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Research Article

THE SYNTHESIS OF SPHERICAL SHAPE AMINO FUNCTIONALIZED PEI-TGIC COVALENT ORGANIC FRAMEWORKS: SYNTHESIS, CHARACTERIZATION, AND METHYL ORANGE ABSORPTION

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ABSTRACT

In here, the synthesis of covalent organic framework (COF) from the reaction of polyethyleneimine (PEI) and triglycidyl isocyanurate (TGIC) in dimethylformamide at 90 ^{o}C were carried out. The surface are, pore volume and pore size values of PEI-TGIC COFs observed as 23.4 m^2/g, 0.143 cm^3/g, and 22.5 nm, respectively. Moreover, the surface charge of PEI-TGIC COFs increased to +46.1±2.6 mV from +18.3±1.7 mV, after protonation of amine groups of PEI-TGIC COFs. Moreover, the potential usage of PEI-TGIC based COFs in absorption methyl orange (MO) dye from aqueous media was testing. It was observed that, the PEI-TGIC COF absorbed 156.6±4.9 mg/g MO, and the protonated PEI-TGIC (p-PEI-TGIC) COFs absorbed 202.4±5.3 mg/g MO from aqueous media in 30 min. The MO absorption by PEI-TGIC COF fitted with pseudo-first-order kinetic model, whereas MO absorption by p-PEI-TGIC COF fitted with pseudo-second-order kinetic model.

Keywords: *Covalent organic framework, COF, PEI-TGIC, methyl orange absorption*

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1. INTRODUCTION

In recent years, scientists have set out from nature's ability to create complex systems; have made great progress in the production of many materials with advanced functions by combining units in different shapes and structures [1-3]. By way of example, many materials have been synthesized from zero dimension materials [4] to three-dimensional materials [5], inorganic materials [6] to organic materials [7], irregular amorphous materials [8] to regular crystalline materials [9], non-porous materials [10] and porous materials [11] by using weak bonds such as p-p bonds [12] and stronger bonds such as covalent bonds [13]. For porous structure synthesis, exciting progress has been made in coordination chemistry and material science, and metal organic frameworks (MOFs), which are coordinated polymers have been synthesized using metal ions and organic ligands [5]. In addition, with recent significant developments, new generation amorphous materials of various pore sizes have been synthesized such as hyper crosslinked polymers (HCPs) [14], internal microporous polymers (PIMs) [15], conjugated microporous polymers (CMPs) [16], cryogels [17] and son on [18]. With these developments in the synthesis of porous structures; the synthesis of covalently bonded crystalline porous structures has been a new field of research for researchers. Studies have shown that the most important strategy for this purpose is the use of rigid units with multiple connections by covalent bonds [19]. Finally, in 2005, the first covalent organic frameworks (COFs) were synthesized by Yaghi and co-workers, with crystallin, and porous structure and high surface area [7].In brief, COFs are two- or three-dimensional porous crystal structures synthesized by regulation of organic subunits [7, 20, 21]. Although they were used for gas absorption [22] and separation [23] when first synthesized, advances in this area have enabled COFs to be used in a wide range of applications, from solar collectors [24] to optoelectronic devices [25], sensors [21] to catalysts [20], and environmental applications [26] to medical applications [27].

Dyestuffs are organic pollutants which are widely used in textile, paper, printing industry and home paints, produced about 7×10^5 metric tons annually and sold in the market with more than 100.000 types [28, 29]. Wastewater containing dyes is one of the most problematic organic pollutants due to their high toxicity, suspended structures, and color. Reduction of light penetration as a result of coloring of dyes adversely affects activity for photosynthetic organisms in aquatic life [30-33]. However, it can be toxic to some living things in aquatic life, in the presence of aromatics, metals, chlorides, and so on [30-33]. Because of their synthetic origin and complex structure, dyes are stable and difficult to biologically degrade. Dyes can be classified as, anionic - direct, acid and reactive dyes; cationic - basic dyes; and nonionic - disperse dyes [30]. Among these, water-soluble reactive and acid dyes are the most problematic dyes [34, 35]. In addition, despite the low concentration of basic dyes, giving too much color with negatively affects water and water organisms [36, 37].

In this study, the prepared of isocyanurate based amine functionalized (PEI-TGIC) COFs were successfully synthesized in dimethyl formamide at 90 ^{o}C. The prepared COFs were treated with HCl to protonation of amine groups on PEI-TGIC COFs. The PEI-TGIC COFs were characterized by using Fourier Transform Infrared (FT-IR) spectrometer, surface area and porosity measurements, zeta potential, and thermogravimetric analyzer (TGA) measurements. Moreover, the prepared PEI-TGIC based COFs were used as an absorbent for methyl orange removal from aqueous media.

2. EXPERIMENTAL

2.1 Materials

The branched polyethyleneimine (PEI, 50% in water, Mn:1800, Aldrich) and triglycidyl isocyanurate (TGIC, Aldrich) were used for synthesis of covalent organic frameworks.

Dimethyl formamide (DMF, 99%, Merck) was used as solvent for COF synthesis. Hydrochloric acid (HCl, 36.5%, Sigma Aldrich) was used to protoation of PEI-TGIC COFs. Potassium chloride (KCl, 99%, Merck) was used for zeta potential measurements. Methyl orange (MO, ACS reagent, 85% dye content, Fluka) was used for absorption studies.

2.2 Synthesis of PEI-TGIC covalent organic framework

The synthesis of PEI-TGIC COF was carried out in DMF at 90 ^{o}C by using epoxy – amine ring opening reaction [17]. In brief, 3.93 mmol of TGIC was dissolved into 100 mL of DMF and 23.8 mmol of PEI (2 mL of PEI solution %50 in water), and stirred at 90 ^{o}C, at 800 rpm mixing rate for 2 h. The prepared PEI-TGIC COFs were precipitated in excess amount of acetone, and washed with acetone, acetone-water, water, and acetone again, to remove unreacted reactants. The prepared and washed PEI-TGIC COFs were dried by using heatgun and stored at closed tubes for further usage.

Moreover, the prepared PEI-TGIC COFs were treated with 1 M HCl acid to protonation of amine groups of to obtain higher positively charged PEI-TGIC COFs. Then, protonated PEI-TGIC (p-PEI-TGIC) COFs were washed with water once, acetone twice, and dried by using heat gun.

2.3 Characterization of PEI-TGIC covalent organic framework

Functional group determination of TGIC and PEI-TGIC COFswere carried out by Fourier Transform Infrared (FT-IR, Nicolet iS10, Thermo) spectroscopy with using attenuated total reflectance (ATR) module. The range of wavelength is in between 4000 and 650 cm^{-1}.

The thermal behavior of PEI-TGIC and p-PEI-TGIC COFswere determined and comparedeach other with thermogravimetric analysis through using Thermogravimetric Analyzer (TGA, /DTA 6300, Exstar).Initially, moisture is removed from the sample through heating from 25 ºC to 100ºC. Then the temperature alteration is set to raise 10ºC per minute from 90ºC to 1000ºC.

Zeta Potential Analyzer (BIC, Brookhaven Inst. Corp.) is used for the determination of the particle charges. The aqueous solutions of PEI-TGIC and the p-PEI-TGIC COFwere diluted with 10^{-3}M KCl solution to prepare for analysis of zeta potential.

Particle size and shape are observed through using Scanning Electron Microscope (SEM, JEOL JSM-5600). The synthesized, washed and freeze-dried PEI-TGIC COFs were placed into carbon tape attachedaluminum stub and coated with gold to a few nanometer thicknesses under vacuum. The images were taken with an operating voltage of 20 kV.

Specific surface area, pore volume, and pore size determination of PEI-TGIC COF were carried out with Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods by using Micrometritics, Tristrar II, Surface area and porosity device. Before analysis, the PEI-TGIC COF was dried in freeze-dryer (Christ Alpha 1–2 LD plus), and prior to measurementspassed through N_2 gas for 8 h to remove moisture and other contaminants at 80 °C using a Flow Prep 060 Degasser.

2.4 Absorption studies

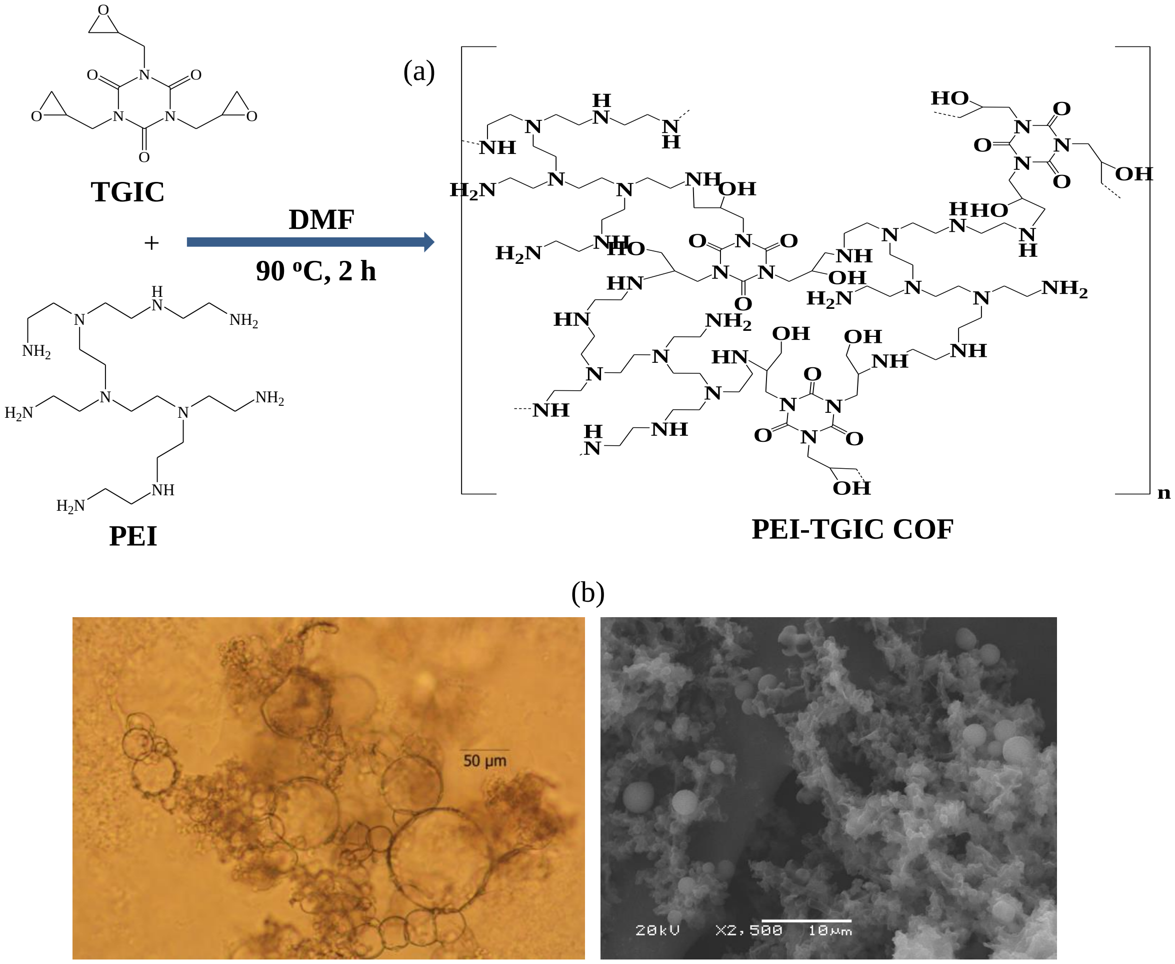
The absorption study of MO from aqueous solution was done by following literature with some modification [17]. For this purpose, 0.05 g of each PEI-TGIC and p-PEI-TGIC COFs were used as absorbents. Besides, the 100 mL of 250 ppm MO aqueous solution were prepared and 0.05 g of each PEI-TGIC and p-PEI-TGIC COFs were added into solutions after taking zero time samples from solutions. Then, the samples from solution were taken in certain time intervals and were read by using UV–vis spectrophotometer (UV–Vis, T80+, PG Instruments) after 25 times dilution at 464 nm wavelength. The absorbed amount of MO dyes from prepared PEI-TGIC, and p-PEI-TGIC COFs were determined from the decreasing on absorbance values of diluted samples at 464 nm wavelength for MO.

3. RESULTS AND DISCUSSION

3.1 Synthesis and characterization of PEI-TGIC COFs

In recent years, the reactions of epoxy and amine groups are widely used for modification and synthesis of new polymeric structures [38]. In brief, the reaction involves the nucleophilic addition reaction of amine to epoxy groups [39]. The hydrogen atoms of primary and secondary amine groups provide to opening of oxirane ring of the epoxy components with nucleophilic addition reaction [40-42]. In here, the branched PEI molecules was used with the 1:2:1 ratio of primary, secondary, and tertiary amine groups content to reacted with tri epoxy groups contain TGIC molecule to synthesis of PEI-TGIC COFs. The molecular structure of PEI and TGIC, and schematic presentation of reaction between PEI and TGIC are given in **Figure-1 (a)**. It was seen from **Figure-1 (a)**, the amine primary and secondary amine groups on branched PEI molecule bonded with epoxy groups of TGIC with the nucleophilic addition reaction. On the other hand, the obtained optic microscope and SEM images are given in **Figure- 1 (b)**.

Figure-1. (a) the schematic presentation of synthesis of PEI-TGIC COF, and (b) the optic microscope and SEM images of PEI-TGIC COFs.

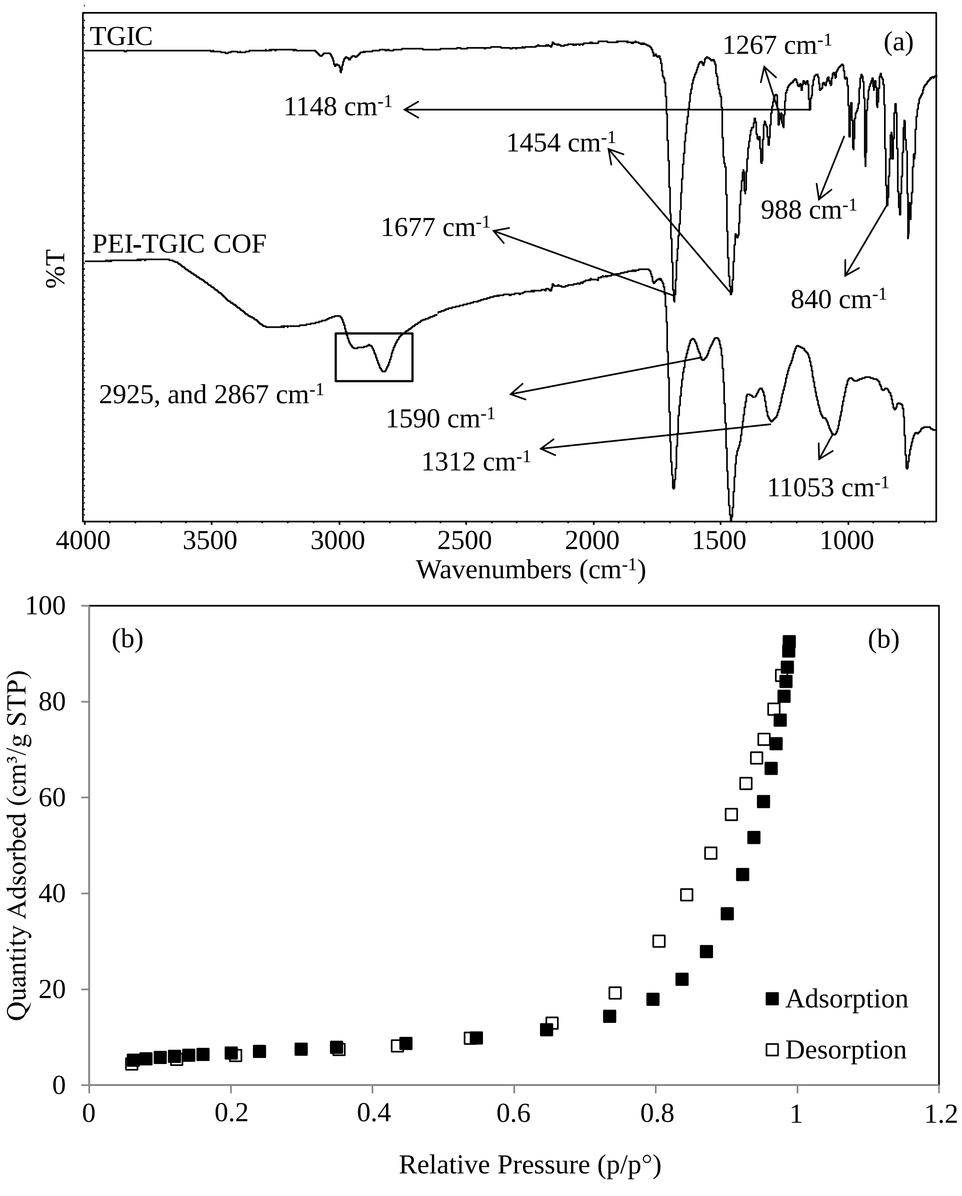


It was clearly seen from optic microscope and SEM images of PEI-TGIC COFs, the COFs are spherical shape with poly dispersed size ranges. The optic microscope images of PEI-TGIC COFs were taken from the aqueous solution of COFs, and it was seen that, the sizes of

COFs between 20-100 µm in aqueous media, whereas the SEM images which are taken from dried from of PEI-TGIC COFs shown that the sizes of PEI-TGIC COFs are between 0.5-5 µm. It can be said that, from optic microscope and SEM images the prepared PEI-TGIC COFs can be swollen easily in aqueous media with almost 20 fold increasing on size of dried from. On the other hand, the yield % of reaction was gravimetrically calculated as 78±4.1 % from the mass of reactant and product.

To confirm of synthesis of PEI-TGIC COF, the FT-IR spectrum of TGIC and PEI-TGIC were recorded and compared for the observing disappeared and appeared peaks after PEI-TGIC COF synthesis. It was clearly seen from **Figure-2 (a)**, the FT-IR spectrum of TGIC shown some characteristic peaks such as C=O stretching at 1677 cm^{-1}, CH_2 stretching at 1454 cm^{-1}, 1267 cm^{-1} asymmetric epoxy ring stretching, 1148 cm^{-1} C-N-C peak from aromatic ring, 988, and 840 cm^{-1} asymmetric epoxy ring bending, respectively. On the other hand, it was clearly seen that, the peaks from epoxy ring is disappeared and turned to –OH peaks at 1310, and 1053 cm^{-1}, and the peaks from amine groups at 1590 cm^{-1} was also observed after synthesis PEI-TGIC COFs.

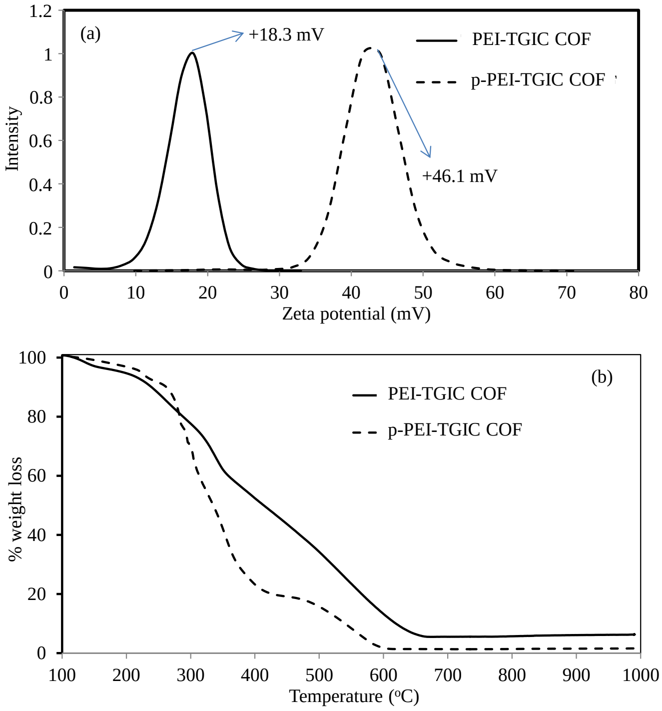
Figure- 2. (a) The FT-IR spectrum of TGIC and PEI-TGIC COF, and (b), N_2 adsorption/desorption graph of PEI-TGIC COF.



Besides, the surface area, pore size and pore volume values of PEI-TGIC COFs were determined by using N_2 absorption/desorption measurements and corresponding graph is given in **Figure 2 (b)**. The shape of obtained hysteresis loop were H3, and it H3 type hysteresis loopindicated that the narrow slit-shaped pores were obtained in prepared PEI-TGIC COFs [43, 44]. Moreover, the surface area was determined as 23.4 m^2/g from N_2 absorption/desorption measurements of PEI-TGIC COFs with using BET method. Also, the pore volume and pore size values of PEI-TGIC COFs were determined as 0.142 cm3/g, and 22.5 nm, respectively, from N_2 absorption/desorption measurements of PEI-TGIC COFs with using BJH method. The porous structure of prepared provides a considerable number of reactive sites on PEI-TGIC COFs.

Besides, the prepared PEI-TGIC COFs were treated with 100 mL of 1M HCl at room temperature about 2 h to protonate amine groups. The change on surface charges were determined by using zeta potential measurements and corresponding graph is given in Figure 3 (a). It was observed that, the surface charge of PEI-TGIC COF is determined as +18.3±1.7 mV, whereas increased to +46.1±2.6 mV after HCl treated to prepare p-PEI-TGIC COF. The increasing on surface charges approximately 2.5 fold confirm that the amine groups of PEI-TGIC COF was successfully protonated.

Figure- 3. The changing on (a) surface charges, and (b) thermal stability of PEI-TGIC after protonation.

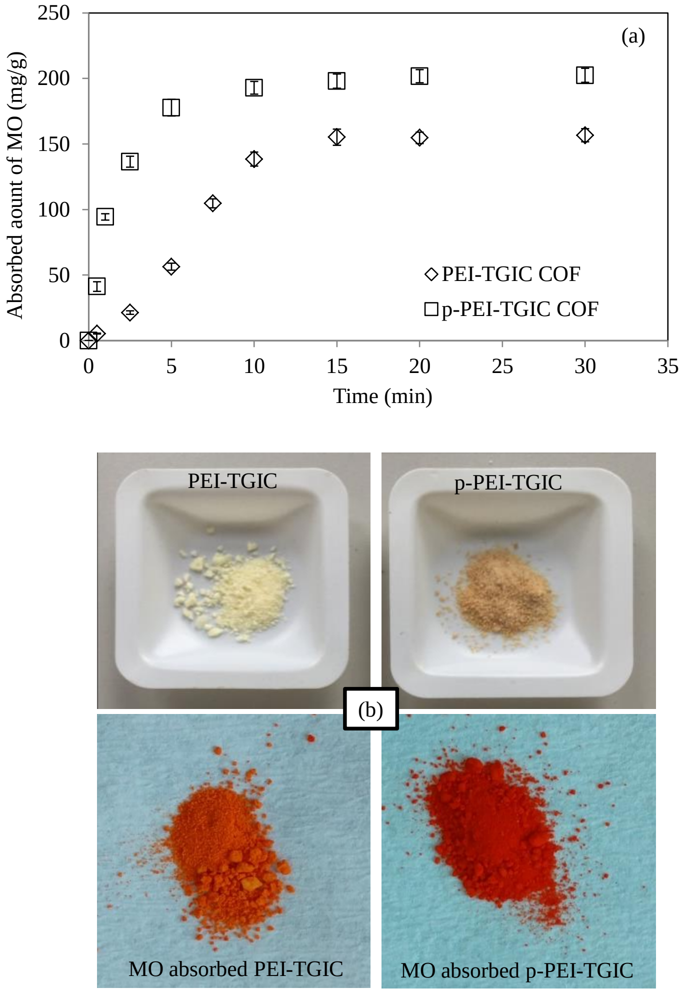


Furthermore, the thermal stability of PEI-TGIC, and p-PEI-TGIC COFs were compared each other from their corresponding TGA thermograms in **Figure 3 (b)**. The bare PEI-TGIC COFs shown three degradation steps as started for first degradation step is between 100-154 ^{o}C with 3.2% weight loss, the second degradation step is between 213-326 ^{o}C with 30.7% weight loss, and the last degradation step between 350-611 ^{o}C with 93.6% weight loss, and finally the 93.7% weight loss was observed at 1000 ^{o}C. Differently from bare form of PEI-TGIC, the p-PEI-TGIC COFs shown lower thermal stability in three degradation steps as observing of the first degradation step is between 100-228 ^{o}C with 2% weight loss, the second degradation step I between 258-405 ^{o}C with 80.6% weight loss, and the third degradation step is between 473-602 ^{o}C with 98.4% weight loss, whereas it was observed 98.6% weight loss at 1000 ^{o}C, respectively.

3.2 The potential usage of PEI-TGIC COFs as an absorbent

In literature, there is so many publication has been reported about removing of toxic organic dyes such as oxidation, reduction, and absorption/desorption or organic dyes [45-47]. The oxidation or reduction of organic dyes has some disadvantages such as using some catalysts as metal nanoparticles, or extinguishment of reusability potentiality of dyes. On the other hand, the absorption or desorption of organic dyes from waste waters provide reusability potentiality of organic dyes with desorption processes. Therefore, the potential usage of prepared PEI-TGIC and p-PEI-TGIC COFs were investigated for MO dyes from aqueous media. The absorption of MO studies was carried out from 100 mL 250 ppm MO solution with the addition of 0.05 g of PEI-TGIC and p-PEI-TGIC COFs. The absorbed amount of MO was calculated by reading of the taken samples from MO solution in certain time intervals with UV-Vis spectrometer at 464 nm wavelength for MO dyes. The samples were 25 times diluted before reading on UV-Vis spectrometer. The corresponding graph is given in Figure 4 (a). It was observed from **Figure-4 (a)** that, the PEI-TGIC COFs were absorbed 56.4±26 mg/g MO in 5 min, and 156.6±4.9 mg/g MO dyes from aqueous media in 30 min (in equilibrium). On the other hand, the absorbed amount of MO by p-PEI-TGIC was determined as 177.6±6.3 mg/g in 5 min, and 202.4±4.3 mg/g in 30 min. It was observed that, the rate of absorption and amount of absorbed MO higher for p-PEI-TGIC COFs than bare PEI-TGIC COFs, due to higher positive surface charges of p-PEI-TGIC interactions with negatively charged MO dyes.

Figure- 4. (a) The adsorption graph of PEI-TGIC, and p-PEI-TGIC COFs MO dyes [0.05 g COF, 100 ml, 250 ppm MO], and (b) digital camera images of PEI-TGIC, and p-PEI-TGIC COFs and theri MO absorbed forms.



The digital camera images of PEI-TGIC, p-PEI-TGIC and their corresponding MO absorbed forms are also given in **Figure- 4 (b)**. It was clearly seen that, the white color of PEI-TGIC COFs turned to brownish color after HCl treatment, and also the orange color of MO absorbed form of p-PEI-TGIC COFs darker then PEI-TGIC COFs that confirm that higher amount absorption of MO dyes by p-PEI-TGIC COFs.

The absorption kinetic of MO by PEI-TGIC and p-PEI-TGIC COFs were determined by using well-knownpseudo-first-order (Eq. 1), and pseudo-second-order (Eq. 2) models, respectively following corresponding equations [48];

$$\log (q_e - q_t) = \log Q_t - (k_1/2.303)t \qquad (1)$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \qquad (2)$$

where; “qe” is absorbed amount of molecule at equilibrium (mg/g), “qt” isabsorbed amount of molecule at at t time (mg/g), k_1 is rate constant for pseudo-first-order model (min_{-1}), and k_2 is constant for pseudo-second-order model ($g.mg^{-1}.min$). The calculated values of qe, k_1 and k_2 values from the plots of log (q_e-q_t) vs t for pseudo-first-order model, and t/$q_t$vs t fro pseudo-second-order model, are summarized in **Table 1** for MO absorption by PEI-TGIC, and p-PEI-TGIC COFs, respectively. It was observed for MO absorption by PEI-TGIC COFs that, 210.6 mg/g and 333.3 mg/g q_e values for pseudo-first-order, and pseudo-second-order kinetic models, whereas experimental q_e value is 156.6±4.9 mg/g. Moreover, the k_1, and k_2 values were also determined as 0.227 min^{-1}, and $1x10^{-4}$ g.min-1.min, with 0.971, and 0.584 corelation coefficient (R^2) values for pseudo-first-order, and pseudo-second-order kinetic models, respectively.

Table- 1. Pseudo-first-order and pseudo-second-order constants and correlation coefficients for adsorption of MO by PEI-TGIC, and p-PEI-TGIC COFs.

Material	Exp.	Pseudo-first-order-model			Pseudo-second-order-model		
	q_e (mg/g)	k_1 (min^{-1})	q_e (mg/g)	R^2	k_2 ($g\ mg^{-1}\ min$)	q_e (mg/g)	R^2
PEI-TGIC COF	156.6±4.9	0.227	210.6	0.971	$1x10^{-4}$	333.3	0.584
p-PEI-TGIC COF	202.4±5.3	0.264	149.7	0.978	$3x10^{-3}$	217.4	0.998

It can be said that from results, the MO absorption by PEI-TGIC COFs fitting with pseudo-first-order kinetic model. On the other hand, the absorption of MO by p-PEI-TGIC COFs q_e values were calculated as 149.7, and 2017.4 mg/g forpseudo-first-order, and pseudo-second-order kinetic models, whereas experimental q_e value is 202.4±5.3 mg/g. The R^2 values with 0.978, and 0.998, k_1 and k_2 values with 0.264 min^{-1}, and $3x10^{-3}$ g.min-1.min were calculated forpseudo-first-order, and pseudo-second-order kinetic models, respectively. It was observed that, the MO absorption by p-PEI-TGIC COFs fitting with pseudo-second-order kinetic model.

The validity of kinetic model can be done from R2 values, and also the Sum of Square Error (SSE %) were also used in literature from the corresponding equation (Eq. 3) [48];

$$SSE\ \% = (\Sigma(q_{e,exp} - q_{e,cal})^2/N)^{1/2} \qquad (3)$$

Where,“N” is the number of data points. “$q_{e,exp}$” and “$q_{e,cal}$” (mg/g) are the experimental and calculated adsorption capacities, respectively. The numerical fitting is good if R^2 is ~1.0 and SSE is ~ 0.0. The SSE values were calculated as 18 and 58.9 for pseudo-first-order, and pseudo-second-order kinetic models for MO absorption by p-PEI-TGIC, and 17.6, and 5 for pseudo-first-order, and pseudo-second-order kinetic models for MO absorption by p-PEI-TGIC COFs. The validity of fitted kinetic models of MO absortion by PEI-TGIC, and p-PEI-TGIC COFs were proven with SSE calculation.

4. CONCLUSION

In this study, it was reported that, the synthesis of novel spherical shape, porous PEI-TGIC COFs with23.4 m^2/g surface area, 0.143 cm^3/g pore volume, and 22.5 nm pore size, and its protonated form p-PEI-TGIC COFs were successfully carried out. The surface charge increased to 46.1±2.6 mV from 18.1±1.7 with the protonation of PEI-TGIC COFs. The prepared PEI-TGIC and p-PEI-TGIC COFs absorbed 156.6±4.9 mg/g, and 202.4±5.3 mg/g MO from its aqueous solution. On the other hand, the absorption kinetic of MO by PEI-TGIC COFs fitted with pseudo-first-order model with 0.971 R^2 values, whereas absorption kinetic of MO by p-PEI-TGIC COFs fitted with pseudo-second-order model with 0.998 R^2 values. Therefore, the cationic-based COFs of PEI-TGIC and p-PEI-TGIC have great potential for the removal of negatively charged dyes, pesticides, herbicides, and heavy toxic metal ions different oxidation states from aquatic environments.

Conflict of Interest Statement

The authors declare no conflict of financial, academic, commercial, political, or personal interests

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