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## Canadian Journal of Scientific Research

### Novel composite materials for water treatment

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#### Abstract

Due to industrialization, water pollution has reached alarming levels, consequently, polymer-based nanocomposites are used to treat wastewater and improve environmental sustainability. The adsorption process is an alternative approach for the removal of pollutants in comparison to other conventional ways of treatment. Polymers provided adaptable characteristics, enhanced processability, amazing durability, a large surface area for rapid decontamination, selectivity to remove various contaminants, and cost-saving water treatment. Magnetic graphene oxide-based nanocomposites (MGOs), which are among the manufactured magnetic adsorbents, have received a lot of interest recently for their successful removal of metal contaminants and dyes from the aqueous phase. The review article discusses natural polymer, synthetic and their modified forms and related uses in wastewater treatment. This review mainly focused on the wastewater treatment using natural polymers and the techniques involved for their extraction from natural sources. The recent trends in polymer extraction from natural sources and the scope for the future research of natural polymers in various sectors are also discussed in detail.

**Keywords:** Polymer composites, Graphene, Wastewater, Nanocomposites, Nanotubes.

*Submitted: 16-06-2024; Accepted: 13-12-2024; Published: 15-12-2024; <https://doi.org/10.66487/5-24-CJSR-1-1-5>*

#### Review article

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#### 1. Introduction

The last few decades have shown a dramatic increase in human population and industrialization that ultimately incases the demand of consumption of freshwater. Hence the water quality is deteriorating day by day because of the heavy metals /dyes (cationic, ionic dyes) that are released from the industries. So as a result, bulk amount of industrial contaminated water is directly discharged into the natural environment and water reservoirs. These dyes or heavy metals are very toxic in nature and highly stable in aqueous environment [1]. These hazardous heavy metals /dyes can enter into the human body through biological food chain and accumulate in the body and cause many diseases including gastric dysfunction, anemia, bone softening and many others. These synthetic dyes /metals have detrimental impact on aquatic organisms as well. These dyes contain chromogenic groups that form a layer on the water surface and does not allow the light to enter the water, hence lower the photosynthesis rate of aquatic plants and disturb the other vital activities of aquatic organisms. Therefore, this polluted water must be treated to remove contamination before discharge into the water streams [2]. Numerous methods, including ion exchange, electrochemical oxidation, Fenton oxidation, reverse osmosis, coagulation/flocculation, zonation, electrocoagulation, biodegradation, and adsorption,

have been developed for the treatment of dye polluted water. These treatments have high removal efficiency but at the same time have many disadvantages like high energy utilization, cost, huge waste etc. [3]. The most frequent adsorbent utilized for this function is activated carbon (AC). When polymers are combined with other natural or inorganic components, a new material is created that has the desired qualities, such as low density, toughness, hardness, thermal properties, chemical and structural stability, or other particular characteristics depending on the intended purpose. Numerous polymer composites, including those based on graphene, carbon, and clay, were developed and are widely used in the water treatment and distillation industries. This overview explains the origin, makeup, and characteristics of these polymers, as well as how they are used to purify water. Based on graphene oxide Due to their distinctive qualities, including high surface area, small size, the ability to modify the surface, excellent conductivity, cost-effective synthesis, and primarily biological compatibility, nanocomposites have drawn a lot of attention and are crucial in separation and purification technology [4].

## 2. Wastewater and its impact on the environment

Nowadays, environmental deterioration is one of the biggest worldwide problems, which has sped up the development of sophisticated technology. One of the biggest contributors to the contamination of natural water sources is the wastewater that results from various industrial activities [5]. Every human community must have access to a clean water supply. The amount of toxic substances entering water sources is dramatically increasing. However, the growing usage of harmful materials has resulted in a significant rise in the load of unwanted compounds in freshwater across the biosphere [6]. Scientists discovered over 700 carcinogenic and extremely hazardous organic and inorganic micro-contaminants as a result of rapid industrialization. These are classified as persistent environmental pollutants that are not biodegradable. Inorganic pollutants that are toxic comprise Cr (VI), Hg, Cd (II), Lead (II), As (V), and others, whereas organic pollutants comprise dyes, paints, and others [7]. Drinking water pollution with hazardous and toxic elements like As (V), F, and a high dissolved solids load is a big problem. The major cause of water-borne illness in children is pathogenic organisms [8]. Both animal and human wastes carrying the coliform bacteria are discharged into water bodies such as rivers and lakes in combination with the inadequate water sanitation infrastructure and drainage channels, resulting in waterborne illnesses. Due to illnesses and a lack of adequate water sanitation systems, 670,000 children leave school each day. Aside from pesticides, other contaminants in bodies of water include trace elements and heavy metals, including zinc, manganese, and copper [9].

### *Natural polymers*

Because of their diverse structural makeup, carbohydrates, plant matter, and bacterial biomass provide a significant supply of natural and monomeric feedstock polymers [10]. Polysaccharides represent the most extensively utilized biopolymers among natural polymers; they are both ecologically nonthreatening and have medicinal uses. Additionally, lignin and cellulose are the two natural polymers found in the highest concentrations on Earth. The majority of polysaccharides come from plants and are made up of at least two monosaccharides joined together covalently by glycosidic linkages [11]. While they are water-insoluble at an environmental pH and are mostly utilised in the food and pharmaceutical sectors, they have a significant potential to absorb water due to their hydrophilic functional groups. In addition, the flexibility of the polymer structure, cross-linking density, and wettability are significant factors that affect how well the polymer nanocomposite absorbs water [12]. After cellulose, chitosan is the second most important natural constituent, and it can be extracted industrially through marine sources in amounts of roughly 1 billion tones. Most biodegradable plastics are produced primarily using this polymer. As a detoxifying agent, anti-inflammatory, and epidermis regenerator in addition to being an adsorbent or ion exchanger and due to its crystalline structure, it demonstrates important characteristics in procuring raw materials, with medical applications [13]. The food and pharmaceutical manufacturers, cosmetics, and the environment. Chitosan is made from the leftovers from the manufacture of fish and

biomass. The semicrystalline starch structure is made up of glucose units connected by glycosidic linkages. [14].

### *Synthetic polymer*

Polymers created by humans are referred to as synthetic polymers. Those substances known as polymers are made up of repetitive structural components called monomers. One of the basic polymers is polyethylene, which comprises ethene or ethylene as such subunit [15]. The linear polymer is referred to as high-density polyethylene (HDPE). The chain-like structures of many polymeric compounds mirror those of polyethylene [16]. Due to environmental concerns, researchers are looking at water-soluble polymers to water purification [17]. In addition to its high conductivity, superior mechanical strength, acceptable biocompatibility, and non-covalent bonding with certain polymers (such as chitosan (CS), poly (N,N-dimethyl acrylamide (PDMAA), etc.), the water-rich GBH resembles real soft tissues. [18].

### *Membrane filtration*

The use of membranes to purify water is a rapidly expanding field of science. Membranes may be categorized as dense or porous depending on how ions and molecules travel through them. The method of membrane filtering produced good results in the removal of heavy metals from wastewater. The fundamental benefit of this procedure is greater removal effectiveness; less area is needed, and operation is simpler. Toxic metal ions have been effectively removed from wastewater using several membrane types, including electrodialysis, reverse osmosis, ultrafiltration, membrane filtration, and nanofiltration. The primary drawbacks of this technology include dealing with the rejection, membrane contamination, and high-power costs, while its key benefits are high efficiency, relatively low energy needs, dependability, and simplicity of operation. General terms, this technique of treatment has been used to successfully treat industrial wastewater sewage, produce drinking water and desalinate saltwater, recover usable components from effluent, and produce salts[4].

### *Adsorption*

Certain elements of a fluid or gas phases are deposited to a surface of the solid adsorbent during the separation process known as adsorption. Many chemical species are removed from wastewater, including heavy metal ions, colours, oils, and soluble organic pollutants. The polyester resins and the particulate fibers from the 800 m sieve were combined in a specific ratio. According to a water absorption test, treated fibers had a lower absorption rate than untreated fibers. Chemical processing of agricultural fibers was found to be appropriate [19]. Adsorbents are typically used as sphere-shaped pellets, rods, moulds, or rock formations with hydrodynamic diameters between 0.5 and 10 mm. They also need to be highly heat stable, have small pores, and have strong abrasion resistance in order to have a wide exposed surface area[20].

### 3. Recent advancement in polymer composites

#### 3.1 Polymer- clay composites

Composites of polymer-cationic clay for desalination and water treatment. As a new pollutant adsorbent with responsiveness to pH, a polymeric grafted clay composite made of montmorillonite, Cationic clay, and polyvinyl pyridine, a stimuli-responsive polymer, was created. The modification of clay to form clay nanocomposites by sonication of polymer (as illustrated in Fig.2.). A higher polymer dosage without polymer leaching, a decreased pH/charge dependence, and a zeta potential were among the notable properties of the composite structure. In compared to commercial adsorbents, its improved characteristics accounted for the substantial performance towards the removal of the inorganic and organic contaminants. The stimuli-responsive polymer specifically absorbed protons at low to intermediate pH levels, which improved the adsorption of contaminants.

#### 3.2 Polymer carbon composites

Due to its distinctive morphological, electronic, optoelectronic, semiconductor, mechanical, chemical, and physical capabilities, carbon nanotubes (CNTs) have attracted attention as a highly prospective adsorbent. They have also been widely used to eliminate heavy metals in wastewater treatment [21]. CNTs are made up of a single layer of carbon atoms which are rolled into hollow, smooth tubes with a diameter of roughly less than 1 nm. They are just one atom thick. The exceptional mechanical, compressive strength, and electrical features of CNTs have been shown to make them a fantastic candidate for a variety of technological applications. Single-walled carbon nanotubes (SW-CNT) or multi-walled carbon nanotubes (MW-CNT), that differ by the number of carbon-based atom cylinder arrays stacked around the hollow nanotube core, are the two forms of carbon nanotubes that have been created and investigated in great detail since the 1990s. Depending on the atomic arrangements of the nanotube cylinders, the characteristics of the two different forms of CNT differ. In general, CNTs are potential candidates for a variety of applications in microelectronics, the biomedical field, and composite repetition in polymers due to their unique structural and functional characteristics, such as electrical conduction, high aspect ratio (i.e., length to width), and extremely small size[22].

#### 3.3 Core-shell nanomaterials

NPs are frequently comprised of multiple layers, including material's core, which is the substance's central portion, the thin layer, which may be branched of various small moieties, flocculants, metal ions, as well as polymeric branches, and also the shell coat, which is made of a material that differs from the core's material. Core-shell nanostructures come in a variety of forms, such as those with a metal core (a single sphere or an assembly of multiple tiny spheres) and a shell

### 4. Applications of carbon nano tubes in wastewater treatment

Particularly as potential possibilities for water filtration, CNTs-based membranes have drawn a lot of

interest. However, due to their adsorption or removal capabilities, CNTs membranes are largely used for water treatment, where membrane contamination and performance restoration are the main challenges. According to reports, the engineered adsorptive CNT-based membrane might overcome the drawbacks of traditional CNT-based nanocomposites or membranes, enabling the removal of micropollutants in a very efficient manner [23].

Compared to single-walled nanostructures, MWCNTs are more often employed in a variety of applications. With the aid of an external magnetic field, the created magnetic modified MWCNTs may be simply peeled off and conveniently spread in the water phase. The use of magnetically modified CNTs for various pollutants found in water sources is now under consideration. Lists various research works carried out to remove heavy metal ions or dyes using magnetic carbon nanotubes, however few studies have been noticed addressing the connection with magnetic modified CNTs and pollutants that occur in wastewater [24].

### Graphene based polymer composites

#### 4.1 Nanoporous Graphene Oxide membranes

Nano pores are created artificially on the surface of GO (Graphene oxide) sheets for the nanotubes GO (Graphene oxide) walls to allow molecules, ions, or atoms smaller than that of the nanoporous can pass through. The high-density and sub-nanometer holes with in nanoporous graphene membranes were achieved using ion irradiation-oxidation etching procedures. The findings showed that when the oxidation etching time was extended, the number of nanopores steadily rose and then stabilized in the range of 0.40 to 0.24 nm. Electrostatic repulsion and size sieving are two components of the separation mechanism. Through the use of ion irradiation-oxidation etching procedures, the nanoporous graphene membranes were created having high-density and sub-nanometer pores. This nanostructured GO membrane was approved to let salt ions to pass through the membrane. In comparison to other materials, the nanoporous GO sheets displayed exceptional water permeability due to their ultra-thin permeability and distinctive pore shape [25].

#### 4.2 Properties of Graphene Oxide

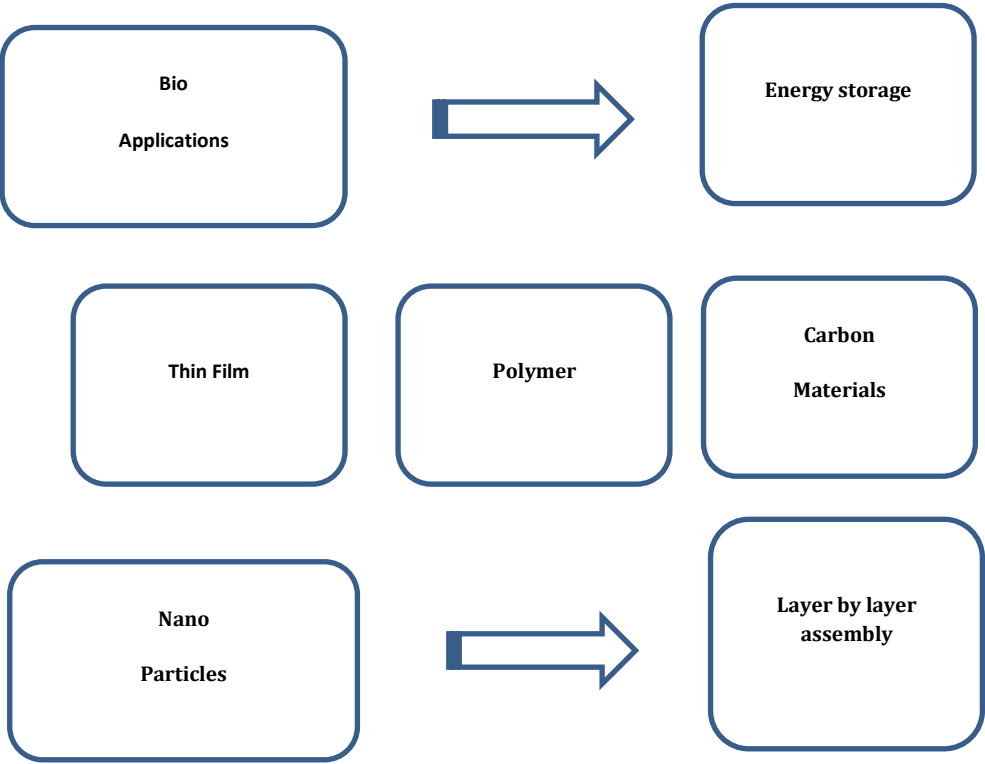
The thermoelectric, electrical, and mechanical characteristics of polymers in its composite can be improved by graphene. To accomplish the required use, graphene needs to be evenly distributed throughout the polymer medium.

### 5. Electrical properties

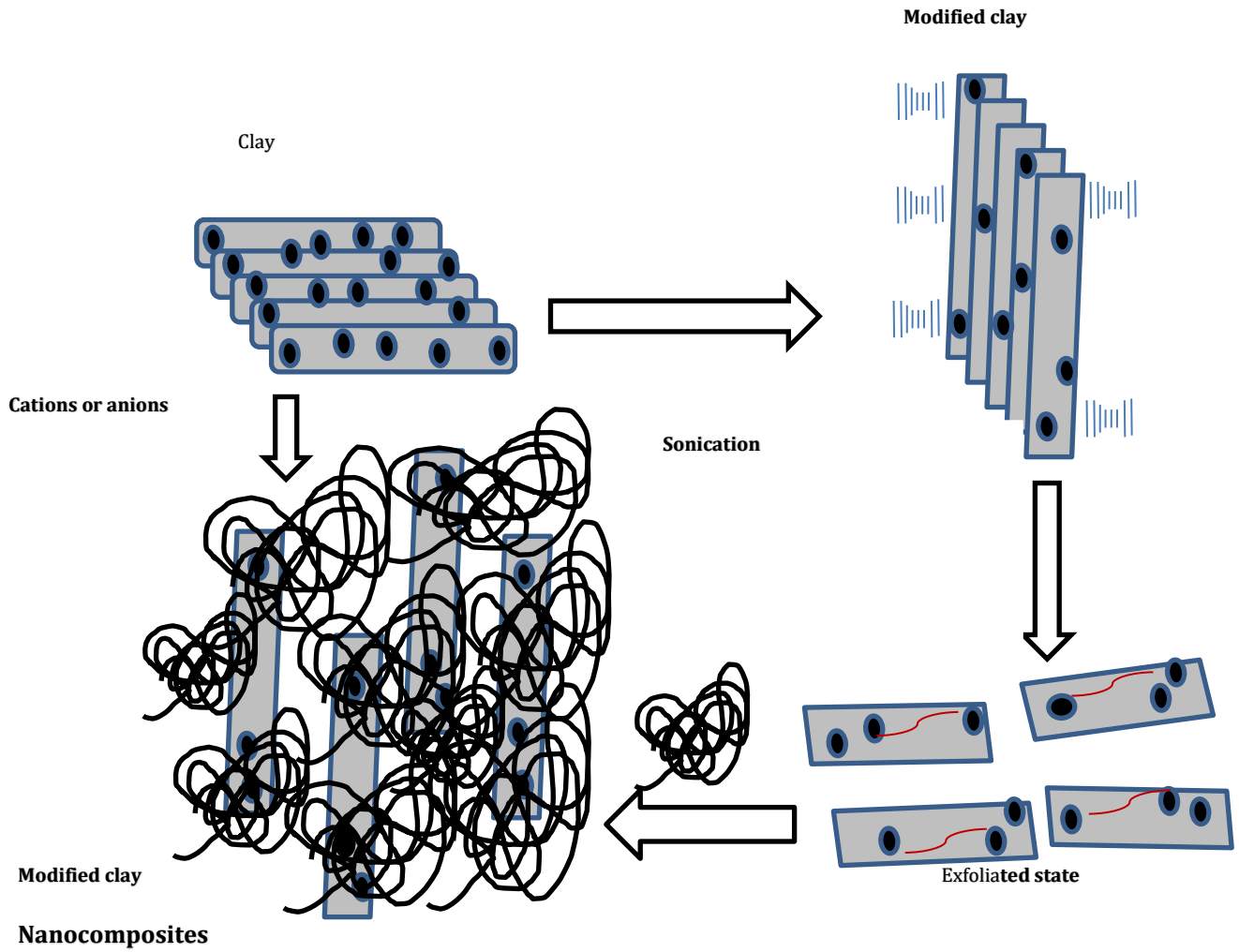
To increase the photocatalytic activity, graphene-based composites with different metals, metal oxides, or their nanoparticles are exploited [26]. The decomposition of methylene blue using photo catalysis with composites of graphene and ZnO nanorods was shown to be enhanced with reduced photo corrosion [27]. It is due to the synergistic interaction between the efficient hybridization at the interface between ZnO nanorods and graphene and the extended lifespan of excess electron-hole pairs produced by photons [28].

**Table1:** Extraction methods of polymers and their application in wastewater treatment.

| Natural Polymers | Extraction/Synthesis method                                                   | Treatment Technology         | Removal Percentage |
|------------------|-------------------------------------------------------------------------------|------------------------------|--------------------|
| 1. Cellulose     | Alkalization, bleaching, Acid hydrolysis process                              | Adsorption                   | 95.90%             |
| 2. Starch        | wet milling process and alkali method                                         | Flocculation                 | 94.00%             |
|                  | Water bath heating method                                                     |                              |                    |
| 3. Pectin        | Mechanical process of roasting, differential attrition, sieving and polishing | Coagulation and flocculation | 54.20%             |
| 4. Gums          |                                                                               | Adsorption                   | 45.00%             |
| 5. Hemicellulose | Maceration                                                                    | Coagulation and flocculation | 70.00%             |
|                  | Pulsed Electric field extraction                                              |                              |                    |
| 6. Tannin        |                                                                               |                              | 95.40%             |
| 7. Inulin        |                                                                               | Coagulation and flocculation | 89.00%             |
|                  |                                                                               | Flocculation                 |                    |



**Figure 1:** Process of synthetic polymer



**Figure 2:** Schematic diagram showing synthesis of nano clay polymer composite

## 6. Mechanical properties

Mechanical qualities of graphene oxide across various conditions and circumstances are referred to as mechanical properties. These qualities also include yielding stress, rigidity, toughness, brittleness, ductility, and intrinsic strength. According to research, decreasing energy stability and the dissolution of the sp<sup>2</sup> carbon network of graphene oxide caused a monotonic decline in intrinsic strength and young's modulus, which caused the band gap to further widen during uniaxial tensile strain. Graphene oxide exhibits homogenous stress distribution, having stiffness and strength measured at 40GPa and 120Mpa, respectively [29].

## 7. Thermal properties

The term "composite" refers to a solid substance made up of many phases, at least one of which has dimensions less than 100 nm or a structure with a nanoscale repetition spacing between the phases. When creating composite structures, physical dimensions within nanoscale range are always used. A composite can have a variety of features thanks to the mixing of numerous materials, including flexural strength and water sorption [30].

## 8. Mechanism of graphene oxide nanocomposites

This section discusses three nanocomposites, including iron oxide-graphene oxide, tungsten oxide-graphene oxide [31]. Nanocomposites based on graphene oxide frequently display comparable performance in the treatment of water [32].

### 8.1 Preparation of graphene oxide

Graphite, which is used to make GO, can be chosen from both natural and artificial sources. It is made up of polycrystalline particles or granules. The most prevalent source of natural graphite is employed in a variety of applications that need chemical alterations [33]. Natural graphite can act as a seeding site for chemical reaction processes because it has multiple localized flaws in its – structure [34]. There are two primary processes in the preparation process; see. First, graphite powder is oxidized to create graphite oxide, which may be easily dispersed in water or another polar solvent because it has hydroxyl and epoxide groups distributed across the basal planes and carbonyl and carboxyl groups at the margins [35]. Second, by sonicating the bulk graphite oxide, monolayer, bilayer, or few-layer GO sheets can be suspended colloidally in a variety of solvents. The crucial step in making GO is choosing the right oxidizing agents to oxidize the graphite [36].

## 9. Characterization of Graphene Oxide

Various techniques may be used to investigate the structures and surface features of graphite oxide and GO (graphene oxide) in detail. Exploring the chemical characteristics of GO may be done very well using solid-state <sup>13</sup>C nuclear electron microscopy (NMR) [37]. Lerf employed this method to develop the GO structural model that is the most widely recognized. It implies that GO's structure consists of aromatic sections with chemically pure benzene rings and parts with aliphatic six-membered chains that

include hydroxyl, epoxide, carbonyl, and carboxyl groups [38].

## 10. Applications for Composites Made of Graphene Oxide

Water Treatment in a recent work, sodium alginate and graphene were mixed to create a nanocomposite adsorbent. A larger free volume, superior separation performance, and a high permeate flow were all displayed by the composite [39]. The design of the hybrid's water channels was well-aligned masonry and brick. The hybrid's structural flaws and free volume cavities have contributed to the water channel's selectivity and permeability in a related work, a nanomembrane for ultrafiltration was created by grafting a temperature-responsive polymer called poly (N,N-2-ethyl amino ethyl methacrylate) with graphene oxide [40]. The poly (N,N-2-ethyl amino ethyl methacrylate) used in this composite caused stimulation to carbon dioxide and argon, resulting in a regulated hole size within the membrane. Poly (N,N-2-ethyl amino ethyl methacrylate) polymer's amine group engaged in a reaction with carbon dioxide in aqueous, protonated, and then deprotonated when argon was introduced to the medium [41]. The cast membrane's separation capabilities changed as a result of this alteration in the polymer's morphological form. Rhoda mine-B and methylene orange dyes were tried to see if the nanofiltration membrane would reject them [42]. These two dyes had average rejection rates of 98.9 and 96.5%, correspondingly. The polymer nanocomposites are natural materials with cheap costs that are employed as adsorbents for several micropollutants [43]. They have interlayered ions in solution or cations and either a positive or a negative layered structure. Many factors, including as porosity, pore volume, and particle shape, affect the utilization of materials as adsorbents. Clays' low wettability and pH dependency are primarily their limitations as adsorbents [44]. To address these issues and enhance their performance in the selective removal of organic and inorganic pollutants from aqueous environments, clay composites were proposed. Clays were employed as fillers or host matrixes to store polymers and enhance their mechanical qualities [45]. Due to their wide range of porous patterns, increased surface areas, lightweight weight, great durability, enhanced flowability, and good selectivity for different contaminants, cost effectiveness, and nearly zero damage during regeneration for reuse [46]. In the field of water treatment, polymer-clay composites have attracted interest. They also gave instructions on how to quickly clean up after using water supply. Polymer-clay composites can be made in a variety of ways, such as exfoliating, coating/wrapping, coagulants, intercalation, or coating/wrapping [47].

## 11. Conclusions

As demonstrated in this study, when mixed with various adsorbent materials, such as carbon-based materials, clays, and other polymers, both natural and manufactured polymers demonstrated exceptional adsorptive capabilities. Research on polymer composites paved the way for a path toward pollution-free environments. A polymer composite structure showed rapid and simple manufacturing, robust mechanical performance, and additional active affinity for organic pollutant adsorption. Extensive research was

conducted to alter the polymer architectures in order to obtain superior adsorption ability, durability, and selectivity of diverse organic and inorganic pollutants. Despite all the research papers that have been studied, polymeric materials for water purification and desalination have not yet performed to their full potential, especially when it comes to the mass manufacture of these adsorptions. The following are the views for achieving the best performance from the adsorbents:

1. Developing low-cost methods to combine Nano adsorbent materials with biosorbent carriers.

2. By researching innovative functional materials or creating hybrid technologies, more functional groups may be added that can boost adsorption effectiveness.

3. Finding additional agricultural wilds to use as adsorbents to lower manufacturing costs and maintain the adsorbent-based business. Mechanisms for chemisorption Reduction and oxidation Electrostatic interaction Complicating or chelating Ionic transfer.

4. Numerous Review of Chemistry, Detailed study of the adsorption process is necessary to understand the theory behind adsorption behavior and, as a result, to improve the effects of different adsorbents in a variety of contexts.

5. Increasing the biomass resources' capacity for recycling and pretreatment before being employed as adsorbents; selecting the organic compounds produced on the adsorbents and improving the selectivity of the adsorbents; decreasing the operational costs to use adsorbent materials on a broad scale, which may be done by offering novel ways to remove pollutants.

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