INFORMATICS JOURNALS

Online ISSN : 3049-3455

Mineral Metal Energy Oil Gas and Aggregate

Contents available at: *www.informaticsjournals.com/index.php/2MEOGA*

2MEOGA

Metals and Organic Compound-Based Polymer Composite Beads to Remove Multiple Colouring Agents from Water and Other Aqueous Media

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Abstract

Adsorbent composite polymer beads are prepared by mixing a bimetallic organic compound and Polysulfone for the removal of multiple dyes and colouring agents from aqueous solution. The invention comprises of following steps: a) Synthesis of an adsorptive bimetal organic compound; b) Synthesis of polymer homogenous solution and development of a composite polymer beads - bimetallic organic compound via phase inversion of the homogenous solution and obtaining varying diameter beads; and c) Using the developed polymeric composite beads in batch and packed column continuous flow systems to remove single and/or multiple coloring agents from water and other aqueous mediums.

Keywords: *Dye removal, Bimetallic polysulfone beads, Adsorption, Polymeric composite, Phase inversion*



पेटेंट कार्यालय, भारत सरकार
The Patent Office, Government Of India

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(पेटेंट नियमावली का नियम 74) | (Rule 74 of The Patents Rules)

पेटेंट सं. / Patent No. : 500802

आवेदन सं. / Application No. : 202231061764

फाइल करने की तारीख / Date of Filing : 30/10/2022

पेटेंटी / Patentee : Zelence Industries Pvt. Ltd.

प्रमाणित किया जाता है कि पेटेंटी को, उपरोक्त आवेदन में यथाप्रकटित *SYNTHESIS OF GO/FE-MN EMBEDDED POLYSULFONE BEADS FOR THE REMOVAL OF TOXIC METALS FROMAQUEOUS SOLUTION* नामक आविष्कार के लिए, पेटेंट अधिनियम, 1970 के उपबंधों के अनुसार आज तारीख अक्टूबर 2022 के तीसवें दिन से बीस वर्ष की अवधि के लिए पेटेंट अनुदत्त किया गया है।

It is hereby certified that a patent has been granted to the patentee for an invention entitled *SYNTHESIS OF GO/FE-MN EMBEDDED POLYSULFONE BEADS FOR THE REMOVAL OF TOXIC METALS FROMAQUEOUS SOLUTION* as disclosed in the above mentioned application for the term of 20 years from the 30th day of October 2022 in accordance with the provisions of the Patents Act,1970.

अनुदान की तारीख / Date of Grant : 18/01/2024

Controller of Patents

टिप्पणी - इस पेटेंट के नवीकरण के लिए फीस, यदि इसे बनाए रखा जाना है, अक्टूबर 2024 के तीसवें दिन को और उसके पश्चात प्रत्येक वर्ष में उसी दिन देय होगी।

Note. - The fees for renewal of this patent, if it is to be maintained, will fall / has fallen due on 30th day of October 2024 and on the same day in every year thereafter.

1.0 Invention

The presented invention relates to the synthesis, preparation and application of bimetallic Metal Organic Compound (bMOC) - polymer-based composite beads for the adsorption of multiple colouring agents in continuous flow mode. The formed beads are used to efficiently remove multiple dyes and colouring agents from water and other aqueous media.

1.1 Background and Technical Field

The presence of colouring agents in water and other aqueous media is an enormous environmental concern. Textile, dyeing, paper and pulp, tannery, and paint industries are large users of colouring agents; therefore, effluents from these industries, as well as those from dye-producing plants, tend to include dyes and colouring agents in adequate concentrations.[1] These colour-imparting agents are an unpleasant form of pollutant because they are hazardous through oral consumption and inhalation, skin and eye irritation, and skin sensitisation, causing problems such as skin irritation and sensitisation, as well as carcinogenicity. They can give water a colour that is perceptible to the naked eye and thus highly undesirable from an aesthetic standpoint. The aquatic environment is affected by disrupted light transmission and thereby affecting biological metabolism processes, resulting in the extinction of aquatic flora and fauna in ecosystems. Hence, it becomes important to check these colouring pollutants in an aqueous system.

In this regard, a cheaper approach of conventional adsorption of these pollutants over an adsorbent can be applied. This particular adsorbent can target these colouring agents, but similar to other adsorbents, application and removal of the adsorbent after adsorption is difficult.[2,3]

Hence, in this invention, the adsorbent is mixed into a polymer to obtain a composite bead that can be easily handled, applied and extracted after the adsorption process. The invention involves: a) Synthesis of an adsorptive bimetal organic compound; b) Synthesis of polymer homogenous solution and development of a composite polymer beads - bimetallic organic compound via phase inversion of the homogenous solution and obtaining varying diameter beads; and c) Using the developed polymeric composite beads in batch and continuous flow systems to remove single and/or multiple coloring agents from water and other aqueous mediums. This invention also features a fixed bed column packed with composite beads in intermittent baffle walls to enhance the efficiency of the system.

1.2 Summary of the Invention

The innovation lies in the synthesis of an adsorbent-polymer composite powder synthetic material to capture multiple dyes and colouring agents from water and other aqueous media. The invention describes the method of application. Fabrication and matrix formation are discussed in detail.

In one aspect, synthesis of a bMOC has been described by a standard solvothermal method involving a solvent medium (Ultrapure water or Dimethylformamide (DMF) or Dimelthylsulfoxide (DMSO) or Ethanol (EtOH) or Methanol or N-Methyl-2-pyrrolidone (NMP)), metal salts (Iron and/or Aluminum or copper or cobalt) and an organic acids (1,3,5- benzene Tricarboxylic acid (BTC) or 1,4- benzene Dicarboxylic acid(BDC) or Fumaric Acid (FA)) to bind it all together. It is well within the scope of the present invention to tune the composition and other synthesis parameters of MOC to attain the targeted removal for multiple dyes and colouring agents (Rhodamine B (RhB) or Methyl Orange (MO) or Methylene Blue (MB) or Crystal Violet (CV), or Malachite Green (MG)).[18-21]

In another aspect, the synthesis of homogeneous polymer solutions (Solid polymer in liquid solvent medium) and additives has been described. The requirements for the target of the composition may fall within the scope of this invention. Solid polymers like Polysulfone (PSF) or Polyethersulfone (PES) or Polyvinyl Alcohol (PVA) or Polycarbonate (PC) or Polyvinyl Chloride (PVC), solvent medium (i.e. Water or Dimethylformamide (DMF) or Dimelthylsulfoxide (DMSO) or Isopropanol (IPA) or Methanol or N-Methyl-2-pyrrolidone (NMP) and Polyethylene glycol (PEG-400 or 600 or 1000) as additive.[26-29]

It is further in the scope of the present invention involving the synthesis of bimetallic organic compound -polymer composite beads with varying ratios of optimised compositions of bMOC from (1) and homogenous polymer solution from (2). The various ratios of bMOC: Solid Polymer (W%) have been selected for optimisation of the adsorption process.

It is further in the scope of the present invention, the designed composite beads being used for absorptive

removal of dyes and colouring agents (Rhodamine B (RhB) and/or Methyl Orange (MO) and/or Methylene Blue (MB) and/or Crystal Violet (CV) and/or Malachite Green (MG)).

It is further in the scope of the present invention to apply the product, i.e. bimetallic Metal Organic Compound (bMOC) - polymer-based composite bead, to be used in batch and continuous flow systems for the removal of dyes and colouring compounds.[30-32]

2.0 Description of Drawings

1. This shows the actual polymeric composite bMOC beads before application.
2. Adsorption of dyes by polymeric composite bMOC beads can be seen floating and settling in the conical flasks.
3. The Fourier Transformation Infrared Spectroscopy (FTIR) spectra depict the characteristic signatures of the individual dyes adsorbed and compare them with the unused beads in Figure 1.
4. The removal percentage has been denoted in this representation of % Removal v/s dose plot for different dyes as Rhodamine B, Crystal Violet, Methylene blue, Malachite green and Methyl orange.
5. Schematics representation of the beads as media in a packed column for adsorption of dyes as Rhodamine B, Crystal Violet, Methylene blue, Malachite green and Methyl orange.
6. Bead sizes as shown by Vernier calliper measurements.

3.0 Detailed Description

3.1 Definitions

In this invention, a method to synthesise bMOC-Polymer composite beads and their application for multiple dye removal in a process has been described. It is well within the scope of this present invention to use MOC and polymer additives found useful in applications other than this work. All the scientific and technical terms have their usual meaning.

3.2 Bead Synthesis and Development Process

Step 1:

The synthesis has been divided into four parts (subsections 2.1, 2.2, 2.3 and 2.4) or processes, with the first two simultaneous processes (subsections 2.1 and 2.2), a third process (subsection 2.3) with a combination of the previous two processes and a final process (subsection 2.4) after achieving the third process as desired. It should be understood that this mechanism can be applied elsewhere, although the composition of each material is within the scope of this work.

Step 2:

Synthesis of bimetallic aluminium/Iron/copper/cobalt (BDC/BTC/FA) MOC was obtained in a following manner. Further in detail, Aluminium Nitrate Nonahydrate (0.002-0.010 moles), Ferric Nitrate Nonahydrate (0.002-0.020 moles), Dimethylformamide (DMF) and BDC (0.003-0.070 moles) were completely dissolved in 40-100 ml of DMF.[14-17] All the chemicals are dissolved completely. The obtained solution was placed in a 50-150 mL Teflon-lined cup in a hydrothermal autoclave and was subjected to a temperature of 170 - 200 °C for 24 - 60 hours. The product, yellowish-white precipitate, was filtered and washed with Ethanol, followed by DI water to remove unreacted components. Finally, the product was dried overnight at 50 °C and stored for further investigation.

Step 3:

A polymer such as Polysulfone or polyether sulfone or poly vinyl chloride or polycarbonate (in 10-30 % by weight), a solvent Dimethyl formamide or N-Methyl-2-pyrrolidone or Dimelthylsulfoxide or Ethanol (DMF/NMP/EtOH in 70-95 % by weight), an additive such as polyethylene glycol (600) (1-5 % by weight) were mixed in a beaker, heated (50-70 °C) and stirred until clear and homogeneous polymer solution was obtained. The solution was left to age for a period of 10-24 hrs.

Step 4:

The obtained bMOC product and the polymer solution (5-75 % by weight), where bMOC composition is preferably 5-25 %, more preferably in 10-20 % and most suitable in 14-18 % of polymer weight, were mixed (for 10-24 hrs) to form a uniform solution with no visible lumps or unevenness. The solution from the previous process was now drop-casted in the liquid solution (Deionised water) in the form of beads. The desired shape of the beads is spherical with an outside diameter ranging from 0.5 to 3 mm. The so-formed solid beads were decanted and again immersed in Deionised water for 12-24 hrs to remove any remaining solvent from previous stages.

Step 5:
The formed bimetallic metal organic compound-polymer-based composite beads are tested in a batch system for the removal of multiple dyes and colouring agents. The dye solution of 5-30 mg/L of RhB or MO or MB or CV, or MG was used for adsorption onto bMOC. A dose of 10 to 125 g/L of the bimetallic metal organic compound-polymer-based composite beads was tested.

Step 6:
The formed bimetallic metal organic compound-polymer-based composite beads are now packed into a column with intermittent baffle walls, where the height of the baffle walls is 40 to 60 % of the column diameter, to obtain a desired flow and effective contact time. The setup has two units comprising a column of fine aggregates, suitably sand, and a column comprising the designed composite polymer beads. The test was carried out at an inlet flow rate of 2 to 10 mL/min and 5-30 mg/L of dye concentration (RhB or MO or MB or CV, or MG), and a change in concentration was observed at the outlet of the column.

3.3 Examples

Example 1:
In detail, Aluminium Nitrate Nonahydrate (0.002M), Ferric Nitrate Nonahydrate (0.002M), and BDC (0.002M) were completely dissolved in 80 ml of DMF. The obtained bMOC was mixed homogeneously with a polymer solution of Polysulfone (10%), DMF (89%) and PEG (600) (1%). The as-formed beads were tested for the removal of Rhodamine B dye, and efficiency was observed to be 85-90 %.

Example 1a:
In detail, Aluminium Nitrate Nonahydrate (0.002M), Ferric Nitrate Nonahydrate (0.002M), and BDC (0.002M) were completely dissolved in 80 ml of DMF. The obtained bMOC was mixed homogeneously with a polymer solution of Polysulfone (20%), DMF (79%) and PEG (600) (1%). The as-formed beads were tested for the removal of Rhodamine B dye, and efficiency was observed to be 85-87 %.

Example 1b:
In detail, Aluminium Nitrate Nonahydrate (0.002M), Ferric Nitrate Nonahydrate (0.002M), and BDC (0.002M) were completely dissolved in 80 ml of DMF. The obtained bMOC was mixed homogeneously with a polymer solution of Polysulfone (30%), DMF (69%) and PEG (600) (1%). The as-formed beads were tested for the removal of Rhodamine B dye, and efficiency was observed to be 80-85 %.

Example 2:
In detail, Aluminium Nitrate Nonahydrate (0.002M), Ferric Nitrate Nonahydrate (0.002M), and BDC (0.004M) were completely dissolved in 80 ml of DMF. The obtained bMOC was mixed homogeneously with a polymer solution of Polysulfone (10%), DMF (89%) and PEG (600) (1%). The as-formed beads were tested for the removal of Rhodamine B dye, and efficiency was observed to be 95-99 %.

Example 3:
In detail, Aluminium Nitrate Nonahydrate (0.002M), Ferric Nitrate Nonahydrate (0.002M), and BDC (0.006M) were completely dissolved in 80 ml of DMF. The obtained bMOC was mixed homogeneously with a polymer solution of Polysulfone (10%), DMF (89%) and PEG (600) (1%). The as-formed beads were tested for the removal of Rhodamine B dye, and efficiency was observed to be 90-95 %.

Example 4:
From example 2, the doses were studied for the removal of multiple dyes and colouring agents. A dose of 10 to 125 g/L of the bimetallic metal organic compound-polymer-based composite beads was tested on a batch scale. The dye solution of 5-30 mg/L RhB or MO or MB or CV, or MG was used for adsorption onto bMOC beads. At a concentration of 25 mg/L of the dyes, the dose of 50 g/L, the removal was obtained as 99, 98, 99, 95, and 92% and at the dose of 75 g/L, the removal % was obtained as 99, 99, 99, 98 and 97% respectively in the duration of 30 minutes.

Example 5:
From example 2, the formed bimetallic metal organic compound- polymer-based composite beads are now packed into a column with intermittent baffle walls, where the height of the baffle walls is 40 to 60 % of the column diameter, to obtain a desired flow and effective contact time. The setup has two units comprising a column of fine aggregates, suitably sand, and a column comprising the designed composite polymer beads. The test was carried

out at an inlet flow rate of 2 to 10 mL/min and 5-30 mg/L of dye concentration (RhB or MO or MB or CV, or MG), and a change in concentration was observed at the outlet of the column. A flow rate preferably in 0.006 to 0.010 L/min showed 99% removal efficiency with an effective bed contact time of most suitably 1-2.5 minutes.

4.0 Claims

1. An adsorbent bimetallic metal organic compound- polymer-based composite beads capable of adsorbing multiple dyes and colouring agents having a concentration up to 25 mg/L in aqueous medium.
2. An adsorbent bimetallic metal organic compound-polymer-based composite beads in claim 1, wherein the said material is composed of (a) a bimetallic organic compound powder and (b) a homogeneous polymer solution.
3. Adsorbent metal organic compound powder in claim 2a is a result of a synthetic chemical solution that includes metal salts, organic acids and solvents.
4. Adsorbent metal organic compound powder in claim 3, wherein said adsorbent metal organic compound powder comprises the synthetic chemicals consisting of metal salts in 1 to 10 parts, an organic acid in 2 to 20 parts, and an equivalent weight of the solvent in 7 to 70 parts.
5. Adsorbent metal organic compound powder in claim 4, wherein the metal salts are two metal salts in combination.
6. An adsorbent bimetallic metal organic compound-polymer based composite beads in claim 2, wherein said metal organic compound powder comprises 14-18 % of the said polymer solution weight.
7. An adsorbent bimetallic metal organic compound-polymer based composite beads in claim 2b, wherein said homogeneous polymer solution includes preferably Polysulfone in 5 to 20 parts, a solvent by weight in 80 to 95 parts and an additive in 1 to 5 parts.
8. An adsorbent bimetallic metal organic compound-polymer based composite beads in claim 6, wherein the composite solution is drop-cast into a liquid to form spherical beads have a diameter of 0.5 to 3.0 mm.
9. An adsorbent bimetallic metal organic compound-polymer-based composite beads in claim 1 capable of adsorbing multiple dyes and colouring agents having a concentration up to 25 mg/L in aqueous media in a batch and continuous flow system.
10. An adsorbent bimetallic metal organic compound-polymer based composite beads in claim 8 wherein, the batch system has mobilised composite beads in a dosage of 50 to 100 g/L, with a retention time of 10 to 60 minutes.
11. An adsorbent bimetallic metal organic compound-polymer based composite beads in claim 8 wherein the continuous flow system has immobilised composite beads and a flow rate preferably in 0.006 to 0.010 L/min.
12. An adsorbent bimetallic metal organic compound-polymer based composite beads in claim 8 in a continuous flow system has immobilised composite beads with intermittent baffle walls (with height 40-60 % diameter of column), with an effective bed contact time of most suitably 1-2.5 minutes.

5.0 Comparative Study with Existing Patents and Papers

5.1 US20210139348: Activated Carboniron /Cerium Oxide Nanocomposite Suitable for Dye Removal

Activated carbon, e.g., from waste tires, modified by bimetallic Fe and Ce

Nanoparticles can provide a high surface area and active sites for enhanced dye adsorption. Such nanocomposites can offer magnetic removal from aqueous solutions containing, e.g., Methylene Blue or Rhodamine B. Adsorption equilibrium data fit well to the Langmuir isotherm model, with an adsorption capacity was 324.6 mg/g. Rhodamine B adsorption by such activated carbon-Fe—Ce magnetic adsorbents has an endothermic character and pseudo-second-order kinetics. In ethanol solution, rhodamine B was desorbed at high efficiency and such materials, which could be recycled up to 5 cycles. Such magnetic nanocomposites are adsorbents for treating dyes such as rhodamine B in wastewater, even in large-scale adsorption systems. Polyamides can be grafted to such nanocomposites.

Response:

US20210139348 from King Fahd University of Petroleum and Minerals discloses an "Activated carbon-Fe—Ce magnetic nanocomposite" which comprises iron (10-15 %), carbon (66-72 %), Cerium (7-14%) and oxygen (8-18

%), where Iron is in composition of Fe(II) and Fe(III) with 75% of Fe(III). The process involves precipitating iron oxide, cerium oxide, activated porous carbon and polyamide bound together to form a magnetic nanocomposite. The magnetic nanocomposite has been used to remove methylene blue and rhodamine B. The nanocomposite may use additives, but does not involve an organic component as an integral part/basic building block of the adsorbent structure. The above patent also does not involve the formation of polymeric beads and their subsequent application in the removal of dyes in batch and continuous flow systems with single/multiple dyes. This makes the adsorbent material handling and separation easier from the dye solution.

5.2 CN104030389 - Method for Removing Dyes in Water by Utilising Magnetic Metal-Organic Framework Material

The invention provides a method for removing dyes in water by utilising a magnetic metal-organic framework material, and relates to the method for removing the dyes in the water. The method is mainly used for solving the problems of complicated processes, low treatment efficiency and high cost of the existing method for removing dyes in water. The method comprises the following steps: 1) preparing the metal-organic framework material to obtain the metal-organic framework material; 2) preparing the magnetic metal-organic framework material to obtain the magnetic metal-organic framework material; 3) removing the dyes in the water, namely firstly, adding the magnetic metal-organic framework material into to-be-treated water, stirring for certain time at a certain stirring speed and carrying out magnetic separation by utilizing a magnet to finish the removal of the dyes in the water. The method is mainly used for removing dyes from the water.

Response:

CN104030389 by Northeast Forestry University uses ratio of $Fe(NO)_3$ to 1, 3, and 5-phthalic acid in 1: (0.5-0.6) dissolved in high-purity water in step 1 and adding $Fe(NO)_3$ + sodium acetate in step 2 and sealing it in a steel reaction kettle under electrothermal blowing constant temperature of 190-220 DEG C in each case followed by removing, washing and drying the magnetic MOF. The patent uses a high temperature, and the magnetic composite is limited to iron-1,3,5-pthalic acid for removing crystal violet and does not disclose the removal of other dyes. The above patent also does not involve the formation of polymeric beads and their subsequent application in the removal of dyes in batch and continuous flow systems with single/multiple dyes. The patent also does not disclose the application of a magnetic composite in a continuous flow system and the recovery mechanism thereafter.

5.3 CN101798123A: Application of Bimetal Composite Oxide in Adsorbing Acid Violet 90 in Dye Wastewater

The invention discloses the application of a bimetal composite oxide in adsorbing acid violet 90 in dye wastewater. The bimetal composite oxide is prepared by baking magnesium-aluminium binary hydrotalcite. A baked product of a hydrotalcite-like compound, namely the bimetal composite oxide, is used for adsorbing the acid violet 90 in the dye wastewater and has a large adsorption capacity and a high removal rate, and a material after adsorption is easy to recycle.

Response:

CN101798123A discloses a LDH material as magnalium binary hydrotalcite is [Mg_2 + 1-xAl_3 + x$(OH)_2$] (CO 32-) X/2MH_2O], which is synthesised by roasting at 450-650 DEG C and forms a bimetal composite oxide. This invention specifically targets the synthesis of the adsorbent material and the removal of Acid black dye and claims the same. The patent does not involve the concept of an organic component in the main composite oxide network and describes the material in the LDH classification roasted at a very high temperature. The patent does not disclose the use of composite oxide for the removal of other dyes, as well as the recovery of the used adsorbent.

5.4 Paper: Magnetic Metal–Organic Framework Composites for Environmental Monitoring and Remediation

Environmental pollution remains one of the topical issues confronting scientists in the 21st century. The deployment of appropriate technology is among the promising routes of curbing the anthropogenic menace. Magnetic Metal–Organic Framework (MMOF) composites, a

combination of metal–organic frameworks and magnetic metal nanoparticles, result in the formation of composite materials with outstanding synergy properties that have been harnessed in several studies for environmental mitigation.

In this review, the detrimental effects of pollution on man and the environment are brought to the fore.[4-7] The general methods for synthesising MMOF composites and the classification of MMOF composites based on their composition, with appropriate examples, are highlighted. In-depth analysis of physicochemical properties of MMOF composites that are harnessed for the detection and remediation of environmental contaminants is discussed. Furthermore, the practical applications of these auspicious composites to detect some environmental pollutants and remediate their effects on the environment are extensively explored. Finally, the new frontiers and prospects of MMOF composites in global environmental pollution mitigation are presented.

Response:

1. The above paper is a review of the composites of metal-organic frameworks with magnetic materials. The well-known metal-organic framework is a broad classification of materials that share a metal and an organic component in their basic structure. These materials vary as per the composition and targeted application. In our study, no such magnetic material was synthesised, and the application is limited to the removal of multiple dyes and colouring agents.
2. This invention has an advantage over other works in the application of the adsorbent material and recovery after use, if compared to magnetic MOF. The designed polymer beads with bimetallic organic compounds give an edge over existing adsorbent materials with easy application, even in continuous flowing systems.

5.5 Paper: Iron-Based Metal Organic Framework for Efficient Removal of Methylene Blue Dye from Industrial Waste

The present investigation assesses the applicability of Fe-BDC metal organic framework for the removal of the toxic dye methylene blue from industrial waste. The adsorption characteristics and dye removal efficiency of Fe-BDC MOF have been determined by investigating factors such as the effect of contact time, concentration of the dye, amount of adsorbents, and temperature. Up to 94.74% dye removal was attained by increasing the dose of adsorbent and temperature. Maximum 94.74% dye removal was achieved after 24 h, on adding 25 mg of Fe-BDC MOF to the dye solution of MB having a concentration of 5 mg/L. Langmuir, Freundlich and Temkin isotherm models have been used to evaluate the ongoing adsorption. Freundlich adsorption isotherm was found to be best fitted for the adsorption process. Based on pseudo-first-order, pseudo-second-order and intraparticle diffusion kinetic equations, different kinetic parameters have been obtained. Pseudo-second order kinetic model with rate constant (k2) 4.9 × 10–2 g/mg·min, is found to be best fitted for the adsorption of methylene blue on Fe-BDC MOF, indicating that the removal of dye takes place dominantly through the chemisorption process.

Response:

1. The above paper focuses on the synthesis of an iron-based metal-organic framework using a BDC acid. Whereas, this invention involves more than one metal in different ratios, i.e. optimised compositions, and to derive a better efficiency with multiple colouring agents.
2. The current invention has an advantage over other work in the application of the adsorbent material and recovery after use. The designed polymer beads with bimetallic organic compounds give an edge over existing adsorbent materials with easy application and recovery.
3. The methylene blue removed in this paper is up to 5 mg/L (94.74% removal efficiency). Our study targets multiple dye concentrations of 20-25mg/L and claims the same with greater removal efficiency of 95-99 %.

5.6 Paper: Highly Efficient Removal of Dye Pollutants by MIL-101(Fe) Metal-Organic Framework Loaded Magnetic Particles Mediated by Poly L-Dopa

A magnetic Metal-Organic Framework (MOF) composite, MIL-101(Fe)@PDopa@Fe_3O_4, was synthesised as the stable adsorbent for the removal of Methyl Red (MR) and Malachite Green (MG) from wastewaters. A very thin film of 3,4-dihydroxy-L-phenylalanine (L-DOPA) was used as

an efficient and environmentally friendly binder between Fe_3O_4 particles and MIL-101(Fe). Characterisation of MIL-101(Fe)@PDopa@Fe_3O_4 was accomplished by various spectroscopic, microscopic and thermal analysis techniques. Magnetic properties of the composite were studied using by vibrating sample magnetometer (VSM). Influencing factors such as pH, ionic strength, contact time, adsorbent dosage, temperature, and initial dye concentration on the adsorption ability of the MIL-101(Fe)@PDopa@Fe_3O_4 were investigated. The very excellent adsorption capacities (833.33 and 1250 mg/g for MG and MR, respectively) were achieved. Adsorption kinetics, thermodynamics, and isotherms studies indicated that MG and MR adsorption followed the Langmuir isotherm model and pseudo-second-order kinetic model. The Adsorbent was successfully used to remove industrial colours from real textile wastewater. The MIL-101(Fe)@ PDopa@Fe_3O_4 was found to be recyclable for the removal of MR and MG.

Response:

1. The above paper describes the synthesis of MIL-101(Fe)@PDopa@Fe_3O_4 (iron-based magnetic metal organic framework) for the removal of MG, MR.
2. This invention involves more than one metal in different ratios, i.e. optimised compositions and derives a better efficiency with multiple colouring agents. The current invention has an advantage over other work in the application of the adsorbent material and recovery after use. The designed polymer beads with bimetallic organic compounds give an edge over existing adsorbent materials, with easy application and recovery of the adsorbent after use.

5.7 Paper: Synthesis of the Magnetic Core–Shell Bimetallic and Tri-Metallic Metal–Organic Framework Nanocomposites for Dye Adsorption

Bi-metallic and tri-metallic Metal–Organic Frameworks (MOFs) supported on the Magnetic Activated Carbon (MAC) were synthesised for the reduction of Methylene Blue (MB) concentration in the aqueous solutions. The adsorbent nanocomposites were characterised by applying the general tests, including XRD, FTIR, FESEM, TEM, BET, and VSM. The XRD achievements demonstrated that the crystalline structure of MOFs was derived on the MAC by the presented method. The core–shell morphology with nano-scale size of the magnetic carbonaceous MOFs was detected in TEM and FESEM micro-images. The acceptable magnetic strength of the prepared adsorbents was proved by using the VSM analysis. The important operating conditions, including pH and temperature, were also evaluated, while the other parameters were kept constant. The pseudo-second-order kinetic model was matched with the experimental data to show the kinetic behaviour of the multi-component MOFs. The isotherm studies showed that the good agreement between the experimental data with both the Langmuir model and the maximum capacities was calculated to be about 66.51 and 71.43 mg/g for the bi-metallic and tri-metallic nanocomposites, respectively. Regeneration experiments indicated that the fabricated adsorbents have an excellent reusing adsorption capacity, which can be a proper selection for industrial applications.

Response:

1. This paper synthesised magnetic activated carbon (MAC) and three different magnetic MOFs as mono-metallic MOF (Ni-MOF@MAC), bi-metallic MOF (Ni-Co-MOF@MAC), and tri-metallic MOF (Ni-Co-Cu-MOF@MAC). In our study, we have used iron and aluminium to synthesise a bimetallic organic compound which has an optimised ratio of composition and synthesis. The material is neither magnetic in nature nor a composite with a magnetic material.
2. The above material uses magnetic activated carbon synthesised at 800 DEG C and then coats it with the said MOFs, whereas this invention has a simple process to synthesise polymer-bimetal MOF beads. The designed polymer beads with bimetal organic compound give an edge over existing adsorbent materials with easy application in packed bed continuous flow systems and recovering adsorbent after use.

6.0 Overall

The term metal organic framework, bimetal organic framework, is a common standard nomenclature for a material containing a metal/s and organic/s in an ordered structure.

The difference lies in the synthesis method, composition, ratios of each component, temperature, solvent, etc. In this study, the Aluminium-iron bimetallic organic compound was synthesised, and a composite

bead was formed with a polymer. This composite is non-magnetic in nature. The as-formed material is then used to remove multiple dyes and colouring agents in batch and continuous flow mediums.

The claim broadly comprises two parts 1. Material composition and procedure steps to the synthesis of composite polymer beads, and 2. Removal of dye/s (up to 25 mg/L) with this particular material only.

7.0 Bibliography

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