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Utilization of ZIF based nanomaterials for clean environment purposes

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Abstract: *The ZIF and the plethora of nanocomposites of varying types of it are capable to the protection of the natural environment. By utilizing several processes known as adsorption, photocatalysis, oxidation, antibacterial activity, ZIF can be utilized in fuel purification, removal of heavy metal from water, managing nuclear waste, desulfarizations, adsorption of different toxic gases, and dye degradation. For these, ZIFs become important in the case of cleaning environment. By using adsorption, these have the capacity to separate gases from environment that are toxic. By oxidation, ZIF can do oxidative desulfarizations, which make ZIF efficient in cleaning environment by removing sulfur. ZIF can degrade dyes through photocatalysis which is useful in industrial water purification. As ZIFs are hydrophobic, removing halogens and rhodamine B from water is possible by utilizing ZIFs. The use of ZIF-based nanomaterials in clean environment purposes is the principal focus of our research.*

Keywords: Adsorption; environment; photocatalysis; purification; ZIF.

1. INTRODUCTION

One kind of Metal Organic Framework (MOF) is termed to as Zeolitic Imidazolate Framework (ZIF). A MOF might have one, two, or even three dimensions, and yet belong to the same chemical family. In the form of frameworks, they are composed of metal ions or clusters that are coupled to organic ligands. These frameworks are what give them their structure. They belong to a class of coordination polymers that are distinguished by their porous structure, which is also the reason why they are classified as such. These organic ligands may be referred to as "struts" or "linkers," depending on the circumstances in which they are being discussed. ZIFs, which are subclasses of MOFs, have topological characteristics that are analogous to one another. Bennett was the first person to publish a research on melt-quench ZIF in 2015, when he did so [1]. Because of this, he became a trailblazer in this industry. To effectively create ZIF glass, he made use of the melt-quench manufacturing technique. According to research that was only recently made public, a good number of the ZIF materials have a high resistance to heat and chemicals, are porous, and have the potential to be used in a wide variety of applications. This has led to the discovery of a wide range of possible applications, which is a direct result of this. Imidazole-based linkers are employed to connect the tetrahedral single-metal nodes that were used in its production. These nodes were used in its fabrication [2]. When utilizing this procedure, it is feasible to construct tetrahedral structures, which are quite like the structures that can be found in zeolites. As a direct consequence of this, the structures that make up ZIF are made up of gigantic cages that are linked to one another by a substantial number of very small windows. Catalysis and gas separation are two applications that might benefit from the usage of these materials due to their excellent resilience to heat and chemicals. It contains a significant quantity of carbon, nitrogen, as well as a variety of transition metals. In addition to zeolites' resilience to heat and chemicals, these materials also feature the capacity of both MOFs and zeolites to change the size of the pores in their structures. These materials are known as hybrid materials [3]. As an immediate and unavoidable consequence of this, a material of superior quality will be generated. The degradation of rhodamine B from wastewater required the use of bimetallic ZIFs, which facilitated the acceleration of the extraction process [4]. These ZIFs were used in the process. Bi_2O incorporated grapheme oxide was used because of its ability to enhance the rhodamine B dye's potential for absorption on the surface of the graphene oxide [3]. It was determined that ZIF-90-SH was the most effective adsorbent for removing mercury ion (Hg II) ions from an aqueous solution while maintaining a temperature of room temperature throughout the process [5]. While the treatment, a solution that was mostly composed of water was used. Using ZIF-90, which involves the addition of thiols, it is possible to remove Hg II from water [6]. This process requires the use of thiols. Because of the remarkable adsorption properties it has, ZIF-93 is capable of successfully separating carbon dioxide (CO_2) and nitrogen (N_2) mixtures from one another. Because of this capability, it is ideal for applications in the industrial sector due to the possible advantages that it offers. A larger dynamic separation capacity was shown to be associated with a longer CO_2 retention lifetime, according to the results of a few different experiments. This association was shown to have a statistically significant relationship [7]. It has been shown that the employment of ZIF-8 and ZIF-67 is the most effective method for rapidly absorbing and eliminating sulfur mustard. Extensive study has provided evidence to support this claim. In a very short period of time, it has been shown that the zeolitic imidazolate frameworks ZIF-8 and ZIF-67 are capable of efficiently removing sulfur mustard from the environment [8]. ZIFs are able to remove pollutants from the air through a variety of adsorption methods (Figure 1), for instances, electrostatic interaction, coordination reaction, hydrophobic adsorption, hydrogen bonding, ion exchange reaction, diffusion, lewis acid-base interaction etc. [9]. This adsorption possess enables them to do so in a way that is reasonably efficient. This is one of the reasons why they are so successful [10]. Because MOFs materials, such as ZIF, include a high level of microporosity, it is possible to employ these materials for the adsorption and storage of a wide variety of various gases for example CO_2 [11]. The utilizations of various ZIFs for environment safety issues are the objectives of our research.

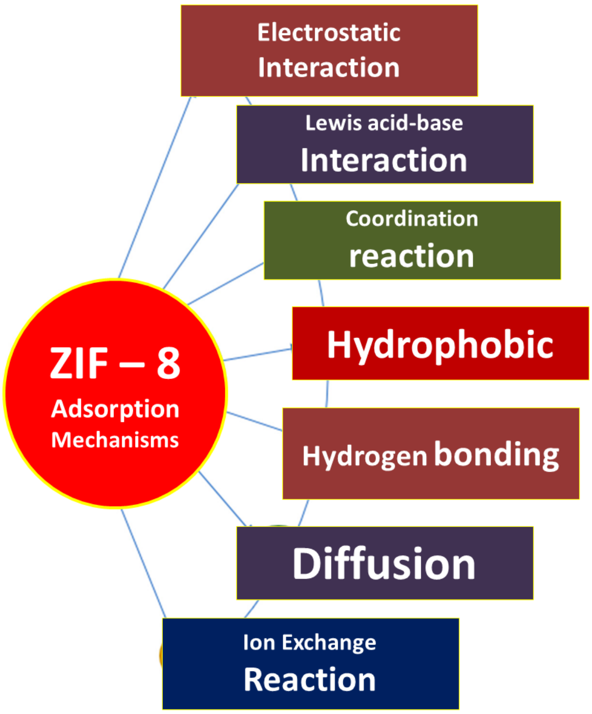

Fig. 1: Adsorption mechanisms of ZIF-8.

2. REMOVAL OF POLLUTANT FROM WATER

2.1 Adsorption

ZIFs are very hydrophobic and stable, providing them a better choice for filtering pollutants from water[12]. Various types of ZIFs can absorb various components from water. Co/Zn based ZIFs can adsorb I_2, Cl_2 and Br_2 from water [13]. Its large capacity makes ZIF-8 an attractive adsorbent. Some materials, such as ZIF-8 and ZIF-71, could be used to separate furanic molecules from alcohols. ZIF-8 is a popular adsorbent due to its high capacity. Furanic compounds can be separated from alcohol-based solvents using ZIF-8 and ZIF-71 materials. These non-ideal interactions between the adsorbent and the adsorbed phase (i.e., the solid-liquid equilibrium) appear to be more favorable than the non-ideal interactions between vapor and liquid equilibrium, making distillation slower and costly to maintain [14]. ZIF-8 [15] and ZIF-90 [16] can adsorb small alcohol molecules large surface area and reliability of ZIF-67 (a representative cobalt-based ZIFs material) makes it an excellent adsorbent for the removal of 1-naphthol from aqueous solutions [17]. Also, phenol can be removed by adsorptive removal from water by using it [18]. When it comes to aqueous solutions, ZIF-8 has removed phthalic acid (H_2-PA) and diethyl phthalate (DEP) [19]. Zn/Co ZIF adsorbents can be used to separate Rhodamine B (RhB) from water. Compared to ZIF-8 and ZIF-67, it has the highest adsorption ability for RhB [20]. Adsorbents for separating Rhodamine B from wastewater were made using nitrogen-doped carbons that were in-situ glucose-coated ZIF-8 [21][22]. Roselle red dye is adsorbable by ZIFs, which contain core-shell microspheres [23]. However, ZIF-7 can adsorb many types of gases such as propane and ethylene. It can also absorb butane and propane [24].

2.2 Photocatalysis

Both ZIF-11(Zn) and ZIF-8(Zn) are photo-catalytically active against bacteria. ZIF-8 can inactivate *E. coli* to a large extent. ZIF-8 has a much greater photocatalytic inactivation impact on *E. coli* than ZIF-11. As a result of ZIF-8's strong photocatalytic properties (Figure 2), this occurs [25]. ZIF-8, on the other hand, is more successful in inactivating *E. coli* from water. Methylene blue (MB) is a widely used organic dye that is extremely difficult to degrade in waste streams. Under 500Whg lamp illumination in the open air and at room temperature, the photocatalytic activities of ZIF-8 photocatalysts were studied. In the photocatalytic reaction with ZIF-8, the UV-vis absorption spectrum of the undecomposed MB in solution showed that the concentration of MB dropped significantly with time [26]. ZIF-8 is now capable of engaging in wide-spectrum photocatalytic degradation of gaseous HCHO thanks to the addition of N=C=O groups that have been functionalized into the molecule [27]. As a result, it can degrade benzyl alcohol in water.

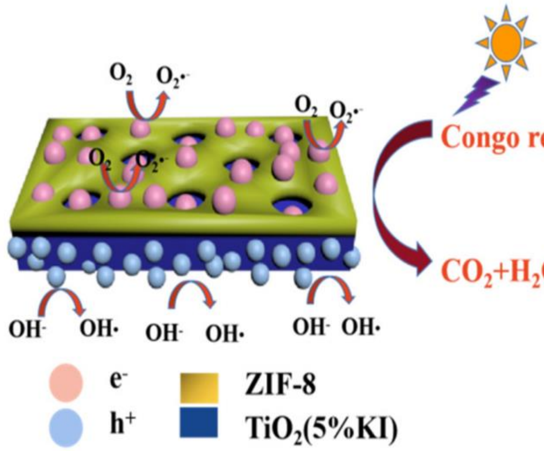

Fig. 2: Schematic of the photocatalytic mechanism of ZIF-8@TiO_2 (5% KI) [28].

3. FUEL PURIFICATION

In terms of selectivity, ZIF-8 is the best choice. It has been shown that the adsorption and purification of biofuel may be studied using molecular simulations in 6 kinds of ZIFs (ZIF-8, ZIF-25, ZIF-71, ZIF-90, ZIF-96, and ZIF-97). ZIF-97, ZIF-96, and ZIF-90 may form H-bonds with ethanol (EtOH) and H_2O due to polar functional groups. When the concentration of adsorbate increases, the number of H-bonds rises. No H-bonding is formed due to non-polar or very weakly polar functional groups of ZIF-8, ZIF-25, and ZIF-71 have non-polar or very weakly polar functional groups. Thus, during the low-pressure range, EtOH uptake decreases by ZIF-97, ZIF-96, ZIF-90, ZIF-71. At infinite dilution, the isosteric heat of adsorption follows the same magnitude. In biofuel purification, the selectivity of EtOH over H_2O decreases as EtOH composition increases. There is more selectivity in hydrophobic ZIF-8 and ZIF-25 than hydrophilic ZIF-90, ZIF-96 and ZIF-97 [29]. The fundamental and process components of a high-performance method for separating and purifying 2,5-dimethylfuran (DMF) have been developed from thermodynamically non-ideal reactor exit mixtures containing furans (DMF and MF) in small amounts (less than 10%) dissolved in an organic solvent. These mixtures exit the reactor as a byproduct of the production of furans. The procedure in issue is one that separates and purifies 2,5-dimethylfuran (BuOH). The DMF-selective behavior of numerous ZIF/MOF adsorbent materials was made obvious by analyzing their binary DMF/BuOH adsorption, and it was revealed that ZIF-8 was an exceptionally intriguing adsorbent because of its high capacity and DMF/BuOH selectivity. Because ZIF-8 has both of these components, the aforementioned findings may be attributed to the existence of ZIF-8 [14]. ZIFs are promising candidates for the separation of CH_4/H_2, CO_2/CH_4, and CO_2/H_2 mixtures, according to computer simulations that were carried out with atomic-level precision. In addition, ZIFs have the potential to separate mixtures of CO_2 and CH_4. The use of equilibrium molecular dynamics simulations and grand canonical Monte Carlo simulations, respectively, allowed for the calculation of estimates of the self-diffusivities and adsorption isotherms of gas mixtures in ZIFs. Utilizing the findings from atomistic simulations, an investigation of the ZIF membranes' adsorption selectivity, diffusion selectivity, and permeation selectivity was carried out [30][31]. By this it is assumed that ZIF may be a proper separator and it may purify CH_4 by separating other gases.

4. REMOVAL OF HEAVY METALS FROM WATER

Nevertheless, coordination chemistry and redox pathways may make it possible for metals to circumvent biological processes such as transport and compartmentalization and instead bind to specific cell components. This can result in dysregulation of the machinery that controls trafficking and the homeostasis of ions in the body. It is possible for cell malfunction, the oxidative breakdown of biological macromolecules, and finally cell toxicity to occur when heavy metals bind to DNA and nuclear proteins in an unfavorable manner. It is necessary to develop methods that are both cost-effective and capable of removing minute quantities of heavy metal ions from water to protect the health of humans and the environment. In order to remove heavy metal ions from wastewater, a number of different processes, including chemical pre-treatments such coagulation-flocculation, photocatalysis, and membrane separation, have been used [32]. Various types of nanomaterials have been proven efficient in heavy metal adsorption [33]. For heavy metal removal, adsorption has been demonstrated to be a successful and cost-effective method because of its ease of use, few secondary products, reversibility, and ability to produce high-quality effluent at low energy and maintenance costs. Cu(II) adsorption capacity of ZIF-8 has been reported to be up to 800 mg g^{-1}, making it one of the most advanced adsorbents for copper capture [32]. Cubic, leaf-shaped, and dodecahedral zeolite filters (ZIFs) were evaluated for their ability to exclude As (III). The experiment indicated that despite differences in specific surface area and shape, all three adsorbents had outstanding As(III) adsorption capabilities. It was shown that the highest adsorption capacities of cubic ZIFs, leaf shaped ZIFs, and dodecahedral ZIFs were 122.6, 108.1, and 117.5 mg/g, respectively, when pH 8.5 was used to match the adsorption isotherms. Three ZIFs reduced As(III) from 200 g/L to below 10 g/L in 2h at a 0.2g/L adsorbent dose [34]. In wastewater treatment, nFe@ZIF-8 is used to remove Pb (II) through selective adsorption and reduction. Within 60 minutes at a pH of 5, nFe@ZIF-8 removed more than 95.3 percent of Pb(II) from the aqueous solution at an initial concentration of 50 mg L^{-1} Hg II has been absorbed using a new monolithic adsorption material ZnS-ZIF-8 [35]. Unique ZnS-ZIF-8 monolith exhibits exceptional capture efficiency toward Hg II in the presence of competing, diverse metal ions within a short time frame. According to the Langmuir model, the Hg II removal capacity was up to 925.9 mg/g [36]. ZIF-8 composite is also utilized for Pb^{2+} adsorption from water [37][38][39]. If we want to remove Pb from water, we should use a nanocomposite made with ZIF@$NiTiO_3$ [40].

5. REMOVAL OF NUCLEAR WASTE/ RADIOISOTOPES FROM WATER

Adsorbents with antifouling characteristics can be made from chitosan-graphene oxide-ZIF (GCZ8A) foam. It can recover Uranium from seawater due to its high specific surface area (200.79m^2/g) and nitrogen/oxygen functional groups. The adsorbent obtained an adsorption capacity of 121.7 mg/g at the fifth cycle. In natural seawater, the GCZ8A adsorbent has high Uranium - uptake capacity (12.24 μg g^{-1}) and a 66.31 % Uranium (VI)-removal rate [41]. ZIF-8 nanocrystals can absorb radioactive iodine [42]. It is also possible to separate radioactive iodine utilizing nanocrystals of ZIF-67 on siliceous mesocellular foam [43]. Utilizing Fe@ZIF-8 as a promising adsorbent for the removal and abruption of Uranyl(VI) ions from aqueous solutions, With a latent adsorption capacity of 270.7 mg g^{-1}, the material is highly selective for U(VI) at pH = 4.5 [44]. To remove Uranium, highly porous zeolitic imidazolate frameworks (ZIFs) have been utilized (VI). ZIF-8 (540,4 mg/g) > Zn/Co-ZIF (527,5 mg/g) > ZIF-9 (448,6 mg/g) > ZIF-67 (368,2 mg/g) show a decreasing propensity to remove Uranium (VI) [45].

6. CO_2 ADSORPTION

ZIFs are utilized for CO_2 adsorption applications [46][47]. ZIFs are characterized by a structure that is both stiff and porous. In this case, the interaction between the quality of the pores and the functionality of the walls, which is defined by the various imidazolate functional groups, leads to an increased capacity for CO_2 collection [48]. ZIFs absorb carbon dioxide based on their size and shape. For the adsorption of CO_2 to proceed, -stacking interactions as well as hydrogen-like bonds are required. The adsorption of CO_2 does not impact its geometry. However, it does affect the structure of some ZIF structures significantly [49]. Adsorption on ZIFs can be used to separate and store CO_2 at low temperatures. As a result, each of the two CO_2 adsorption sites is situated in a tiny cavity produced by the zinc's six-membered rings and their benzimidazolate-binding molecules.

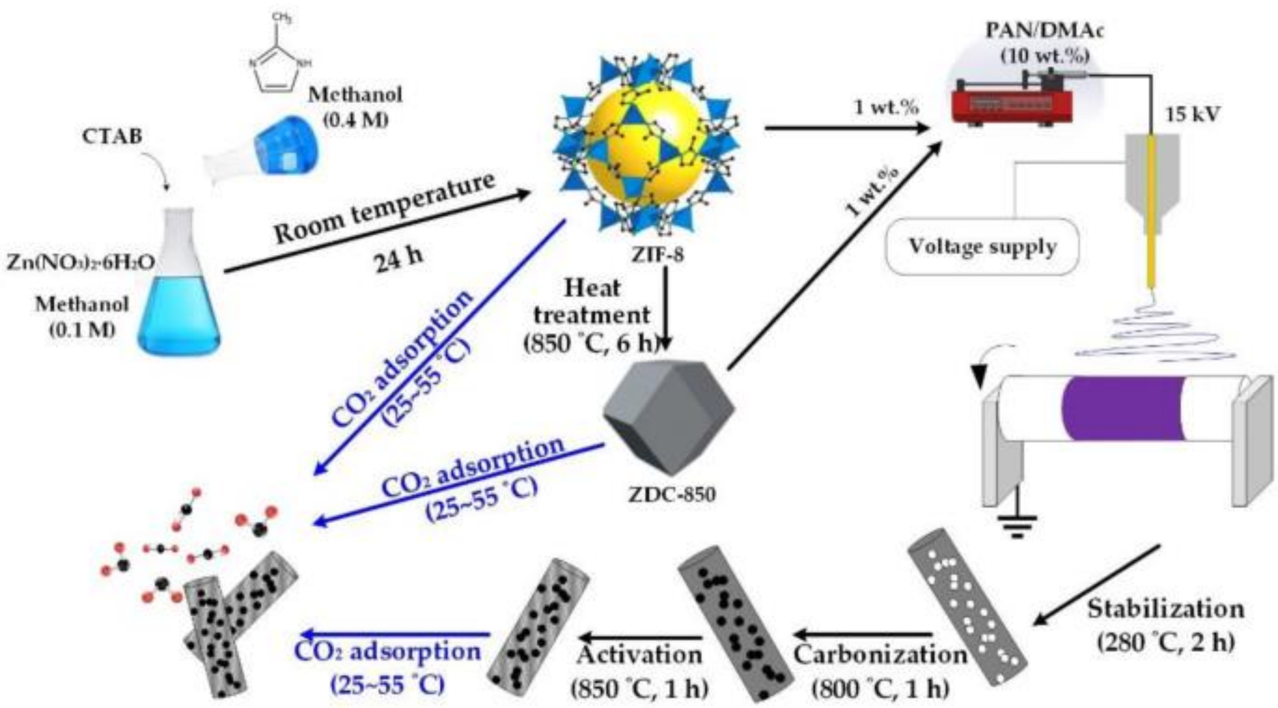

Fig. 3: Synthesis of ZIF-8 and its CO_2 adsorption process [50].

Zinc 4-membered rings or the topological beta-cage of ZIF-7, there is no significant CO_2 adsorption. Some of the CO_2 adsorption sites in ZIF-7 and ZIF-8 are identical. The benzimidazolate ligand controls ZIF-7 CO_2 adsorption [51]. ZIF-7's structural flexibility is affected by CO_2 adsorption because CO_2 migrates between its different guest-hosting holes under pressure [52]. Using the density functional theory (DFT), three different sized ZIFs with small, medium, and big cages may be used to anticipate the behavior of adsorbed carbon dioxide. With and without CO_2, the water hydration strength and organization inside the material are investigated. CO_2 is mostly found on the cage's inner surface due to single and multipoint interactions in a ZIFn cage (n = 1, 4, 6). Here with highly accessible surfaces, such as ZIF6, their adsorption is the most intense [53]. Both ZIF-7 and ZIF-94, both of which have topologies with smaller holes than their counterparts (ZIF-11 and 93, respectively), display bigger adsorptions than their counterparts. However, under higher pressures, the opposite may be true for these two structures. In this specific scenario, the adsorption of the structures that have holes of a larger size is greatly enhanced [47]. Additionally, the ZIF-8 is capable of adsorbing and capturing CO_2 (Figure 3) [54].

7. OXIDATIVE DESULPHURIZATION

Co-ZIF-67 is a molecule that was developed to accomplish the removal of dibenzothiophene (DBT) from gasoline. This was the compound's primary goal. When we used to activate Co-ZIF-67/M-A1 (SBET = 2478.8 m^2/g), we were able to acquire an adsorption capacity of 550 mg/g at 65 °C and a Madsorbent/Vfuel ratio of 0.8 mg/mL. This was achieved by heating the material. After completing four distinct applications, recycling was ultimately successful [55]. After a great deal of research, testing, and investigation, it was discovered that ZIF-8 has a greater resistance to H2S [56]. The DBT adsorption capacity of the NCNT/ZIF-8 was 81.2 mg/g, which was much higher than that of pure ZIF-8. This remarkable performance may be due to the additive effects of NCNT and ZiF-8, the presence of basic groups in the structure of NCNT, as well as the substantial increase in surface area and pore volume. After going through three cycles of adsorption and desorption, it hardly showed any signs of losing its adsorption capacity [57]. Mercaptans are a kind of chemical that may be eliminated via the use of ZIF-8's decontamination capabilities. The hierarchically porous ZIF-8 had a greater number of active Zn sites, and therefore, it exhibited a better capacity for the adsorption of mercaptan from gasoline while still maintaining a reasonable selectivity. In addition to that, the exterior possessed a big surface area [58]. To adsorb and get rid of sulfur mustard (HD) as quickly as possible, ZIF-8 and ZIF-67 have been used. An HD simulant known as 2-chloroethyl ethyl sulfide was used in several the studies so that the researchers could have a better understanding of how the polarity of the solvent affects adsorption. After that, the adsorption and removal of CEES and authentic HD from aqueous solutions was accomplished with the help of ZIF-8 and ZIF-67. It has been shown that a positive correlation exists between the polarity of the solvent and the adsorption capacities of ZIF-8 and ZIF-67. In addition, 97% of CEES was promptly adsorbed by ZIF-8 and ZIF-67 within one minute at a temperature of 25 degrees Celsius in a solution that was 9:1 (v/v) water to ethanol [59].

8. CONCLUSION

Nanomaterials based on ZIF may have a variety of different features, including photocatalytic capabilities and adsorption properties. ZIF's significance in environmental applications is increased by the implication of this behavior. The degradation and separation of pollutants from our air, water, and other surroundings is within the capabilities of some kinds of nanomaterials. In most cases ZIFs utilize the adsorption property in clean environment purposes of these. Mainly by adsorption they can remove toxic gases from air as well as water, can remove Furanic molecule from alcohol, can remove heavy metal form water, and can remove nuclear waste from environment.

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