Novel nanocomposite based on poly (xanthoneamide-triazole-ethercalix) and TiO$_2$ nanoparticles: preparation, characterization, and investigation of nanocomposite capability in removal of cationic water pollutants

Vahid Hasantabar$^a$, Moslem Mansour Lakouraja, Hamed Tashakkorian$^b$ and Mona Rouhi$^a$

$^a$Faculty of Chemistry, Polymer Chemistry Laboratory, Department of Organic Chemistry, University of Mazandaran, Babolsar, Iran; $^b$Paramedical Department, Cellular and Molecular Biology Research Center (CMBRC), Health Research Institute, Babol University of Medical Sciences, Babol, Iran

ABSTRACT
A new multifunctional nanocomposite based on poly (xanthoneamide-triazole-ethercalix) (PXTE) and TiO$_2$ nanoparticles (PXTE–TiO$_2$), which is a novel class of multiphase material containing nanosized inorganic material within polymer matrix, was prepared and characterized fully in this article. At first, PXTE was synthesized through click reaction, and then PXTE–TiO$_2$ nanocomposite was prepared by chemical immobilization of PXTE onto the modified TiO$_2$ nanoparticles. Nuclear magnetic resonance, Fourier transform infrared, X-ray diffraction, scanning electron microscopy, differential scanning calorimetry, and thermal gravimetric analysis were applied for characterization of synthesized materials. Dye and ion removal capability of PXTE–TiO$_2$ nanocomposite were investigated by batch method for methylene blue and cadmium ion. The results showed that thermal stability and potential applicability of PXTE–TiO$_2$ nanocomposite make it as a good candidate for wastewater refinement.

1. Introduction
Although organic synthetic dyes are widely used as colorants in leather, textiles, foodstuff, liquid crystalline displays, ink-jet printer, and electro-optical devices; and as a result, makes our world more spectacular, but they bring serious environmental problems too. In addition to the starting material used in preparation and processing of pigments; handling and also production of many organic compounds which are used as pigments are hazardous and risky for human life beside the mutagenicity and carcinogenicity of dyes itself.[1–4]

Generally, hazardous chemicals such as dyes and pigments are troubous from environmental point of view and must be removed from waste effluents; in this regard dyes removal or the decolorization of wastewater is an essential necessity for environmental safety.[5,6]

In the recent literature, some technologies are more pronounced for the decontamination of dye containing effluents. For instance, chemical methods like as oxidative processes, Fenton oxidation, H$_2$O$_2$, ozonation, and electrochemical process, also biological procedures similar to; decolorization by white-rot fungi and/or other microbial cultures, and physical methodologies such as membrane filtration, coagulation/flocculation, and adsorption have gained much attention.[7–11]

However, these techniques have some drawbacks which limit the applicability of these methods.[12,13] Among these techniques, adsorption method has attracted more approval for the removal of dyes due to its simplicity and high efficiency.[14] Different classes of organic and inorganic adsorbents were employed so far,[15–18] but the adsorption capacities were not satisfactory.[19,20] To achieve the high adsorption capability, new high performance adsorbents are still under investigation.

Furthermore, along challenges for dyes toxicity, heavy metals are another problem that threatens life safety. Nowadays, specific consideration is given to the production control and effluents discharge of toxic heavy metal-ion contents, like lead, cadmium, copper, silver, mercury, chromium, or arsenic to natural waters, which may cause high risk to human health and horrible diseases.[21–23]

Calix[4]arenes have been used extremely as building blocks for the preparation of various adsorbents for pollutant removal.[24] Calix[4]arene derivatives are classified in group of metacyclophanes and are cyclic tetramers composed of four phenolic and four methylene moieties.[25] They have been interested both as complexation hosts for cations and adsorptive structures for removal of many risky species such as dyes. This category of compounds was found to be exceptionally selective for various metal
cations in specific applications such as nuclear-waste remediation.\[26–28\] To take advantage of calix[4]arenes, researchers applied them in the formulations of absorbent polymers. However, in spite of all of the advantages such as increasing thermal stability, solubility, and selectivity of the mentioned polymers, there are some apprehensions about their solubility and disjunction of some chemical structures in the absorption medium; which is not ignorable on the basis of pollution parameters. So, immobilization of calix[n]arene frameworks onto a specific bed not only reduces their solubility but also can increase the adsorption efficiency in remediation of undesired industrial compounds and will improve the applicability.\[29\]

In this study, new functionalized nanocomposite based on modified TiO\textsubscript{2} nanoparticles and poly (xanthone-amide-triazole-ethercalix) (PXTE) bearing active triazole and calixarene moieties having specific cavity was prepared for selective complexation with heavy metal ions and to entrap dye molecules. In the preparation of PXTE, click reaction has been used to link calix segment to the bioactive xanthone scaffold \[30\] through triazole ring formation. Then, to meet the mentioned advantages, PXTE–TiO\textsubscript{2} nanocomposite was prepared from PXTE and modified TiO\textsubscript{2} nanoparticles. After preparation and characterization of the nanocomposite (PXTE–TiO\textsubscript{2}), its application in complexation and/or trapping of cadmium ion (Cd\textsuperscript{2+}) and removal of methylene blue (MB) was investigated.

2. Experimental

2.1. Materials and instruments

Sodium azide, methanol, sodium hydroxide, toluene, triethyl amine, chloroacetyl chloride, NaHCO\textsubscript{3}, DMF, CuCl, concentrated ammonia, THF, TiO\textsubscript{2} nanoparticles, (3-Glycidyloxypropyl) trimethoxysilane (GPTMS), and DMSO were purchased from Merck, Fluka and Aldrich companies. Toluene dried with sodium metal and other solvents and compounds were used as received. Calix dipropargyl (Calix-DPr) \[28\] and 2,7-diaminoxanthone (DAX) prepared based on literature.\[30\] Melting points were determined with an Electrothermal 9100 melting point apparatus. IR and \textsuperscript{1}H NMR spectra were recorded on Bruker Fourier transform infrared (FT-IR) spectrometer and Bruker Avance III 400 MHz NMR spectrometer using tetramethylsilane (TMS) as an internal standard, respectively. XRD spectra were investigated using XRD, GBC, Cu Ka radiation (\(\lambda = 1.54\) Å), spectrophotometer. For UV–vis measurements, Cecil (Cambridge–England) UV–vis spectrophotometer was applied. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were recorded on a Perkin-Elmer Pyris Diamond and Pyris 6 TGA Consumables, respectively. Thermo Fisher Scientific ICE 3300 atomic absorption spectrometer was employed for determination of the metal ion.

2.2. Synthesis

2.2.1. Preparation of 2,7-(N-2-chloroacetamide) xanthone (NCIX)

In a 50-mL round-bottomed two-necked flask, 1.13 g (5 mmole) of DAX was added to the mixture of 25 mL dry toluene and triethyl amine (1.73 mL, 12.5 mmole) at 100 °C. Then, chloroacetyl chloride (1 mL, 12.5 mmole) was surcharged to present mixture. The reaction kept in these conditions while being stirred under N\textsubscript{2} for overnight. The mixture was then collected by filtration and immediately washed with 5% NaHCO\textsubscript{3} aqueous solution which gave 1.42 g (yield = 75%) of pure NCIX after drying in oven 60 °C for 4 h (mp = 263–265 °C).

\textbf{FT-IR (Kbr, cm\textsuperscript{-1}):} 824, 1300, 1480, 1548, 1622, 1689, 2949, 3087, 3288 cm\textsuperscript{-1}.

\textbf{\textsuperscript{1}H NMR (400 MHz, DMSO-d\textsubscript{6}):} 4.31, 7.69, 8.01, 8.50, 10.66 ppm.

\textbf{\textsuperscript{13}C NMR (100 MHz, DMSO-d\textsubscript{6}):} 43.96, 115.36, 118.97, 119.42, 121.23, 127.75, 135.34, 152.31, 165.39 ppm.

2.2.2. Preparation of 2,7-(N-2-azidoacetamide) xanthone (NAzX)

To the solution of NCIX (5 mmol, 1.90 g) in 25-mL DMF in a round bottom flask, sodium azide (2.2 equiv., 0.72 g) was added and the mixture stirred at 60 °C overnight. After that water was added to the flask while mixture was cold to room temperature. Then, white yellowish solid was collected by filtration and dried at room temperature for 24 h (1.67 g, yield = 85%) (decomposed above 235 °C).

\textbf{FT-IR (Kbr, cm\textsuperscript{-1}):} 545, 632, 826, 1307, 1479, 1548, 1621, 1691, 2110, 2923, 3082, 3318 cm\textsuperscript{-1}.

\textbf{\textsuperscript{1}H NMR (400 MHz, DMSO-d\textsubscript{6}):} 4.11, 7.67, 8.01, 8.49, 10.48 ppm.

\textbf{\textsuperscript{13}C NMR (100 MHz, DMSO-d\textsubscript{6}):} 42.22, 114.56, 118.97, 119.42, 121.23, 127.75, 135.34, 152.31, 163.39 ppm.

2.2.3. Synthesis of PXTE

In a 25-mL flask, to a solution of calix-DPr (5 mmol) and NAzX (5 mmol) in DMF (20 mL), was added a suspension of CuCl (98.5 mg, 20 mol%) in H\textsubscript{2}O (2 mL) in drop wise manner. Then, NE\textsubscript{t}3 was added gradually until color of mixture changes from brown to light green. The reaction mixture was stirred at 60 °C for 12 h. After that, the mixture was diluted by water (20 mL) and then concentrated ammonia (5 mL) was added and stirred for another 1 h. The mixture was filtered and the resulting solid material was washed with H\textsubscript{2}O, methanol, and THF. Finally, the obtained polymer was further purified using continuous extraction by soxhlet in MeOH.
FT-IR (KBr, cm\(^{-1}\)): 550, 633, 824, 985, 1125, 1205, 1305, 1480, 1551, 1625, 2870, 2959, 3416 cm\(^{-1}\).

\(^1\)H NMR (400 MHz, DMSO-d\(_6\)): 1.15, 4.30, 5, 5.50, 7.08–7.50, 7.65–8.41, 8.47, 9.07, 10.66 ppm.

2.2.4. **Modification of nano TiO\(_2\)**
Modification has been carried out in dry toluene (20 mL) at reflux temperature. Nanoparticles of TiO\(_2\) (1 g) were first suspended in the organic medium and after addition of GPTMS (1 mL), the mixture was stirred overnight at reflux temperature. The GPTMS grafted TiO\(_2\) nanoparticles were collected by centrifugation, washed three times with toluene to remove excess silane coupling agent and finally dried under vacuum overnight at 50 °C.

FT-IR (KBr, cm\(^{-1}\)): 417–767, 1108, 1631, 2868, 2932, 3421 cm\(^{-1}\).

2.2.5. **Preparation of PXTE–TiO\(_2\) nanocomposite**
For preparation of nanocomposite, synthesized PXTE (0.2 g) was charged in 10 mL DMSO in round bottom flask (25 mL) and then NaOH (0.1 g) was added. Reaction mixture stirred at room temperature for 30 min and then 1 g of modified nano TiO\(_2\) was added to the flask and the mixture sonicated for 30 min at room temperature. After that, flask transferred to oil bath (80 °C) and mixture stirred at same temperature overnight. Then, suspension mixture was centrifuged and washed three times with DMSO to remove non-supported polymers. Finally, the precipitate was washed sequentially with distilled water and acetone for removal of NaOH and residual DMSO from composite. The milky solid material was dried at 50 °C in vacuum oven for overnight and then weighed (1.1 g).

FT-IR (KBr, cm\(^{-1}\)): 468–733, 956, 1029, 1125, 1203, 1303, 1440, 1476, 1627, 1691, 2863, 2904, 2950, 3251, 3420 cm\(^{-1}\).

### 2.2.6. Dye and ion removal

2.2.6.1. **Adsorption procedure for the MB and Cd\(^{2+}\) batch method.** The adsorption capacity of the nanocomposite for MB and Cd\(^{2+}\) as typical pollutants in aqueous media was determined by batch wise methods. According to literature, since photocatalytic property of TiO\(_2\) nanoparticles under ultraviolet is effective in dye removal and ineffective in ion removal,\(^{[31]}\) for better understanding the adsorption efficiencies of the introduced nanocomposite in removal of MB and Cd\(^{2+}\), the same conditions were applied in adsorption experiments. So, the parameters such as amount of dosage, pH, contact time, and concentration of dye and ion were optimized (Tables 1 and 2). The experiments were conducted in 25-mL Erlenmeyer flasks with glass caps which contain particular amounts of the adsorbents as well as particular concentration of adsorbed solution.

To obtain adsorption equilibrium, solutions were stirred on a stirrer operating at a constant speed (200 rpm) at 25 °C for a fixed time. The adsorbent was filtered and the adsorbed dye and ion was analyzed from filtrate liquid by the UV–vis spectrophotometer (\(\lambda = 665 \) nm) and atomic absorption spectrometer, respectively. The obtained data in batch studies were used to calculate the percentage of dye and ion removal using the following mass balance:

\[
R(\%) = \frac{C_i - C_f}{C_i} \times 100
\]

Where \(C_i\) (mg/L) is the initial concentration of solution before sorption and \(C_f\) (mg/L) is the final concentration after the sorption of dye and ion.

The amount of dye and metal adsorbed \(Q_e\) (mg/g) was determined using the following mass balance relationship:

\[
Q_e = \frac{C_i - C_e}{m} \times V
\]

### Table 1. Optimization of adsorption parameters for MB sorption.

| Dosage (mg)\(^a\) | \(R\) (%) | pH\(^b\) | \(R\) (%) | \(C_i\) (ppm)\(^c\) | \(R\) (%) | Time\(^d\) | \(R\) (%) |
|-------------------|----------|---------|----------|-----------------|----------|----------|----------|
| MB sorption       |          |         |          |                 |          |          |          |
| 6                 | 83.86    | 4       | 55.42    | 20              | 87.95    | 30 min   | 46.36    |
| 10                | 87.95    | 7       | 87.95    | 40              | 59.45    | 1 h      | 58.37    |
| 20                | 91.36    | 11      | 90.75    | 60              | 43.45    | 2 h      | 74.38    |
| 30                | 92.95    | –       | –        | 80              | 36.25    | 3 h      | 87.95    |
| –                 | –        | –       | –        | 100             | 29.68    | 4 h      | 87.95    |

**Isotherm and kinetic models**

- Langmuir: \(Q_m = 153.84\) \(K_l = 0.26\) \(R^2 = 0.99\)
- Freundlich: \(n = 6.37\) \(K_f = 76.54\) \(R^2 = 0.99\)
- Pseudo-first-order: \(Q_0 = 61.40\) \(K_1 = 1.2 \times 10^{-2}\) \(R^2 = 0.99\)
- Pseudo-second-order: \(Q_{e,cal} = 94.33, Q_{e,exp} = 87.95\) \(K_2 = 3.17 \times 10^{-4}\) \(R^2 = 0.99\)

Note: The bold numbers are optimum values.

\(^a\)pH 7, \(C_i = 20 \) ppm.

\(^b\)Dosage = 10 mg, \(C_i = 20 \) ppm.

Notes:

- pH 7, \(C_i = 20 \) ppm.
- Dosage = 10 mg, pH 7.
- Dosage = 10 mg, pH 7, \(C_i = 20 \) ppm.
reaction of azide with chloride in good yield. For preparation of polymer, the click reaction of Calix-DPr with NAzX has been performed in the presence of CuCl and triethyl amine as mentioned in our recent work [33] (scheme 1). The presence of the amide and triazole linkages in main chain of the polymer proposed to improve the thermal properties of the polymer and cause enhancement in metal complex formation. In continue, it has been designed to prepare nanocomposite of the synthetic polymer with modified TiO₂ nanoparticles. In this regard, 20 wt.% of polymer was treated with modified TiO₂ nanoparticles in DMsO under sonication and then stirring overnight at 80 °C (scheme 2).

Structural features of the monomers, polymer, and nanocomposite were verified by FT-IR and NMR spectroscopies. The IR absorption peak about 2100 cm⁻¹ in Calix-DPr and NAzX spectra confirmed the presence of acetylenic and azide groups, respectively, and disappearance of these vibrational peaks in the polymer (PXTE) spectrum verified that polymer has been prepared successfully (Figure 1). As seen in 1H NMR spectrum of PXTE, amide proton of xanthone segment was observed at 10.66 ppm and hydroxyl groups of calix unit detected at about 9.07 ppm. In addition, proton of triazole ring at 8.47 ppm, CH₂ bridges of calix at 4.30 ppm, and CH₂ of etheric linkage and xanthonic scaffold about 5 ppm were confirmed the FT-IR spectral data of synthesized polymer (Figure 2). From FT-IR spectrum of nanocomposite, it is obviously suggested that immobilization of PXTE onto modified TiO₂ nanoparticles was accomplished. Peak pattern at 400–800 cm⁻¹ was similar to that of modified nano TiO₂ and is related to Ti–O–Ti, and decrease in intensity of peaks at about 1100–1200 cm⁻¹ is due to loss of epoxide-etheric bonds during opening of epoxide rings. Furthermore, the other peaks at nanocomposite spectrum are related to PXTE characteristic vibrations that confirm conjunction of PXTE to nano TiO₂ bed (Figure 3).

Table 2. Optimization of adsorption parameters for Cd²⁺ sorption.

| Dosage (mg)  | R (%) | pH  | R (%) | Cᵢ (ppm)  | R (%) | Time  | R (%) |
|--------------|-------|-----|-------|-----------|-------|-------|-------|
| 5            | 49.67 | 4   | 18.92 | 20        | 51.07 | 30 min| 21.90 |
| 10           | 51.07 | 7   | 51.07 | 40        | 50.09 | 1 h   | 38.30 |
| 20           | 52.89 | 11  | 57.42 | 60        | 42.55 | 2 h   | 49.45 |
| –            | –     | –   | –     | –         | –     | 80    | 36.56 |
| –            | –     | –   | –     | –         | –     | 100   | 29.70 |

Isotherm and kinetic models

|                      | Qₑ  | Kᵢ  | R²      |
|----------------------|-----|------|---------|
| Langmuir             | 208.33 | 0.04 | 0.97    |
| Freundlich           | 16.98 | 0.54 | 0.91    |
| Pseudo-first-order   | 81.90 | 3.2 × 10⁻² | 0.99 |
| Pseudo-second-order  | 51.81, Qₑ, 51.07 | 1.23 × 10⁻³ | 0.99 |

Note: The bold numbers are optimum values.

*pH 7, Cᵢ = 20 ppm.

*aDosage = 10 mg, Cᵢ = 20 ppm.

*bDosage = 10 mg, pH 7.

*bDosage = 10 mg, pH 7, Cᵢ = 20 ppm.

3. Result and discussion

Heterocyclic five-membered rings such as [1,2,3]-triazole are chemically stable in harsh oxidative and hydrolysis conditions. Generally, [1,2,3]-triazoles have been prepared by [2 + 3] dipolar cycloadition reaction of corresponding organic azide and terminal alkyne, also called as ‘Click reaction’ which has attracted much attention in the field of materials especially supramolecular chemistry and sensors.[32] To achieve a convenient and efficient synthesis of PXTE, the following synthetic strategy was applied. The click reaction components, Calix-DPr and DAX, were prepared according to our previously reported strategy. [28–30] NCIX was obtained by reaction of DAX with chloroacetyl chloride in dry toluene in the presence of triethyl amine and then NCIX transformed to NAzX by replacement where V is the volume of the solution (L); Cᵢ is the equilibrium concentration (mg/L); and m is the mass (g) of the adsorbent.

![Figure 1. FT-IR KBr pellets of PXTE, Calix-DPr, and NAzX.](image-url)
5. Scanning electron microscope

Scanning electron microscopy (SEM) was applied for determination of the morphology and size of the synthesized materials. Figure 5 displayed SEM images of PXTE, modified TiO₂, and PXTE–TiO₂ nanocomposite. As seen in SEM image of modified TiO₂, it can be observed that the TiO₂ particles appear in uniform sphere-like shape with nanosize. SEM graph of PXTE shows that this polymer has not relatively uniform distribution with sporadic particles diameter from 50 to up than 300 nm. This SEM image also indicates that PXTE particles are in agglomerates form with smooth surface. It is obvious that the SEM of PXTE–TiO₂ nanocomposite represents different morphology compared with the bare PXTE particles and has morphology similar to modified TiO₂ with small aggregated globules having an average particle size about 100 nm.

6. Thermogravimetric analysis

TGA thermograms of PXTE, modified TiO₂, and PXTE–TiO₂ nanocomposite were carried out under nitrogen atmosphere to consider degradation of polymer and estimation of sedimentation on TiO₂ in modified TiO₂ and PXTE–TiO₂ nanocomposite (Figure 6). In the TGA curve of PXTE, degradation occurred in two steps, first at about 350 °C that related to scission of aliphatic bonds and second at about 500 °C that is due to aromatic rings destruction and with increase of temperature to 600 °C weight remained fix to 40% initial weight. TGA of modified TiO₂ shows one weight loss at about 360 °C.
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It is concluded that immobilization of polymer on TiO$_2$ bed is about 11%.

7. Differential scanning calorimetry

DSC of materials was done under N$_2$ atmosphere from 25 to 350 °C. In DSC curve of modified TiO$_2$, three endothermic peaks are present near to 90, 250 and 290 °C. The first one is related to solvent evaporation and the next peaks assigned to destruction of aliphatic bonds and epoxide rings, respectively. DSC of PXTE showed one endothermic and two exothermic peaks. The endothermic peak is related to solvent and humidity evaporation. The exothermic peak at 150 °C is probably $T_g$ and the other one at 225 °C related to $T_f$. For PXTE–TiO$_2$ nanocomposite only one endothermic peak is appeared that is related to solvent exhaust. It can be concluded that rigidity of synthetic polymer (PXTE) after immobilization on nano TiO$_2$ increased (Figure 7).

8. Adsorption study of the MB and Cd$^{2+}$

As demonstrated in experimental section, for optimization of adsorption parameters, some tests were done and the results are summarized in Tables 1 and 2.

8.1. Effect of adsorbent dosage

Four doses in MB removal and three doses for cation removal were tested in which 10 mg adsorbent was selected as the best option for both. No significant changes

Figure 4. The XRD pattern of modified TiO$_2$, PXTE, and PXTE–TiO$_2$ nanocomposite.

Figure 5. SEM of modified TiO$_2$ (a), PXTE (b) and PXTE–TiO$_2$ nanocomposite (c).
8.2. pH effect on the adsorption

pHs 4, 7, and 11 were investigated in adsorption tests. According to the pH evaluation, acidic pH has low adsorption efficiency because of protonation of hydroxyl, NH and nitrogen’s of triazole rings, and presence of electrostatic repulsion. In contrast, in basic condition, increment of adsorption is due to active adsorbing sites and electrostatic attraction that can increase the adsorption efficiency. Also, hydroxides of metal ions that are commonly insoluble may coprecipitate. Practically, to prevent metal hydroxide formation, pH 7 was selected as neutral and optimized pH, since adsorption was satisfied and no interferences were observed.

8.3. Initial concentration

The samples with 20, 40, 60, 80, and 100 ppm concentrations were tested. According to adsorption efficiency, the 20 ppm was the best choice. Reduction of adsorption efficiency by increase of concentration is probably due to saturation of active sites by adsorbed dye molecules and ion.

Figure 6. TGA and DTG curves of PXTE, modified TiO₂ and PXTE–TiO₂ nanocomposite.

Note: Heating rate = 10 °C/min.

Figure 7. Differential scanning calorimetry of modified TiO₂, PXTE, and PXTE–TiO₂ nanocomposite.

Note: Heating rate = 10 °C/min.
Where \( C_e \) and \( Q_e \) are the equilibrium concentration (mg/L) and equilibrium adsorption capacity (mg/g), respectively. \( Q_m \) is the maximum ion adsorption capacity (mg/g) and \( K_L \) is the Langmuir constant related to the adsorption energy (L/mg). The isotherm constants were calculated from the linear plot between \( C_e/Q_e \) and \( C_e/Q_m \).

\[
\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m}
\]

8.5. Adsorption isotherms

For designation adsorption mechanism, Langmuir and Freundlich isotherms were studied in this work. The Langmuir isotherm theory is often used to describe the equilibrium adsorption isotherms of homogeneous system.[34] The non-linear equation of Langmuir isotherm model is expressed as:

\[
C_e = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m}
\]

The Freundlich model that is the oldest equation describes the adsorption of a reversible heterogeneous surface and is not limited to a monolayer adsorption capacity. This model mentions that the sorption energy decreases exponentially from the center of adsorbent.[34] The Freundlich equation is:
8.6. Adsorption kinetics

Studying of adsorption kinetics is important for stating of adsorption efficiency. The adsorption kinetics of MB and Cd\(^{2+}\) with the nanocomposite were studied by two kinetic models:

Lagergren pseudo-first-order;

\[
\log Q_t = \log Q_e - \frac{K_1}{2.303} t
\]

where \(Q_t\) and \(Q_e\) are the adsorption capacities at time \(t\) (min) and at equilibrium, respectively. \(K_1\) is the kinetic rate constant for the pseudo-first-order model.

pseudo-second-order model:

\[
\frac{t}{Q_t} = \frac{1}{K_2 Q_e} + \frac{1}{Q_e} t
\]

where \(Q_e\) (mg/g) is adsorption capacity of the metal ions on an adsorbent at time \(t\) (min); \(K_1\) (min\(^{-1}\)) and \(K_2\) (g mg\(^{-1}\) min\(^{-1}\)) are the kinetic rate constants for the pseudo-first-order and the pseudo-second-order models, respectively.[35] Kinetic parameters of these models for the nanocomposite in different contact times (30–240 min)
prepared in two steps: (a) click polymerization of NAzX and calix-DPr in the presence of CuCl and triethylamine (b) nanocomposite preparation by conjunction of PXTE onto modified nano TiO2. In characterization of introduced materials, improvement of thermal stability and applicability were observed. Thermal stability of polymer after nanocomposite formation was increased. Also, owing to the presence of TiO2 nanoparticles, introduced nanocomposite gained crystalline nature which is verified by XRD diffraction. The SEM image of PXTE–TiO2 nanocomposite presented crystalline morphology similar to modified TiO2.

9. Conclusions

In the present work, novel PXTE–TiO2 nanocomposite was synthesized and utilized for ion and dye removal from aqueous media. PXTE–TiO2 nanocomposite has prepared in two steps: (a) click polymerization of NAzX and calix-DPr in the presence of CuCl and triethylamine (b) nanocomposite preparation by conjunction of PXTE onto modified nano TiO2. In characterization of introduced materials, improvement of thermal stability and applicability were observed. Thermal stability of polymer after nanocomposite formation was increased. Also, owing to the presence of TiO2 nanoparticles, introduced nanocomposite gained crystalline nature which is verified by XRD diffraction. The SEM image of PXTE–TiO2 nanocomposite presented crystalline morphology similar to modified TiO2.

Scheme 3. Postulated mechanism for ion and dye removal.
with small aggregated globules in average particle size about 100 nm. Capability of this new introduced nanocomposite in MB and Cd$^{2+}$ removal were studied, and results showed that the composite can be a good candidate for wastewater refinement.

**Disclosure statement**

No potential conflict of interest was reported by the authors.

**Funding**

The financial supports by Research Council of University of Mazandaran.

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