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Photocatalytic and adsorptive remediation of hazardous environmental pollutants by hybrid nanocomposites

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ABSTRACT

The combination of metal-organic frameworks (MOFs) with nano-carbon materials is an emerging field among the researchers now a days. The addition of carbon materials (CNTs/GO) increases the Physico-chemical characteristics of parent MOFs. In this mini review the photocatalytic and Fenton-like oxidation behavior of these hybrid nanocomposites has been discussed. Additionally, the efficient remediation of a number of pollutants (VOCs, heavy metals and toxic gases) through adsorptive removal from atmospheric environment has been presented. Finally, the recyclability and stability of MOFs-C along with future perspectives are also presented at the end of this review.

1. Introduction

The escalating environmental pollution has threatened the environmental moieties such as, fresh water bodies, humane health and atmosphere to a greater extent globally [1–4]. Specially, the pervasive existence of heavy metals (Hg(II), Cr(III), As(III), Cu(II) and Pb(II) etc.) natural and synthetic organic pollutants, has gained worldwide growing research concerns and interest [5–9]. The conventional waste-water treatments modalities cannot remove these contaminants effectively, therefore leading to pervasive scums in groundwater, surface water, and even in drinking water. A number of adverse effects on human health and aquatic life has been documented even these contaminants are present at trace levels (ng/L-μg/L) in complex mixtures [10].

In recent times, the development in the area of metal-organic frameworks (MOFs) have attracted a great deal of interest in dealing the matter stated above [11–13]. The MOFs are constructed by the combination of metal clusters or metal ions through coordination with organic linkers to build multi-dimensional (1D, 2D and 3D) architectures [14]. These hybrid architectures have ultrahigh porosity and unique structure. A structural diversity exists among different MOFs as a result of metal ion and organic ligand [8]. The greater specific surface area and ultrahigh porosity of MOFs have added to the wide range of applications in adsorption, luminescence, environmental remediation, energy generation, biomedical imaging, and catalytic degradation etc. [11–13, 15,16].

In view of this, we made an attempt to present a cutting edge mini-review on contemporary advances of MOFs/Carbon materials in environmental indemnification by focusing on MOFs/GO and MOFs/CNTs for eradicating a variety of pollutants from the atmospheric environment. Furthermore, the role of these hybrid materials as the authoritative catalysts for photocatalysis and Fenton-like oxidation, efficient adsorbents for VOCs and toxic heavy metals and gases are discussed. Additionally, the recyclability and reusability of these systems are also summarized, which expedite further developments of these promising materials for pollution remediation in the future.

2. Catalytic transformation of pollutants by MOFs-C

2.1. Photocatalysis

Recently, to remove environmental pollutants environmentally friendly and cost effective technology has been used. Some work has been done on the MOFs-C for photocatalytic degradation of organic pollutants (e.g amoxicillin, atrazine and nitroaromatic compounds) [17] heavy metals [18] and degradation of dyes [19]. The nanocomposite (Ce-Uio-66/RGO) was prepared by one-pot solvothermal method and
under visible light irradiation; it improved the reduction of fifteen kinds of nitrobenzene (NB) [19]. NB photo-reduction with different catalysts was in order as Ce-Uio-66/RGO (0.15h⁻¹) > Ce-Uio-66 (0.03 h⁻¹) > RGO (0.002h⁻¹). It was also shown that all these compounds were effectively converted with conversion rate 70%–88% in 1–5 h. It was also found that even after seven recycle use, they gave very good selectivity (99%) for the reduction of aromatic amines. Mechanism possible for the NB reduction to aniline under visible irradiation and by using hybrid nanocomposites are shown in Fig. 1. As NB has benzene structure, it can be conjugated easily with two-dimensional RGO. The electrons and holes in the conduction band of Ce-Uio-66/RGO become excited. Photoexcitation can also be performed on ligand(H₂BDC) and electrons generated are transfer to Zr−O clusters, as a result reactive Zr³⁺ is formed. NB is reduced by Zr³⁺ to aniline and Zr²⁺ are produced. However, it was thought when NH₂-Uio-66(Zr) was irradiated with visible light, no Zr³⁺ ions were produced because Zr-oxo clusters possess very negative redox potential [20]. It was also proposed that, it’s not possible for ligand NH₂-Uio-66(Zr) to show ligand to metal charge transfer mechanism pathway for Zr³⁺ formation because in this MOF the HOCO-LUCO transitions are only ligand-based [21]. However, under visible light irradiation, EPR signal related to Zr³⁺ in NH₂-Uio-66(Zr) was detected hence confirms photocatalytic activity belongs to Zr³⁺ and produced by LMCT mechanism [22]. So in these processes presence of Zr³⁺ is still questionable, which requires more in-depth and detailed work for clarification.

Additionally, electrons by photo-generation can be transferred to RGO surface, while MOFs Ce³⁺ ions can enhance transfer of electrons from RGO to Uio-66(Zr). Recombination of holes and photo-generated electrons from RGO and Ce³⁺ ions can be efficiently avoided by these processes and leaving holes from the valence band can be quenched by RCH₂OH to have reductive H⁻¹ ions. So it’s possible that reductive H⁻¹, Zr³⁺ and photo-generated electrons could together work on NB, gave photo-reduction which is significantly enhanced.

3. Fenton-like oxidation

Normally, as the heterogeneous catalyst iron based minerals and composites are applied for Fenton-like oxidation. These catalysts, even at neutral pH are used to remove or transform water pollutants. In recent years, much attention is given to use of Fe-based MOFs-C (e.g., MIL-88A(Fe)/GO, MIL-53(Fe)/RGO and MIL-100(Fe)/GO in Fenton like oxidation [23–25]). Excellent catalytic activity is shown by these hybrid catalysts and different kinds of dyes RhB, MO and Congo red) could be completely oxidized by them in 2–240 min. Composite MIL-100(Fe)/GO was recently prepared in one step hydrothermal method [24]. It was observed that at pH 3.0 and in 240 min MO was completely and efficiently degraded in catalytic Fenton like system and with unavoidable leakage of soluble Fe ions. After 240 min of reaction the amount of leached Fe(III) ions reached to 3.72 mg/L and 30% of MO was removed by dissolved iron by homogeneous Fenton oxidation. It was observed that MO and its oxidized products were not completely mineralized (approx 30%–40% of total organic carbon), but MIL-100(Fe)/GO was very stable and reusable even after 3 runs successively. It’s important to note that greater than 95% MO can also be removed by reused composites, even leached Fe(III) was approximately 12 mg/L. From results under acidic conditions the possible catalytic mechanism pathway is shown in Fig. 2: (1) reactants (MO and H₂O₂) rapidly diffuse in active centers through composites open network; (2) organic groups used to adsorb MO from solution by π-π interactions, results in pollutants enrichment close to reactive centers; (3) the catalysts active sites converted adsorbed H₂O₂ to surface bound OH radical to be used for heterogeneous catalysis, which may oxidize MO for fast elimination and transformation. Moreover, in bulk solution, dissolved Fe can do H₂O₂ decomposition and can generate OH radicals for homogeneous oxidation. The MIL-53(Fe)/RGO was used to degrade RhB by irradiation of visible light with H₂O₂. This catalyst system removed RhB in 60 min in pH range 2–6 and H₂O₂ oxidation removed only 10%. RGO loaded on hybrid material was optimized as 5 wt% and it gave a high catalytic rate of 0.078 min⁻¹ and with respect to MIL-53(Fe), it was 3.1 times higher. However, light scattering and blocking is possible due to excesses quantity of RGO and could result in low rate of charge carrier photo-generation, finally RhB photocatalytic efficiency is inhibited. Trapping experiments explains that active species are photo-generated OH radical, holes and electrons, which helps in complete degradation. Fig. 3 explains the application of MIL-53(Fe)/RGO on RhB in catalytic Photo-Fenton oxidation. Under visible light irradiation, the photocatalytic activity of MOFs is very much affected by Fe–O clusters. The photo excited MIL-53(Fe) produce reactive electrons and holes. The energy is transferred by photo-induced electrons to nano-layers of conductive GO, which has the ability to keep separate electron-hole pair effectively hence charge carriers life time is prolonged. The H₂O₂ is converted to OH radicals by electrons generated by photons on GO layers; on the other hand, abundant OH radicals are also produced by H₂O₂ by use of Fe present on composite surface so that RhB can be oxidized. When RhB gone through catalytic Fenton-like process under visible light irradiation by MIL—88A(Fe)/GO same mechanism was
observed [23]. In comparison only 40% of RhB was removed, when reaction was catalyzed by only parent MIL-88A(Fe). When same hybrid materials with 9.0 wt% GO (Optimized) content, used in catalytic Photo-Fenton oxidation, completely removed in 80 min. The MIL-88A(Fe) incorporated with GO increased its surface area affectively from 15.9 m²/g to 408 m²/g and more micro pores were produced between two components. As a result, RhB photocatalytic rate by MIL-88A(Fe)/GO was 8.4 times faster than the bare MOFs. Moreover, over pH range 1.0 – 9.0 the catalytic performance was superior. Also, after 3 to 5 successive runs show reusability excellent. These observations suggest, they are promising for real water treatment application. For improved catalytic removal and transformation of pollutants, role of GO sheets for MOFs/GO mainly depends on three properties: (1) By irradiation of visible light, photo excited electrons on MOFs surface are shifted to GO with excellent conduction, hence interfacial charge transfer is improved and photo-induced electron-hole pair charge recombination is inhibited. For pollutant degradation, electron can react with O₂ (Photo-Fenton and photocatalysis) and with H₂O₂ (Photo-Fenton) and form very reactive O₂⁻ and OH radicals. Moreover, photo-induce holes can directly oxidize pollutants and can also react with OH⁻ to give very reactive O₂²⁻ and OH radicals. The especial 2D network of GO sheets allows reaction to occur on both GO and MOFs, hence more active sites are available. It’s also possible that GO sheets incorporation also increase absorption of light intensity and in visible light region range of hybrid composites. (3) At the GO and MOFs interface, newly formed micro-pores could help reactants mass transfer during oxidation. As GO has aromatic ring structure, it helps in pollutant adsorption and diffusion by π-π interaction. Moreover, during these catalytic reactions MOFs show very important role: (1) to initiate redox reaction, electrons and holes are produced by photoexcitation of organic linkers or active metal-oxo structures by visible light irradiation. Especially, In NH₂-MIL-125(Ti) Ti₃⁺–Ti₄⁺ electron transfer occurs and it could enhance the rate of electron transfer and oxidizing power. (2) The Fe(III) species bound on MOF surface, in H₂O₂ presence, by heterogeneous Fenton-like reaction could react with H₂O₂ to give very reactive OH radicals for oxidation of pollutants.

4. Atmospheric remediation by MOFs-C

4.1. VOCs adsorption by MOFs-C

Most of the studies nowadays are focusing on the MOFs application in...
adsorption of VOCs from atmosphere [26]. The MIL-101(Cr)/GO was synthesized for n-hexane adsorption [27]. From isotherm data it was evident that adsorption behavior could be well described by Langmuir-Freundlich equation \[ q_e = q_{max} K P / (1 + K P^{1/n}) \] Where \( q_e \) is equilibrium n-hexane amount adsorbed in mg/g, \( q_{max} \) is n-hexane maximum adsorption level in mg/g, \( P \) is n-hexane equilibrium pressure in mbar, \( K \) is adsorption equilibrium constant and \( n \) is L-F coefficient. When GO was introduced, surface area was increased (2881.1–3502.2 m\(^2\)/g) and pore volume (1.36–1.75 cm\(^3\)/g). At 298 K, n-hexane maximum adsorption capacity was enormously increased from 500 mg/g (MIL-101(Cr)) to 1042.1 mg/g (MIL-101(Cr)/Go). On the other hand, surface dispersive force was increased due to thick arrays of atoms on GO sheets, could be responsible for efficient adsorption of n-hexane [27]. Organic linkers and GO surface functional groups can also compete for coordination with Cr(III) metal sites, and can cause defects and structural imperfections in MIL-101(Cr) units. So for stronger n-hexane adsorption more unsaturated sites could be present. Additionally, it presented good stability and reversibility, for n-hexane capture, even after five consecutive adsorption and desorption runs at 298 K. Recently, acetone [28] and carbon tetrachloride [26] great health concern typical VOCs, were also well adsorbed by these promising materials. The maximum adsorption capacity of carbon tetrachloride and acetone on MIL-101(Cr)/GO at 298 K and 161.8 mbar reached 20.10 mmol/g and 2368.1 mg/g at 303 K respectively. As compared to MIL-101(Cr), these values showed an individual rise of 44.4% and 15.8%. Similarly, L-F isotherm was well being fitted with these adsorption processes. Mechanistic work suggested that the enhanced adsorption in MIL-101(Cr)/GO was because of increase in specific area, defects and dispersion forces after GO introduction [26,28]. The Cu-BTC/GO was reported to show high adsorption capacity (9.1 mmol/g at 298 K) for toluene [29] and as compared to parent Cu-BTC it has an increase of 47%. Similarly, increase in pore volume and surface area was also considered responsible for improved performance.

4.2. Other toxic gases adsorption by MOFs-C

Recently, it was reported for adsorption and removal of H\(_2\)S, MOFs-C are excellent [16], NH\(_3\) [30,31] and NO\(_2\) [32]. Among these efforts, widely investigated was Cu-based MOFs/GO and for these gases showed high adsorption capacities (e.g., 200 mg/g for NH\(_3\), 140 mg/g for NO\(_2\) and 199 mg/g for H\(_2\)S). Efficiency of these hybrid materials is affected by many influencing factors like loaded GO content, pH, humidity and temperature. It was being observed that for adsorption capacity determination GO ratio had an important role. In a recent work, it was reported that MOF-5/GO capacities were enhanced from 43.3 mg/g (1.75%GO) to maximum 130.1 mg/g (5.25%GO) then decreased to 25.1 mg/g (7% GO) in comparison with 16.7 mg/g (MOF-5) and 2.3 mg/g GO [33]. Characterization explained that strong dispersive forces and pore space was created due to small GO loadings for H\(_2\)S capture, and number of unsaturated sites are also increased, which are used for H\(_2\)S adsorption. However, MOF-5 was distorted and pore structure was destroyed due to more GO amount and adsorption capacity was decreased. When HKUST-1/activated carbon [16] and HKUST-1/GO [34] were used for H\(_2\)S adsorption, similar results were obtained. The breakthrough capacity for HKUST-1 and GO was 92 mg/g and 9 mg/g respectively, in comparison, with 5% GO optimization maximum value reached to 199 mg/g [34]. Also, after three regeneration runs of HKUST-1/activated carbon for CH3SCCH 3 adsorptive removal, demonstrated excellent reversibility [16]. Regenerated composites were very stable, confirmed by FT-IR and XRD, confirmed that for air pollution remediation these materials are very promising candidates. Two main mechanisms of adsorption were adopted from in-depth mechanistic studies, i.e., toxic gases strong coordination in MOF-based materials active metallic centers results in reactive adsorption and micro-pores in these hybrid materials results in physisorption.

5. Stability and recyclability of MOFs-C

For practical application and commercial feasibility, stability and reusability of functionalized materials during pollution removal is very important. In case MOFs-C, great attention is gained by reusability evaluation for “MIL” series of hybrid materials MOFs (e.g MIL-125(Ti), MIL-68(In)–NH2, MIL-68(Al), MIL-101(Cr) and MIL-53(Fe)) and GO. Methanol and ethanol are commonly used reagents for regeneration. These composites demonstrated very high recyclability or reusability again and again and after 3 to 5 consecutive adsorption or desorption of dyes very slight reduction in performance occurred, and other water pollutants; and VOCs [35–37], organic contaminants [38] and Cr(VI) catalytic transformation [39]. Many different characterization techniques were used to further confirm the best stability of reused nano-composites like N2 adsorption isotherm, XRD, XPS, FT-IR and SEM/TEM. For example, no change in molecular and crystal structure of MIL-88A(Fe)/GO and MIL-53(Fe)/GO was detected by FT-IR and XRD after their use for catalytic oxidation of RhB in water [23]. When reused MIL-101(Cr)/GO after ethanol washing was used for elimination of naproxen similar results were obtained [36]. Recently, MWCNTs, MIL-53(Fe) and ZIF-8 formed a hybrid material and it also showed superior stability and reusability when used for adsorption of organic pollutants from water and it was clear from the XRD, XPS, FT-IR and SEM analysis [40]. So, for remediation of polluted environment these highly recyclable and effective MOFs-CS could be applied.

6. Conclusions and future recommendations

Herein, the rigorous efforts are being put forward for the mitigation of hazardous contaminants from wastewater. Conventional techniques used for the remediation of water/wastewater have certain limitations such as high cost, incompatibility, lack of versatility and their own environmental risks for the real-time elimination of organic, inorganic and metal-based pollutants, which hinder their wide range use in various fields of environmental decontamination. These allegations can easily be addressed by the use of MOFs-C based remediation technologies, which can readily encounter the stringent environmental regulations. These remediation technologies have the capacity of sustaining the requirements of integrity and stability of the systems. The currently used water treatment technologies and critical soil analysis advocate that surfactants can prove to be the future of wastewater treatment. Because the micelles architecture can capture hydrophobic organic pollutants in their core and inorganic pollutants in their exterior. A wide number of surfactants have already proved a promising candidate for the decontamination of soil and water from pharmaceuticals, heavy metals, personal care products, and dyes. Advance research on cost-affordability and development of bio-surfactants can make wastewater treatment technology greener and economical.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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