International Journal of Engineering Technology and Management Sciences
Website: ijetms.in Issue: 3 Volume No.7 May - June – 2023
DOI:10.46647/ijetms.2023.v07i03.027 ISSN: 2581-4621

Application of polyaniline-manganese nano-composite for water pollution control

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Abstract
Water resources are currently being contaminated as a result of the rapid rise of industrialization, urbanization, population growth, and climate change. The biggest risk for many nations is a lack of clean, fresh water. The focus and attention of numerous scientists and governmental organizations have recently turned to water purification techniques. For efficient and effective sanitization of water bodies, academics from all over the world are focusing on water purification technologies centered on nanotechnology. Due to their great surface area, high chemical reactivity, excellent mechanical strength, and low cost, nanoscale composite materials offer a significant potential to cleanse water in a variety of ways. Polymer nano-composites (Polyaniline-Mn) have been selected as an effective and economical solution for wastewater pollution treatment. An effectiveness of polymer nano-composites for water purification is provided in this research.

Keyword: Nanocomposite, pollutant, permeability, SEM, TEM.

1. Introduction:

The term "polluted" refers to water that has been harmed by manmade toxins[1]. These contaminants either make it unusable for a particular human use, like drinking water, or significantly alter its capacity to support its biotic ecosystems, like fish. The addition of substances or energy sources that directly or indirectly change the nature of the water body in a way that adversely affects its legal usage is a practical definition of water pollution. Water pollution, also known as aquatic pollution, is the contamination of water bodies, typically brought on by human activity, which has a detrimental impact on the uses of the water. Aquifers, reservoirs, lakes, rivers, seas, and groundwater are all examples of bodies of water. As toxins get into these bodies of water, contamination occurs. Sewage discharges, industrial activities, agricultural activities, and urban runoff including storm water are the four main sources of contaminants. Legislation, the right infrastructure, management strategies, and management plans are all necessary to control water pollution[2]. Improved sanitation, sewage treatment, industrial wastewater treatment, agricultural wastewater treatment, erosion control, sediment control, and urban runoff control are some examples of technological solutions. Due to their precise binding action, nanocomposites are able to remove bacteria, viruses, and both inorganic and organic contaminants from wastewater (chelation, absorption, ion exchange). Metal nanocomposite, metal oxide nanocomposite, carbon nanocomposite, polymer nanocomposite, and membrane nanocomposite are some examples of the nanocomposite materials out of which Polyaniline-Mn nanocomposite having good capacity to control water pollution, that actively contribute to the purification of water.

There are mainly three types of water pollution:

Ground Water Pollution:

Groundwater, one of our least visible but most significant natural resources, is created when rainwater falls and seeps deeply into the earth, filling the fissures, crevices, and porous areas of an aquifer. For drinking water, around 40% of Americans rely on groundwater that has been pumped to the surface of the planet[3]. When contaminants enter an aquifer and make it unsuitable for human use, such as trash leached from landfills and septic systems to pesticides and fertilizers, groundwater becomes contaminated. It can be expensive and difficult, if not impossible, to purge toxins from groundwater fig. 1. An aquifer that has been contaminated might not be useable for hundreds or perhaps thousands of years. As groundwater seeps into streams, lakes, and seas, it can potentially disperse contaminants far from the original contaminating source.

Fig: 1. Ground water pollution

Surface water pollution:

Surface water, which makes up around 70% of the planet, is what gives our oceans, lakes, rivers, and all those other blue areas on the globe their blue color. More over 60% of the water distributed to American houses is surface water from freshwater sources, meaning sources other than the ocean[4]. Farm waste and fertilizer runoff have caused them to significantly increase in pollution. Toxins are also contributed by the discharge of municipal and industrial garbage fig. 2. Additionally, there is all the unorganized trash that businesses and individuals throw directly into waterways.

Fig: 2. Surface water pollution

Ocean Water Pollution:

80 percent of marine pollution, also known as ocean pollution, comes from land, whether it is far inland or near the coast. From farms, factories, and towns, streams and rivers transport pollutants like chemicals, fertilizers, and heavy metals into our bays and estuaries, where they are then transported out to sea[5]. The wind also brings in marine waste, particularly plastic, as does water from storm drains and sewage systems. Additionally, both large and little oil spills and leaks occasionally pollute our waters, which are also continuously absorbing carbon pollution from the atmosphere. Up to 25 percent of carbon emissions caused by humans are absorbed by the ocean fig 3.

Fig: 3. Ocean water pollution

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Effect of Water Pollution:

On Human Being:

Deadly water contamination. You can become unwell from contaminated water as well. Nearly 1 billion people get sick each year from contaminated water. Furthermore, because their residences are frequently located closest to the most polluting enterprises, low-income neighbourhoods are disproportionately at danger. Cholera, giardiasis, and typhoid are a few diseases that can be spread by contaminated water[6] fig. 4. Even in developed countries, sewage treatment plant emissions that are unintentional or unlawful, as well as runoff from farms and cities, introduce dangerous bacteria into waterways.

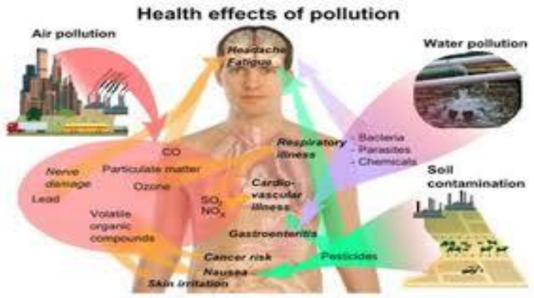

Fig: 4. Hazardous effects on human being

On the Environment:

Marine debris, which can starve, choke, and strangle animals, poses a threat to marine ecosystems as well. Most of this solid waste, including plastic bags and soda cans, is washed into storm drains and sewers before being dumped at sea, turning our oceans into a soup of junk that occasionally clumps together to form floating garbage patches[7]. Over 200 different species of marine life have been harmed by discarded fishing gear and other types of garbage. In the meantime, coral and shellfish are having a harder time surviving due to ocean acidification fig 5. Oceans are growing more acidic despite the fact that they absorb roughly 25% of the carbon pollution produced year by burning fossil fuels. The neural systems of sharks, clownfish, and other marine creatures may be affected by this process, which makes it more difficult for shellfish and other species to form their shells.

Fig: 5. Disturbance of water ecosystem

2. Materials and Method:

The chemicals used such as Ammonia, aniline, ammonium persulphate, manganese dichloride, ethanol, concentrated HCl, aldehyde, diethyl phosphite are of analytical grade, The Distilled water used for experimental work

2.1. Nano-composite: Multi-phase materials called nano composites have at least one phase with diameters between 10 and 100 nm. Nano composite materials have now become viable options to alleviate the drawbacks of many engineering materials. They are reportedly the 21st century's materials. Dispersed matrix and dispersed phase materials are two categories for nanocomposite materials. The nanocomposite are classified on the basis of their contents for example Polymer based and non polymer based Polymer based are classified in to Polyme-polymer, polymer-metal, polymer-ceramic[8]. The non-polymer based are classifier in to Mewtal-metal, Metal-ceramics and ceramic-

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ceramics. Polymer-based nanocomposite (PNCs) have emerged as a significant field of current research and development among various nanocomposites[9-10].

2.2 Methods of preparation-Polyaniline : Here, aniline was oxidatively polymerized. The 0.5 M aniline monomer (99%) solution and the 0.5 M ammonium persulphate (APS) solution were made in two separate beakers using 0.5 M concentrated hydrochloric acid solution. These two were slowly combined while being constantly stirred, and the mixture was maintained in an ice bath for 4-5 hours with the temperature kept between 0 and 6°C, [11] If the powder is not stirred to settle, the dark suspension turns green. This shows that the polymerization reaction began, and that it continued for 10–12 hours at a temperature of 0–6 °C. The result was a paste-like green residue. The finished product was repeatedly cleaned with D.W. and acetone to get rid of the short-chain aniline molecules. The dark-green powder is finally baked at 70°C for 6–8 hours to dry it out. The finished product was ground into conducting PAni, a green powder that was utilised in the following steps of the process.

2.3 Methods of preparation-Nanocomposite : Following the production of polyaniline emeraldine salt (ES), a precise quantity of 0.2 M manganese chloride ($MnCl_2$) solution was carefully and slowly dissolved in polyaniline.[12] The Polyaniline Manganese Chloride Solution was maintained in an R. B. flask and stirred for approximately 3-5 hours using a hot plate and magnetic stirrer (530 RPM). The R. B. flask forms the dark green suspension, and then it is placed in an overnight ice bath. The product was rinsed twice with distilled water and three times with ethanol after filtering. The produced Nano catalyst was heated to 70^{0}C for seven hours.

3. Result and Discussion:

Characterization of nanocomposite:

3.1 Transition Electron Microscopy (TEM 300 Kv)

FEI, Tacna G2, F30, Resolution Point: 2.0 Angstrom Line: 1.0 Angstrom, and Accelerating potential: 300 kV were used to record the HR-TEM (300kV). The TEM images of the synthesised Polyaniline-Mn Nano-catalyst created using oxidative polymerization techniques are shown in the following figure: 6,7 At 100nm, 200nm, and 500nm, the TEM study was performed. The TEM can be used to measure a nanoparticle's size as well as to look at its homogeneity and size distribution.[13] The figure demonstrates the uniform dispersion of Mn particles with a size of 43.16 nm.

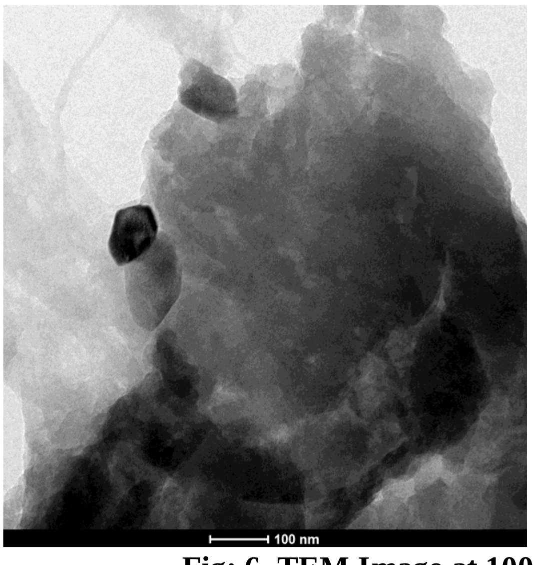

Fig: 6. TEM Image at 100nm

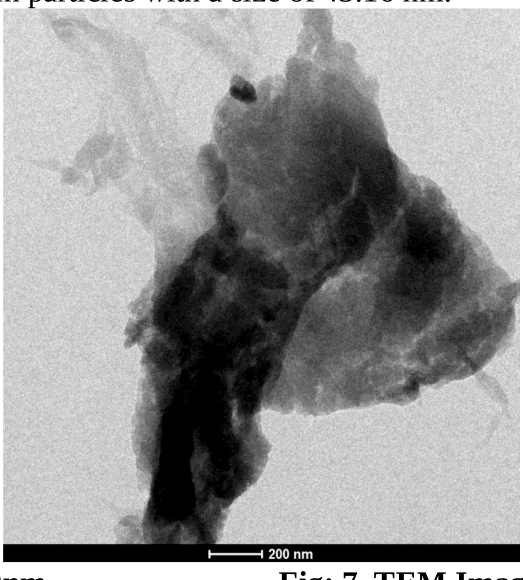

Fig: 7. TEM Image at 200nm

3.2 Scanning Electron Microscopy:

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The JSM-7600F SEI Resolution: 1.0 nm at 15 Kv Field Emission Gun-Scanning Electron Microscopes (FEG-SEM) was used to take the images. In the JEOL JSM - 7600F FEG-SEM, two tested technologies are combined. Determining the morphological traits and surface properties of the compounds is the primary goal of scanning electron microscopy. PANI-Mn Nano-catalyst SEM pictures at various magnifications fig. 8,9. When recording SEM data, the conducting polymers are extremely temperature sensitive. Particles of sizes ranging in the nanometers are clearly characterized, as can be seen from the SEM photos. Because of the high temperature, a polymerization situation is produced in which the interfacial tension lowers as the temperature rises. Polyaniline-Mn Nano rod shape is shown to form. The majority of the particles have a spherical form and are just marginally aggregated.[14] High surface area globular particles are created.

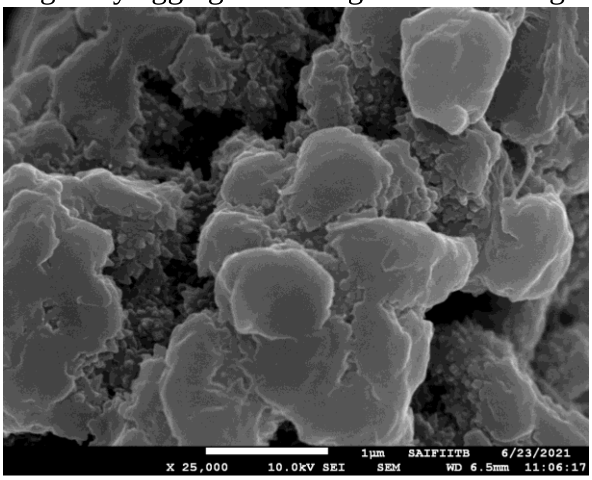

Fig**: 8. SEM Images at 100nm of PANI-MN**

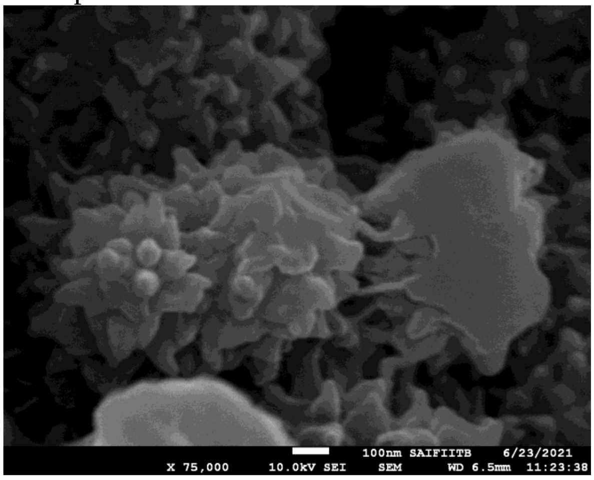

Fig: 9. SEM Images at 1nm of PANI-MN

In order to measure the crystalline size of the Nano-catalyst PANIMn, the oxidative polymerization procedures used to create the Polyaniline-Mn were used to prepare the sample. The FT-IR spectra was used to identify functional groups. By using TEM analysis, the surface morphology and form were examined. Surface structure investigated via SEM analysis. These findings indicated that the Polyaniline-Mn Nano-catalyst had been successfully created.

3.4 Selectivity and permeability: The ability of a membrane to pass fluid necessitates that it be highly porous, extremely thin, and have low channel tortuosity in order to have a high permeability. Selectivity Small, uniform pores and the right surface chemistry are necessary for a high selectivity to separate molecules from the rest of the fluid[15]**.** All membranes almost always tradeoff between permeability and selectivity, with the exception of biological membranes, which, according to their distinct structure and cell regulation, are both extremely permeable and selective. Key membrane characteristics that aid in overcoming the trade-off are appropriately sized pores, a narrow pore size distribution, a thin active layer, and a well tuned interaction between target chemicals and the membrane, according to knowledge of biological and synthetic membranes [16]. The primary target of membrane filtration is natural organic matter, which is made up of a heterogeneous mixture of humic compounds, hydrophilic acids, proteins, lipids, carbohydrates, and hydrocarbons. Membranes used in microfiltration and ultrafiltration only exclude 20–50% of naturally occurring organic materials with mean sizes smaller than 1 nm. However, by size exclusion, reverse osmosis and nanofiltration membranes can block over 90% of organic substances. Individual ion hydration energy is a factor in salt ion rejection. The solute rejection increases with increasing solute hydration. Due to the larger electrostatic repulsion from charged membranes, highervalence ions often have higher rejection rates [17]**.** Selectivity of low-pressure membranes and permeability of high-pressure membranes need to be increased in order to reduce the trade-off relationship. On the basis of fig. 10 it shows that use of nanocomposite.

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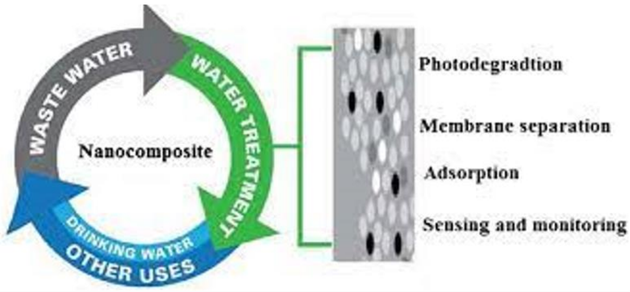

Fig: 10. Use of nano-composite for waste water treatments

3.5 Purification of water using polymer nanocomposites: The use of various PNCs for water filtration is now being investigated. PNCs are used in applications for a variety of reasons, but their distinctive features set them apart from their rivals. Technology for water purification uses a variety of PNCs.

3.6 Techniques for purifying water:

Singh et al. recently studied various water filtration techniques, and these findings are also listed[18]. These approaches are primarily divided into groups based on ways of separation such physical adsorption, chemical deterioration, and biological treatment. Although each method has its benefits and drawbacks, no single technique is effective enough to sufficiently filter the water. Thus, a mix of procedures is advised to ensure adequate water quality. The results of the research have shown that significant efforts are needed to combine various strategies, such as adsorption-biological treatments, to promote biodegradation of dye materials and decrease sludge formation.

3.7 Removing the ions of heavy metals:

Due to anthropogenic sources or geological factors, the majority of surface and ground water are contaminated with several heavy and radioactive elements. The biosphere and food substances have acquired these metal ions. They are also in charge of their biomagnifications and enter the human body through the food chain. Nanocomposites with various hazardous heavy metal ions utilized as adsorbents. The development of economically viable adsorbents for the removal of heavy metals from water and wastewater has been studied by [19]Lim et al. Adsorption, chemical, precipitation, coagulation, flocculation, ion exchange, and membrane filtration are some of the numerous methods used to remove metal. For these processes to produce high-quality treated effluent, suitable adsorbing materials with flexibility in design and operation are necessary. Adsorbents should be regenerate for multiple uses through suitable desorption method at low maintenance cost, high efficiency, and simplicity of operation due to the reversible nature of adsorption process.[20-21] Both physical and chemical interactions take place between the molecules of the adsorbent and adsorbate. In nature, physical adsorption is reversible. While it is challenging to remove the chemisorbed species from the adsorbent surface if the attraction forces are caused by chemical bonding. coupled with adsorption, shares a number of other characteristics. A comparable charged ion bound to an immobile solid particle or composite film is swapped for an ion from solution in the reversible chemical process known as ion exchange. The polymer-based nanocomposite is exceptional at decontaminating metal and comes in a variety of shapes, including candles, mats, membranes, beads, etc.

3.8 Removing the dyes:

PNCs' catalytic capabilities and adjustable surface have a lot of potential for removing dyes, one of the worst pollutants. An alarming water problem and diseases transmitted by water are being caused by the constant discharge of colors into water bodies.[22-24] The majority of dyes have negative impacts on the environment and aquatic life, and they can also induce allergic reactions, dermatitis, skin irritation, and even mutations in people.[25-26]For the elimination of dyes, numerous methods including adsorption, coagulation, filtering, photo, catalytic, and biochemical degradation have been devised. In this context, numerous researchers use polymer nanocomposites for effective dye removal. as dye adsorbents, some significant polymer nanocomposites.

3.9 Removing more contaminants:

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Microorganisms, insecticides, pathogens, and other organic compounds are among the other significant water contaminants. They pose concerns such as the development of disinfection byproducts and antibiotic resistant bacterial species, which has led to the investigation of new disinfection techniques.[27] On direct touch, the nanostructure composite restores cell membrane integrity while killing infections by releasing toxic compounds. They occasionally also generate reactive oxygen species (ROS). Metals have been known to have bactericidal properties since antiquity, but advances in nanotechnology have increased their effectiveness and made it possible to employ them as effective disinfectants. However, using metal particles as a disinfectant also has detrimental effects on health.[28] Although the exact process of disinfection is similarly unknown, it has been suggested that metal atom interactions with DNA base pairs cause hydrogen bonds to break. a cell's DNA molecule.[29] Silver, copper, zinc, iron, lead, aluminium, and gold are a few metals that have shown to be effective disinfectants. Some of them, meanwhile, are hazardous to humans; as a result, non-toxic metals for mammalian cells are utilized instead. Nanocomposite is a potential water decontaminator and substitute for modern chemical disinfectants thanks to the development of nanotechnology.[30] The metal-bound copolymer beads are effective at eliminating a variety of bacterial strains up to 99.9% of them. The microscopic makeup of the polyurethane foam with an Ag coating that is used to purify water.

3.10 Mechanism of Nano-composite to control water pollution:

First, a high surface area nanocomposite is used in the adsorption process. The surface diffusion process occurs on this surface, attracting dye molecules to the nanocomposite's surface area. It should be emphasised that electrostatic attraction, pi-pi interaction, "van der waals" forces, hydrogen bonds, acid-base reaction, and hydrophobic contact are the primary causes of the methyl orange dye's adsorption on the surface of the adsorbent. Out of which the majority of the methyl orange dye adsorption is caused by ion exchange and electrostatic attraction. In electrostatic attraction, SO_3H groups with a negative charge attract an adsorbent surface with a positive charge, and the two are quickly washed away. Ions are exchanged between dye solutions and solid phase adsorbents in the ion exchange mechanism. Following fig. 11 shows the mechanism removal of pollutant from waste water by using Polyaniline-Mn nano-composite.

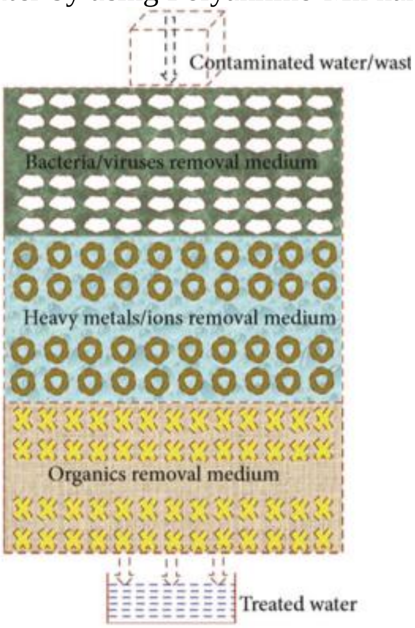

Fig: 11. Mechanism of removal of pollutant from waste water by using nano-composite

Conclusion:

The necessity of the hour and decade is to provide a safer and more secure environment for the next generation. This is owing to the pressure that human activity has placed on nature due to activities like vehicle emissions, climate change, the shrinkage of agricultural area, environmental contamination, etc. The ecosystem is seriously threatened by the chemical and pesticide companies' contamination of the soil and water environment. A review of the literature on nanoparticles has revealed that the special characteristics of nonmaterial's, such as their small size and large surface area, could be effectively used as adsorbents for the treatment of waste sites and water through a variety of processes, including physical and chemical adsorption, complexion, oxidation, and reduction. Bimetallic nanoparticles and surface-modified metal oxide are also employed to boost the photo catalytic activity. Polyaniline-Mn Nano fibrous materials are utilised to treat water and soil borne diseases because of their extraordinarily high surface-to-volume ratio and porosity. Solutions to ensure safe water and soil could be provided by nanoparticles with low toxicity and minimal health hazards, thus ensuring a safer environment.

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