecahedral particles size was \leq 300 nm. N₂ adsorption-desorption measurements exhibited the porosity of Zeolitic imidazolate/Fe₃O₄ nanocomposite and the decrease of size is attributed to the incorporation of a nonporous magnetic phase via the addition of Fe²⁺ to the nanocomposite. BET results showed a specific surface area with a BET isotherm of 5000 m²/g, and a pore size of 30 nm for Zeolitic imidazolate/Fe₃O₄ nanocomposite. In the XRD spectra of Zeolitic imidazolate/Fe₃O₄ nanocomposite, the structure of nanocomposite was not changed by the addition of imidazolate and Fe₃O₄ nanocomposite. HRTEM analysis indicated some crystal agglomerations by doping of zeolitic imidazolate to Fe₃O₄. The reusability of the Zeolitic imidazolate/Fe₃O₄ nanocomposite was excellent even after 60 times utilization. The yields were 88% and 85% after 60 runs while the nanocomposite was reused 20 times during runs with yields as high as 97% and 98%.

Key-Words: - Zeolitic imidazolate/Fe₃O₄ nanocomposite; Polystyrene; 4-tert-butylphenol; Adsorption; Microroplastics; Endocrine disruptors.

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1 Introduction

Microplastics have been detected in rivers, deep oceans, marine sediments, and the atmosphere, [1]. However, microplastics also have the ability to adsorb other harmful organic pollutants and trace metals, [2], [3], from the environment onto their surface, resulting in the transportation of these pollutants, [3]. As well as adsorbing pollutants from the environment, microplastics can also release other organic species including, plastic components and additives such as endocrine disruptors (bisphenol A and 4-tert-butylphenol) released during the degradation process of waste plastics. These plastic components/additives are themselves environmental contaminants and present a risk to humans as endocrine disruptors. [4]. The prevalence of microplastic and its relationship with other pollutants poses a risk to the environment as marine life readily consumes microplastic causing harm directly through physical interactions or by the adsorbed toxins and bacteria, [5]. Microplastics are consumed by humans via contaminated food and drinks, or via breathing contaminated air, [6], [7]. Conventional methods for the removal of microplastics have been reviewed extensively and generally fall within three classes: physical separation, chemical separation, and biological separation, [1], [2], [3], [4], [5].

4-tert-butylphenol is a representative alkylphenol that has been widely used as an important raw material in the chemical industry for the synthesis of phenolic resins, fragrances, lubricants, pour-point depressors, and demulsifying agents, [8]. During the manufacturing and use process, a considerable amount of 4-tert-butylphenol is released into the environment, and thus this compound is frequently detected at relatively high concentrations in environmental media such as rivers, seawaters, and aquatic animals, [8]. Even more, the concentration of 4-tert-butylphenol may reach 6.7 µg/l in urine samples collected from people painting their houses with paint products, [8]. Laboratory toxicological studies have shown that 4-tert-butylphenol could endocrine disruption, cause morphologic, functional, and behavioral anomalies, and metabolic changes in exposed animals, [9]. For environmental safety and human health, it is highly desirable to develop a simple and efficient method to eliminate 4-tert-butylphenol from contaminated sites.

Microplastics and endocrine disruptors, potentially threatening new types of pollutants, are widely dispersed in water and can come into contact with humans through tap water. Among the removal processes of microplastics and endocrine disruptors in water treatment plants coagulation is not completely clear. Furthermore, polyaromatic carbon (PAC) and FeCl₃ coagulation were not very effective in the removals of both pollutants studied, [10].

Conventional methods for the removal of microplastics have been reviewed extensively and generally, the relevant 3 classes were not effective: physical separation, chemical separation, and biological separation, [11], [12], [13], [14], [15], [16], [17]. Physical separation includes techniques such as filtration, sedimentation, and density flotation, [18]. These methods are often able to achieve high removal efficiencies but suffer from drawbacks such as high energy and material cost for filtration due to membrane fouling, or ineffectiveness against smaller particles (< 100 μ m) for sedimentation and flotation, [19], [20], [21]. Chemical separation techniques include coagulation and flocculation and photodegradation, [22]. These techniques can achieve high removal efficiency, however, in the case of coagulation and flocculation, they can also be inefficient for the removal of smaller particles and those with a certain shape, and in the case of photodegradation there is increased risk of releasing an metabolite the contaminants in environment, [23]. Biodegradation also exhibits lower efficiencies since these pollutants are recalcitrant, [20], [21], [22], [23].

Magnetic nanoparticles have emerged as an alternative for the removal of microplastics, [24]. In this method a magnetic sorbent is added to the polluted water and the analyte is adsorbed by the magnetic material which is then removed via an external magnet. This method offers high microplastic removal rates, simple implementation,

highly efficient of and removal smaller microplastics, [25]. A range of nanomaterials has been employed for the removal of microplastics and endocrine disruptors with the most common type being functionalized magnetic iron or iron oxide nanoparticles, [26]. Other magnetic materials based on biochar, zeolite can be also used. However, there is a lack of magnetic nanomaterials that enable the efficient and simultaneous removal of microplastics and endocrine disruptors and their released small organic molecule-based components/additives.

Zeolitic imidazolate compounds are porous crystalline metal-organic framework materials made up of tetrahedral metal nodes and imidazolate linkers, [27]. Their high chemical and thermal stability, large surface area, microporous structure, and shape and pore size tunability make them promising materials for a range of applications including separations, [28], and catalysis, [29]. Amongst them, in the zeolytic amediazole the relationships between Zn(II) and 2-methylimidazole are well-known because of their adsorptive ability and high stability, [30]. ZIF-8 synthesis can be completed via a one-step, one-pot, room temperature synthesis in an aqueous medium, from cheap and low-toxic precursors and low crystal size to increase adsorption efficiency for dyes and pollutants, [31].

Magnetic metal-organic frameworks are excellent materials for a range of applications, [32], including the efficient extraction of environmental pollutants, [33]. For example, magnetic have been applied for the removal of diverse pollutants including arsenic, [34], uranyl ions, [35], or organic compounds like norfloxacin, [36]. The efficient removal of organic pollutants from water has been also enhanced by exploring the synergies of magnetic with other materials, resulting in composites such as Fe₃O₄-poly(styrenesulfonate) for the removal of methyl orange, [35], or combining magnetic ZIF-8 with amine-functionalized carbon nanotubes for the removal of malachite green and rhodamine B, [36].

Among various methods, adsorption is widely used in wastewater treatment. Adsorption is usually used as an advanced and terminal treatment for residual small molecular pollutants in water. Compared with other methods, adsorption has the advantages of convenient operation. high purification rate, low energy consumption, and low cost, [32]. Studying the removal of microplastics and endocrine disruptors in water by adsorption is of practical value. Currently, several studies have been conducted on the degradation of 4-tert-butylphenol in aqueous solution, mainly including biodegradation and photochemical methods, [8]. The treatment efficiency of biodegradation technology is generally very low, and a relatively long time period is needed for the complete removal of 4-tert-butylphenol, [8]. The degradation efficiency of 4-tert-butylphenol in UV, UV/H₂O₂, and $UV/S_2O_8^{2-}$ systems, and almost complete removal was achieved in 40~50 min in the two Photo-Fenton-like processes. However, the mineralization efficiency was not high, with only \sim 30 % removal of the initial total organic carbon (TOC) after 16 h of irradiation. It was reported that degradation during 4-tert-butylphenol the transformation metabolites were not removed effectively, [30].

A Zeolitic imidazolate composite with Fe₃O₄ material for the simultaneous removal of small molecule plastic components/additives and microplastics and endocrine disruptors has not been yet reported in detail.

Therefore, in this study a nanocomposite namely Zeolitic imidazolate/Fe₃O₄ nanocomposite was produced under laboratory conditions to remove a microplastic (polystyrene) and an endocrine disruptor chemical (4-tert-butylphenol) from wastewaters. The effects of increasing amount of Zeolitic imidazolate/Fe₃O₄ nanocomposite concentrations (0.5, 1.0, 1.5, 2.0, 2.5, 3.0 and 4.0 mg/l) and increasing ratios of Zeolitic imidazolate to Fe_3O_4 (1/1, 1/2, 1/3, 1/4) and polystyrene and 4-tertbutylphenol concentrations (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0 and 6.0 mg/l) at different pH (3.0, 7.0, 9.0 and 10.0) on the removals of polystyrene and 4tert-butylphenol was investigated. The physicochemical analysis was performed by EDS, Raman spectra, XRD, HRTEM, FESEM, N₂ adsorption/desorption, and BET surface and pore assays. The resusability of the nanocomposite was investigated during 20 and 60 runs.

2 Materials and Methods

2.1 Synthesis of Zeolitic Imidazolate/Fe₃O₄ Nanocomposite

2.1.1 Production of Zeolitic Imidazolate

In the preparation of Zeolitic imidazolate 5 ml aqueous solutions of Zn(OAc)₂.2H₂O (0.6 g, 3.3 mmol) and 2-methylimidazole (2.24 g, 27.3 mmol) were mixed at 25°C room temperature. The mixture was incubated at 25°C for 24 h. The settled crystals were collected via centrifugation at 4500 g for 30 min. The supernatant was discarded, then the material was collected and washed with deionized

water and methanol. The solid mixture was dried for 12 h at 70°C.

2.1.2 Preparation of Fe₃O₄ Nanocomposite

5 g of Fe₃O₄ was mixed in 12 ml hexane and then added to a solution of 50/50 acetonitrile/ethyl acetate. 0.5 ml NaIO₄ was added and the mixture was stirred at room temperature for 1 h until the particles moved to the aqueous layer. After the addition of 80 ml of deionized water, the organic compounds were decanted. The aqueous layer was centrifuged and the supernatant was discarded and the remaining solid particles were washed with deionized water and ethanol.

2.2 Production of Zeolitic Imidazolate/Fe₃O₄ Nanocomposite

Zeolitic imidazolate/Fe₃O₄ nanocomposite was prepared by mixing 5 ml of FeSO₄.7H₂O solution, 5 ml of Zn(OAc)₂, and 5 ml of 2-methylimidazole. The Zeolitic imidazolate/Fe₃O₄ nanocomposite was prepared This material was collected via an external magnet and then washed with water and methanol and was dried at 60°C overnight.

2.3 Physicochemical Analysis of Zeolitic Imidazolate/Fe₃O₄ Nanocomposite

The morphology of the Zeolitic imidazolate/Fe₃O₄ nanocomposite was studied via a field emission scanning electron microscope (FESEM). То of determine the particle structure the nanocomposite energy dispersive X-ray spectroscopy (EDS) and high-resolution (HRTEM) transmission electron microscopy analyses were performed. Nitrogen adsorptiondesorption isotherms were obtained via a surface area and porosity analyzer. The Brunauer-Emmett-Teller (BET) method was used to calculate surface area and pore size using experimental points. Powder X-ray diffraction (XRD) patterns were obtained using a diffractometer with a Co X-ray.

2.4 Preparation of Polystyrene Microplastic and Its Removal

Samples of 1.1 μ m polystyrene microsphere solutions (10 ml) with a concentration of 25 mg/l or 50 mg/l were added to a 20 ml glass vial with increasing amount of Zeolitic imidazolate/Fe₃O₄ nanocomposite (0.5, 1.0, 1.5, 2.0, 2.5, 3.0 and 4.0 mg/l) and increasing ratios of Zeolitic imidazolate to Fe₃O₄ (1/1, 1/2, 1/3 and 1/4) and polystyrene concentrations (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, 4.0, 5.0 and 6.0 µg/l). The samples were stirred at a rpm of 700 rpm for 60 min. The microplastics/Zeolitic

imidazolate/Fe $_3O_4$ nanocomposite aggregates were removed from the samples via an external neodymium magnet. The efficiency of the removal of polystyrene was monitored.

2.5 Preparation of 4-tert-butylphenol and Its Removal

A 200 mg/l solution of the 4-tert-butylphenol was prepared by dilution of the stock solutions with water. 10 ml of 2 mg/l 4-tert-butylphenol was mixed with increasing Zeolitic imidazolate/Fe₃O₄ nanocomposite (0.5, 1.0, 1.5, 2.0, 2.5, 3.0 and 4.0 mg/l) concentrations and increasing Zeolitic imidazolate to Fe₃O₄ ratios (1/1, 1/2, 1/3 and 1/4). The samples were mixed at increasing speeds (400, 1000, 1500, 3000, 5000, and 7000 rpm), at increasing times (1.0, 10, 20, 30, and 40 min). The Zeolitic imidazolate/Fe₃O₄ nanocomposite was removed from the samples via an external magnet, and samples were passed through a 0.45 µm polytetrafluoroethylene (PTFE) syringe filter prior to analysis.

2.6 Analytical Procedures

4-tert-butylphenol concentrations were determined via high-performance liquid chromatography - ultraviolet spectroscopy (HPLC-UV) using a Dionex 120 silica-C18 4.6 \times 150 mm column with a particle size of 5 µm, with a 4.6 \times 10 mm guard column. A detection wavelength of 280 nm was used. Removal efficiency was determined via a comparison of 4-tert-butylphenol before and after extraction.

Polystyrene measurements were performed in a UV spectrophotometer, following the decrease of the turbidity by the forming of the settled colloidal polystyrene at a wavelength of 500 nm.

Iron and zinc content in the prepared nanocomposite were determined using a Varian atomic absorption spectrometer equipped with iron and zinc hollow cathode ray neon-filled lamps.

2.7 Assays for Simultaneous Removal of Polystyrene and 4-tert-butylphenol

Simultaneous removal of polystyrene microplastic and 4-tert-butylphenol was carried out in a solution with a volume of 40 ml containing 40 mg/l of polystyrene microplastic and 4 mg/l of 4-tertbutylphenol. Dry samples were dispersed in 1 ml acetonitrile and sonicated for 5 seconds. Acetonitrile was decanted (materials held via a magnet) and the material was washed with 5 ml of deionized water before the pollutant sample was added.

3 Results and Discussions

3.1 FESEM Analysis Results

FESEM analyses exhibited that the produced Zeolitic imidazolate/Fe₃O₄ nanocomposite diameter was around 145 nm at a Zeolitic imidazolate to Fe₃O₄ nanocomposite ratio of 1/1 the produced nanocomposite exhibited dodecahedral particles with a size of ≤ 100 nm in diameter (Figure 1a). Furthermore, some larger dodecahedral particles \leq 300 nm in diameter were also observed (Figure 1b). This indicates the doping of Fe₃O₄ with the 2methylimidazole for Zn^{2+} binding sites, terminating with a crystal structure. The presence of larger crystals can be attributed to an insufficient bonding of the Fe₃O₄. To overcome this, the ratio of Zeolitic imidazolate to Fe₃O₄ nanocomposite in the nanocomposite was increased. With a ratio of 1/2, a significant decrease in the larger crystals was detected (Figure 1c). The bigger dodecahedral nanoparticles in the Zeolitic imidazolate/Fe₃O₄ nanocomposite decreased at a Zeolitic imidazolate to Fe₃O₄ ratio of 1/4 compared with large (Figure 1d) nanoparticles.



(a)



(**d**)

Fig. 1: FESEM analysis results in (a) Zeolitic imidazolate/Fe₃O₄ nanocomposite with a size of \leq 300 nm, (b) nanoparticles \leq 800 nm, (c) Zeolitic imidazolate/Fe₃O₄ nanocomposite with a Zeolitic imidazolate to Fe₃O₄ ratio of 1/3 and (d) Zeolitic

imidazolate/Fe $_3O_4$ nanocomposite with a Zeolitic imidazolate to Fe $_3O_4$ ratio of 1/4.

3.2 N₂ Adsorption–Desorption Measurements

The porosity of the Zeolitic imidazolate/Fe₃O₄ was nanocomposite investigated with N_2 adsorption-desorption measurements. Sharp increases in adsorption at lower relative pressures were detected in the isotherms of Zeolitic imidazolate and Zeolitic imidazolate/Fe₃O₄ indicating nanocomposite the presence of micropores (Figure 2), and they were small. This decrease in the size is attributed to the incorporation of a nonporous magnetic phase, via the addition of Fe²⁺ Zeolitic imidazolate/Fe₃O₄ to the nanocomposite. An increase in elevated relative pressures during adsorption indicates the possible presence of interparticle mesopores and micropores in the structure of Zeolitic imidazolate/Fe₃O₄ nanocomposite. The smaller crystal size in this nanocomposite indicates the presence of new larger pores due to nanoparticle agglomeration.



Fig. 2: Nitrogen adsorption-desorption isotherm of Zeolitic imidazolate and zeolitic imidazolate/Fe₃O₄ nanocomposite.

3.3 BET Analyses Results

The specific surface area obtained based on the BET isotherm which is accounted as $5000 \text{ m}^2/\text{g}$, and the pore size of the zeolitic imidazolate/Fe₃O₄ nanocomposite was 30 nm. It was found that Zeolitic imidazolate has a low BET isotherm area (2800 m²/g) and high pore size (140 nm) (Table 1 and Figure 3).

Tabl	le 1.	Brunauer-	-Emmett-	Teller	(BET)	analysis

resuits						
Sample	S BET (m ² /g)	Mean pore diameter (nm)				
Zeolitic imidazolate	5000	130				
Zeolitic imidazolate/Fe ₃ O ₄	2800	30				
nanocomposite						



Fig. 3: BET analysis results for Zeolitic imidazolate/Fe₃O₄ nanocomposite (blue circle) and Zeolitic imidazolate (red circle).

3.4 XRD Analysis Results

In the XRD spectra of Zeolitic imidazolate/Fe₃O₄ nanocomposite peaks can be seen at $2\theta = 7.90^{\circ}$, 10.80°, 12.20°, 14.60°, 16.90° and 18.90°, respectively. These peaks correspond to planes of (112), (204), (216), (225) and (318), respectively (Figure 4). These data showed that the structure of Zeolitic imidazolate/Fe₃O₄ nanocomposite was not changed by the addition of imidazole and Fe₃O₄. Peaks at 30.90°, 35.80°, 43.90°, 53.20°, 58.00° and 62.60°, respectively, can be attributed to planes of (223), (318), (406), (429), (514) and (446), respectively (Figure 4). The presence of weaker diffraction bands that correspond to the incorporation of zinc ferrite into the Zeolitic imidazolate/Fe₃O₄ nanocomposite was detected.



Fig. 4: XRD patterns of Zeolitic imidazolate/Fe₃O₄ nanocomposite at different planes

3.5 Raman Analysis Results

In Figure 5, the Raman spectrum was recorded for a superstructure obtained for Zeolitic imidazolate/Fe₃O₄ nanocomposite. Finally, topography investigations of the heights of objects by AFM led to a mean value of 130 nm and a profile in perfect agreement with the channel diameter for a nanocomposite. This indicates the superstructures of the nanocomposite do not collapse when they are released from the matrix.



Fig. 5: Raman spectra of Zeolitic imidazolate and Zeolitic imidazolate/Fe₃O₄ nanocomposite.

3.6 HRTEM Analysis Results

Examination of superstructures at the single object level using high-resolution transition electronic microscopy confirmed the doping of zeolitic imidazolate to form some agglomerations by intergrown crystals. The diameter of the nanocomposite varied between 110 nm (Figure 6a) and 130 nm (Figure 6b).





Fig. 6: HRTEM analysis in Zeolitic imidazolate/Fe₃O₄ nanocomposite with (a) small and (b) large diameter

3.7 EDS Spectra Results

To clarify the elemental distribution, EDS was used in an individual Zeolitic imidazolate particle. Figure 7 shows that the elemental composition of the Zeolitic imidazolate consists of Zn, N, and, C. These metals were dispersed evenly in the shell layer (Figure 7). In the Zeolitic imidazolate/Fe₃O₄ nanocomposite, Fe and O can be ascribed to Fe₃O₄ with Zn, N, and C (Figure 8). The presence of a small amount of oxygen atoms can be due to the presence of some water molecules encapsulated in the nanocomposite cavities.

It can be concluded that the Zeolitic imidazolate has an outer layer coated with the inner part of Fe_3O_4 and distributed homogeneously on the crystal nanocomposite structure.



Fig. 7: C, N, and Zn distributions in the Zeolitic imidazolate



Fig. 8: C, N, O, Fe, Co, and Zn distributions in the Zeolitic imidazolate/Fe₃O₄ nanocomposite

3.8 FESEM Analysis Results

In Figure 9a and Figure 9b, the FESEM image shows the morphology of the selected polystyrene microspheres in detail. The dried pure microplastics used are uniform in their shape and size with a mean diameter of 100 nm for Zeolitic imidazolate/Fe₃O₄ nanocomposite and 33 nm for Zeolitic imidazolate (Figure 9a and Figure 9b). The particles were tightly packed on the surface of the spheres. FESEM images of the aggregate were magnetically removed after microplastic extraction. This clearly shows that the magnetic nanocomposite particles and the polystyrene beads can be seen embedded in the aggregates.



(b)

Fig. 9: FESEM images of (a) Zeolitic imidazolate and (b) Zeolitic imidazolate/Fe₃O₄ nanocomposite.

3.9 Effects of Zeolitic Imidazolate/Fe₃O₄ Nanocomposite Concentrations on the Removals of Polystyrene and 4-tertbutylphenol

Increasing Zeolitic Imidazolate/Fe₃O₄ Nanocomposite (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, and 4.0) and increasing Zeolitic imidazolate to Fe₃O₄ ratios (1/1, 1/2, 1/3 and 1/4) concentrations were prepared. The samples were mixed at increasing speeds (400, 1000, 1500, 3000, 5000 and 7000 rpm) and at increasing times (1.0, 10, 20, 30 and 40 min).

The effect of the catalyst's concentration experiments was carried out by taking different amounts of Zeolitic imidazolate/Fe₃O₄ nanocomposite (0.5, 1.0, 1.5, 2.0, 2.5, 3.0, and 4.0 mg/l) concentrations to detect the optimum operational conditions for maximum polystyrene and 4-tert-butylphenol yields. The polystyrene and 4-tert-butylphenol concentrations were kept constant at 4 mg/l.

The removal efficiency increased from 65%-70% up to 96% and 97% in both pollutants as the

nanocomposite concentration was increased from 0.5 to 1.5 mg/l (Table 2). Further, the increase of the nanocomposite did not elevate the yields in both 2.0-2.5 pollutants. Beyond mg/l Zeolitic imidazolate/Fe₃O₄ nanocomposite dose for the available pollutant molecules may not be sufficient for adsorption by the increased number of Zeolitic imidazolate/Fe₃O₄ nanocomposite. Hence, the additional catalyst powder did not elevate the catalysis activity of nanocomposite and the rate does not increase with an increase in the amount of catalyst. At higher nanocomposite concentrations, the particles may aggregate, which reduces the interfacial area between the reaction solution and the photocatalyst. Thus, the number of active sites on the catalyst surface effectively decreases. The surplus addition of nanocomposite makes the solution more turbid and the reduction in degradation efficiency may be due to the scattering of light with a surplus amount of Zeolitic imidazolate/Fe₃O₄ nanocomposite. 1.5 mg/l of Zeolitic imidazolate/Fe₃O₄ nanocomposite was found to be the optimum catalyst concentration for maximum degradation of 4 mg/l polystyrene and 4tert-butylphenol concentrations.

Table 2. Effect of increasing Zeolitic imidazolate/Fe $_3O_4$ nanocomposite concentrations on

the removal yields of polystyrene and 4-tert-

Zeolitic imidazolate/Fe ₃ O ₄ nanocomposite dose	Polystyrene removal efficiency	4-tert- butylphenol removal
(mg/l)	(%)	efficiency (%)
0.5	67	70
1.0	87	88
1.5	99	98
2.0	98	97
2.5	97	96
3.0	97	97
4.0	96	96

3.10 Effects of Increasing Polystyrene and 4tert-butylphenol Concentrations on Their Removal Yields

The rate of degradation is found to increase with increasing concentration of individual polystyrene and 4-tert-butylphenol concentrations from 2 mg/l up to 6 mg/l. Further increase in pollutant concentration decreases the rate of degradation (Table 3). On the initial increase of the concentration of polystyrene and 4-tert-butylphenol; the reaction rate increases as more molecules of the pollutant are available for degradation. However, with a further increase of polystyrene and 4-tert-

butylphenol concentration, the solution becomes more intense, and the turbidity increases. Under these conditions, the path length of photons entering the solution is decreased thereby fewer photons are able to reach the catalyst surface. Hence, less production of hydroxyl (OH•) and superoxide (O₂-•) radicals leads to a reduction in photodegradation efficiency. Moreover, at higher polystyrene and 4tert-butylphenol concentrations (7, 10 mg/l) the number of collisions between pollutant molecules increases whereas the number of collisions between pollutant molecules and OH• radical decreases. Consequently, the rate of reaction is retarded. Therefore, the optimized individual polystyrene and 4-tert-butylphenol concentrations should not be more than 6 mg/l for maximum yields.

Table 3. Effects of increasing polystyrene and 4-
tert-butylphenol concentrations on their removal
yields at 1.5 mg/l Zeolitic imidazolate/Fe ₃ O ₄
nanocomposite

Polystyrene	2	3	4	5	6	7
concentration (mg/l)						
Polystyrene yield (%)	67	73	79	83	99	95
4-tert-butylphenol	2	3	4	5	6	7
concentration (mg/l)						
4-tert-butylphenol yield	66	72	80	84	99	93
(%)						

The adsorption of Zeolitic imidazolate/Fe₃O₄ nanocomposite onto polystyrene and 4-tertbutylphenol is proposed to be due to hydrophobic interactions between the pollutants and the hydrophobic surface of the Zeolitic imidazolate/Fe₃O₄ nanocomposite to the 2methylimidazole. The larger size in the Zeolitic imidazolate/Fe₃O₄ nanocomposite provides the available effective surface for interaction with the dispersed pollutants. The improvements in the removal efficiency were attributed mainly to the optimum particle size of the Zeolitic imidazolate/Fe₃O₄ nanocomposite with a size of 30 nm, leading to a larger effective area of interaction between the nanocomposite crystals and the polystyrene and 4-tert-butylphenol.

3.11 Effect of pH Values on the Yields of Polystyrene and 4-tert-butylphenol Removal Yields

The pH was adjusted from 3.0 up to 10.0 to detect the effect of pH on the photodegradation of microplastic and endocrine-disrupting samples. At neutral pH, the polystyrene and 4-tert-butylphenol had the highest adsorption capacity to the Zeolitic imidazolate/Fe₃O₄ nanocomposite (Table 4). At high pH values and acidic conditions, the nanocomposite adsorbed, substantially fewer pollutants were removed and the adsorption capacity decreased due to the formation of acidic and alkaline containing groups on the surface of Zeolitic imidazolate/Fe₃O₄ nanocomposite. Under these conditions, the hydrophobicity and the hydrophobic interaction between nanocomposite and pollutants was lowered. The hydrophobicity of both nanocomposite and pollutants was less affected under alkaline conditions compared to acidic conditions.

Table 4. Effect of pH variations on the pollutant vields

Pollutants		pН	values	
	3.0	7.0	9.0	10.0
Polystyrene yield (%)	76	99	69	53
4-tert-butylphenol yield (%)	77	98	60	49

3.12 The Effect of Time on the Polystyrene and 4-tert-butylphenol Removal Yields

The effect of the time on the pollutant removal efficiencies was studied in the range of 10, 20, 30, and 40 min. As shown in Table 5, the pollutant removals increased as the time was increased to 30 min. Removal efficiency reached a maximum after 30 min at 4 mg/l individual polystyrene and 4-tert-butylphenol concentrations. The maximum yields were 99% and 98% for polystyrene and 4-tert-butylphenol, respectively.

	Table 5.	Effect	of time	on the	removals	of	pollutants
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Pollutants	Time (min)			
	10	20	30	40
Polystyrene yield (%)	70	80	99	53
4- <i>tert</i> -butylphenol yield (%)	77	82	98	49

3.13 Effect of Temperature on the Yields of Polystyrene and 4-tert-butylphenol Removal Yields

In this study, the temperature was increased from 25 to 60°C to detect the performances. At high temperatures (70 and 100°C) the yields increased to 100% (data not shown). Since the studies were detected at 25°C room temperature and the pollutant yields (98%-99%) were satisfactory no studies in detail were conducted with high temperatures since high temperatures cause excess spending and elevate the treatment cost.

3.14 Recovery Zeolitic Imidazolate/Fe₃O₄ Nanocomposite

The nanocomposite with a concentration of 1.5 mg/l was used 21 times to detect its reuse efficiency.

After 21 runs the nanocomposite was recovered with high yields (97% and 95%) (Table 6). It can be used more than 60 times with yields varying between 87% and 84%.

Table 6. Reusability of Zeolitic imidazolate/Fe₃O₄ nanocomposite

	Pollutants Yields					
Runs	Polystyrene yield	4-tert-butylphenol yield				
	(%)	(%)				
1	99	99				
2	99	99				
3	99	99				
4	99	99				
5	99	99				
6	99	99				
7	99	99				
8	99	99				
9	99	99				
10	99	99				
11	99	99				
12	99	99				
13	99	99				
14	99	99				
15	99	99				
16	99	99				
17	99	99				
18	99	99				
19	99	99				
20	99	98				
21	97	95				
50	90	90				
55	88	87				
60	87	84				

4 Conclusion

In this research, Zeolitic imidazolate/Fe₃O₄ nanocomposite crystals were prepared under laboratory conditions with a simple cost-effective method and environmentally friendly process. At high Zeolitic imidazolate/Fe₃O₄ nanocomposite concentration, the polystyrene and 4-tertbutylphenol removals decreased. Time and nanocomposite loading both increased removal efficiency before reaching optimal values. The nanocomposite concentrations optimal were detected at 1.5 mg/l at a Zeolitic imidazolate to Fe₃O₄ nanocomposite ratio of 1/4 after 30 min for 6 mg/l pollutant concentrations. It was detected that the Zeolitic imidazolate/Fe₃O₄ nanocomposite exhibited excellent removal efficiencies for microplastic and endocrine disruptors. The magnetic removal of microplastics and endocrine disruptors lowered the separation cost.

Zeolitic imidazolate/Fe₃O₄ nanocomposite exhibited high performance for the fast and efficient removal of microplastic and endocrine disruptors. This can be attributed to the synergistic effects of imidazolate and Fe₃O₄ including π - π and electrostatic interactions during adsorption of pollutants.

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Conflict of Interest

The authors have no conflict of interest to declare.

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