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Polymer-Clay Nanocomposites and Composites: Structures, Characteristics, and their Applications in the Removal of Organic Compounds of Environmental Interest

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Abstract

Nowadays, many organic contaminants, some of them byproducts from other types of reactions such as dyes or phenolic compounds, or even endocrine disruptors, pharmaceuticals, and personal care products, have been detected in wastewater. Most of them are not controlled and, possibly, can cause harmful effects in aquatic life at environmentally significant concentrations. It is noteworthy, that conventional wastewater treatment plants are not always effective for the removal of these classes of pollutants and so further water treatments are necessary. Therefore, many processes have been investigated for advanced treatment of these effluents as well as for organic pollutants degradation; among these, adsorption process has been used to remove them from wastewater. In addition, there has been a considerable development of new materials with interesting properties, both at large scale and at micro- or nanoscale. Some of these materials are more efficient than others, due to their dimensions in these latter scales, in different kind of applications; specifically, in the field of water treatment. This review is a brief survey of the main characteristics, structures, advantages and recent advances on polymer-clay composites (PCC's) and polymer-clay nanocomposites (PCN's), for environmental applications. In the first part are included some basic concepts: composite materials have components with contrasting yet complementary properties; e.g., organoclays which serve as reinforcement of polymeric matrices and give them a larger contact surface and greater mechanical strength. In particular, PCN's are materials that are used in different applications, for instance to model the morphology of partially crystalline polymers, to remove pollutants from water effluents, to employ them in adsorption processes from water streams, etc. Finally, in the second part, some of developments in the synthesis and applications of these novel materials are discussed; in particular, applications on the field of water pollutants removal through the adsorption process.

Introduction

Water pollution by chief contaminants, such as organic compounds, is of major interest due to their high toxicity and persistence into the environment. For example, endocrine disruptor compounds, pharmaceuticals, personal care products, dyes and pigments and some byproducts of another reactions are persistent and bioactive contaminants, also known as emerging pollutants, continually introduced into the aquatic environment through different sources, which can result in toxic and adverse effects on aquatic organisms and consequently on humans. Some techniques exist to remove these and other micropollutants from water and industrial wastewater: chemical precipitation, conventional coagulation, reverse osmosis, ion exchange, electrodialysis, electrolysis and adsorption. From all of the cited before, adsorption is an economic technique that removes these organic pollutants from water. Nonetheless, it is important to consider the main drawbacks of the adsorption process, which are the regeneration costs, particularly if thermal process is implemented, the type of adsorbent for the treatment of a specific wastewater effluent and also the type of pollutants present in these wastewaters.

One possible strategy to resolve these disadvantages, for example, is the use of clays or clay minerals, polymers and/or activated carbon, which have played an important role in the removal of these organic compounds stated before. Particularly, clay minerals have received a great deal of attention due to their large specific surface area, cation exchange, low cost and toxicity. The adsorption of organic molecules to these minerals is affected by different considerations, such as the exchangeable cations, the distance between the clay mineral layers, and the existence of water molecules between the layers.

In the case of polymers, they are considered multipurpose materials, basically due to their advantageous properties such as easy manipulation, simple production and flexibility. Nevertheless, in some cases, polymers need to be altered in order to fulfill certain performance requirements. One methodology to modify polymer properties is to mix them with solid fillers, such as fibers, platelets, particles, other polymers, clays or clay minerals, resulting in polymeric composites or blends. A composite could be defined as a mixture of two or more materials possessing different physical and chemical properties with a very distinct interface. For composites, it is generally necessary to use a weight fraction of fillers in order to realize significant improvements in their properties. However, this presents both technical challenges and cost implications. Accomplishing property improvement in composites is one of the most important necessities to maximize the overall area of the interface between the matrix and the filler. In this sense, nanotechnology, which involves fillers in the nanometer scale, offers an attractive alternative. Under such conditions, the filler and polymer

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could be in intimate contact almost at the molecular level, possibly yielding substantial improvements in system properties. The possible property improvements could affect thermal, mechanical, electrical, flammability and barrier performance, with only small changes in density and optical properties.

This review covers the various PCN's that have been used as adsorbents for organic pollutants removal. Also, it discusses the synthesis of these materials used as an alternative for the adsorption processes.

Polymer Composites and Nanocomposites

Polymer composites (PC's) consist of different types of short or continuous fibers bound together by an organic polymer matrix. These are often divided into two categories: 1) reinforced plastics and 2) advanced composites. This difference is based on the level of the mechanical properties, for instance, strength and stiffness. Some advantages of these compounds are their lightweight coupled with high stiffness along the direction of the reinforcement. They are constituted of two phases: the continuous phase called matrix, and the dispersed phase that is mainly called as the reinforcing phase.

On the other side, nanotechnology refers to matter manipulation at atomic or molecular scale using nanoscale matter and structures, which can range from 1 to 100 nm. Due to their size, materials present physical and chemical properties that make them unique, such as surface area, volume and the high interfacial reactivity ratio they have. The increase in nanocomposite synthesis has so far shown its versatility, particularly in the science and technology of polymers, fundamentally in applications such as improving barrier properties, flame resistance, optoelectronic properties, cosmetic applications, bactericides and specially water pollution removal [1-3].

Nanocomposites consist of matrices of different materials, which can be polymer, metal or ceramic, and to which is added the charge, e.g., multiwalled carbon nanotubes, activated carbon, reduced graphene oxide, natural clays, graphene-like materials etc., that gives new properties to the material, which helps in a specific application. Among these types, polymeric ones have proven to be the most versatile for their application in several research fields like engineering, building, optoelectronics, medicine, and environmental remediation, in particular removing water pollutants. Overall, nanocomposites have better adsorption capacity, stability and selectivity than other materials in nanometric scale.

Constituents of polymer nanocomposites

As it has been previously stated, PCs can be defined as polymers that have been filled with natural or synthetic compounds to improve their properties. In some other cases, the filler has been incorporated to reduce the cost by acting as a diluent for the polymer, Trindade et al. [4]. In this context, the polymer is called "matrix"; if the filler is in the nanometer range, the composite is called "nanocomposite". These nanocomposites consist mainly of three components, whose characteristics will be described below:

Matrix: The properties of the matrix determine the resistance of the polymeric nanocomposites in most degradation processes, which eventually cause structural failure. These processes include impact damage, delamination, water absorption, chemical attack and deformation at high temperatures. It is because of this, that the matrix is generally the weakest link in the structure of these materials. Thus, according to the resistance of the nanocomposite matrix to the degradative process that can cause a failure of the structure, it can be classified as follows:

Thermostable: Among the matrices in this category are polyester, vinylester, epoxy, bis-maleimide and polyamide resins. Thermostable polyesters are used in fiber-reinforced plastics, whereas epoxy resins have the biggest advanced composite market. The viscosity of these resins is low; however, thermostable resins suffer chemical reactions that intersect the polymer chains, so the matrix is connected in a three-dimensional network. This process is known as curing. Thermostable polymers, due to this intersected three-dimensional structure, tend to have high dimensional stability, high temperature resistance and good resistance to solvents. Considerable progress has been recently made to improve the tenacity and maximum operating temperature of thermostable polymer nanocomposites.

Thermoplastic: Thermoplastic resins, sometimes called engineering plastics, include some polyesters, polyetherimides, polyamide-imides, polyphenylene sulfurs, polyether ether ketones and some liquid-crystalline polymers. They consist of molecules that melt in a viscous liquid at process temperature, usually between 533 and 644 K, and once formed they cool until an amorphous, semi-crystalline or crystalline solid is formed. The degree of crystallinity has great effect in the matrix's final properties. Unlike the curing process, the process of synthesis of thermoplastics is reversible, since when it is reheated to process temperature, the resin can be synthesized in any other desired form. Although thermoplastics have lower temperature resistance and chemical stability, they are more resistant to cracking and impact damage. However, recent advances in thermoplastics synthesis, such as polyether ether ketones, which have a semi-crystalline structure, present excellent resistance to high temperature and solvents.

Moreover, depending on their application, polymer matrices used in nanocomposite synthesis are classified as: general use polymers, engineering plastics, conductive polymers and biodegradable polymers.

General use polymers: These polymers represent the majority of the total production of plastics in the world and are characterized by its use in low-cost applications and generally have low mechanical performance. That is why nanocomposite synthesis with this kind of polymer aids in improving its properties and potentiates its applications. Examples of these are poly(vinylchloride), polyethylene, polypropylene, etc. [5-7].

Engineering plastics: These are materials which can be used, as their name indicates, in engineering applications; to mention a few, structural and equipment parts, as substitute parts, especially metal, due to their better mechanical and chemical properties in relation to general use polymers. Examples of this type of matrix are polyamide and polysulfones [8-10].

Conductive polymers: This type of polymer, also known as synthetic metals, have electric, magnetic and optical properties which can be compared to those of semiconductors. They are also called conjugated polymers because they present conjugated C=C links in their main chains, which allows for the creation of an electron flux under certain conditions. The conductivity of this kind of polymer depends on the polymer chain order at the moment of synthesizing the nanocomposite. Examples of this are polyaniline and poly(ethylene oxide) [11,12].

Biodegradable polymers: This type of polymers, when subject to a certain microbial activity, present cut-off chains. To obtain an optimal biodegradability of the polymer, certain specific conditions are needed, such as pH, humidity, or the presence of some metals. Biodegradable polymers can be obtained from natural sources like corn, cellulose; or sources derived from petroleum or a mixture of petroleum and biomass. An example of this is polyhydroxybutyrate [13].

Filler: Fillers in nanocomposites, also known as charge or

reinforcements, are responsible for their high resistance and rigidity. It is precisely this constituent that is found at nanoscale. Some of the most important composites used are: exfoliated clays, carbon nanotubes, carbon nanofibers, exfoliated graphite (graphene), nanocrystalline metals and some nanoscale inorganic fillers or modified fibers. Of all these fillers, exfoliated clays produce important advantages in the mechanical properties for the modification of polymeric systems [14-16].

Clays: Clays study does not just involve the material, but also the interaction with their environment. This interaction results from the influence of the environment over the clay; for instance, the acid/base character (pH and ionic strength) and the thermodynamic conditions (pressure and temperature) of the surrounding environment. Furthermore, the interaction between clay-like minerals and other composites in the environment can occur in different states of matter (solid, molten solid, liquid, gas and plasma). Therefore, its study is related to the classic disciplines of physics and chemistry of solid and liquid states, as well as developing disciplines in the science of the molten and plasma states.

The main characteristic of clays is that they are studied by many disciplines for basic and applied research. By studying the same sample through different techniques, very important and valuable information is obtained in a very interesting research area, mainly due to the fact that clays are abundant, easily obtainable and very cheap when compared to other materials.

In the particular case of PCN's, clays promote very important technical advantages such as improvements in: i) mechanical properties, ii) barrier properties, iii) thermal properties, iv) degradative properties, v) flame resistance, and vi) rheological properties. To mention but one example, clay can increase the glass transition temperature (T_g) of a polymer, which positively affects the heat distortion temperature.

Interface: The interface in PCN's is the region in which loads are transmitted between the matrix and the filler. The degree of interaction between them is a variable that depends on the nanocomposite's design, and it can range from very strong chemical links to very weak friction forces. This can be controlled by using an appropriate covering in the reinforcement fibers. Generally speaking, a steady interfacial bond makes the polymer nanocomposite stiffer, but brittle. On the contrary, a weak bond decreases stiffness, but enhances toughness. If the interfacial bond is not at least as tough as the matrix, debonding can occur at the interface under certain loading conditions. To take full advantage of the fracture toughness of these nanocomposites, the most necessary coupling occurs between the strong and weak limits. The character of the interfacial bond is also critical to the long-term stability of the nanocomposite, playing a crucial role in environmental behavior, fatigue properties, and resistance conditions.

Polymer-clay nanocomposite synthesis

As it has been stated before, nanocomposites are made of a matrix and reinforcement. The support is a polymer formed by a carbon chain and different types of functional groups bonded to it, which can confer a hydrophobic character to the structure. On the other hand, clay-fillers are usually hydrophilic, which at first sight would make it seem like there is a chemical incompatibility between them, so optimizing clay dispersion and inserting polymeric chains is a necessity in these materials in order to obtain a nanocomposite. A possibility for realizing this is through organic modification of clay which decreases its hydrophilicity, or by using a compatibilizing agent inside the polymer structure; i.e., performing a graft to increase its polarity.
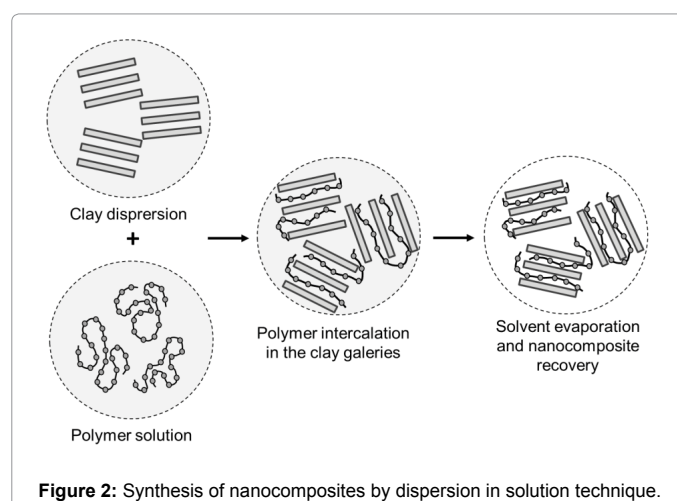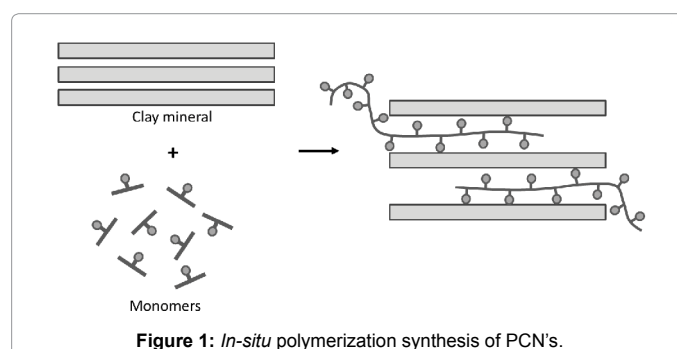
In situ **polymerization:** In this type of PCN's synthesis, the monomer is used as a mean for the dispersion of the charge (clay) and some favorable conditions are set to realize the polymerization between its layers. As clay has greater surface energy, it performs an attraction to monomer units inside its galleries until balance is achieved and polymerization reactions occur between layers with lower polarity, shifting the balance and then having as an objective the diffusion of new polar species between layers, Figure 1.

As an example, Baniasadi et al. [17] used this method to obtain exfoliated polypropylene-based nanocomposites using a bi-supported catalyst. Nonetheless, *in situ* polymerization is limited because a suitable monomer-silicate solvent system is not always available and compatible with current polymer-process techniques.

Dispersion in solution: In this method of synthesis, clay is exfoliated in single layers using a solvent in which the polymer or prepolymer is soluble. The clay's layers can be easily dispersed in the solvent through the increase of entropy due to the layers' disorganization, which exceeds the laminates' organizational entropy value. Afterwards, the polymer is embedded into the delaminated layers and when the solvent is evaporated or the mixture is precipitated, the layers merge with the polymer as filler, Figure 2.

This technique is especially employed with water-soluble polymers. For example, polyvinyl alcohol (PVA) used by Strawhecker and Manias [18], poly(acrylic acid) employed by Billingham et al. [19], and poly(ethylene oxide) by Malwitz et al. [20]. That is due to the polarity of these polymers, which is believed to contribute an enthalpy gain helping intercalation. Therefore, the main requirement of this method is that the chosen polymer should be compatible with the chosen solvent. Remarkably, this method produces a high degree of intercalation only

Figure 1: *In-situ* polymerization synthesis of PCN's.

Figure 2: Synthesis of nanocomposites by dispersion in solution technique.

for specific polymer/clay/solvent systems, suggesting that for a given polymer, one has to find the right clay, organic modifier and solvents.

Intercalation in molten state: In this technique, developed by Vaia et al. [21], the clay is mixed with a thermoplastic polymer matrix in its molten state, Figure 3. Under these conditions, the polymer is taken to the space between the layers forming a nanocomposite. The driving force in this process is the enthalpic contribution of the interactions between polymer and clay, which in this case fulfills the functions of the nanocharge.

Particularly, this method is very attractive, since is the most flexible and environmentally benign from all the existing methods of preparing PCN's. Nanocomposite synthesis comprises compounding and annealing of a mixture of polymer and clay above the melting point of the polymer. During compounding and blending, the polymer melt diffuses into the cavities of the clay. Hence, it allows the processing of PCN's to be articulated directly from the precursors without using any solvent but conventional compounding devices such as mixers and/or extruders.

Some used polymers are polycaprolactone, [22] thermoplastic polyurethane [23], and ethylene vinyl acetate [24]. Also, Wan et al. [25] investigated the effect of silicate modification and montmorillonite (MMT) content on the morphology development, relaxation behavior, and mechanical properties of the poly(vinyl chloride)/montmorillonite (PVC/MMT) nanocomposites. In a similar way, Cabedo et al. [26] prepared ethylene-vinyl alcohol (EVOH) nanocomposites, incorporating kaolinite, by this process.

Between some advantages of this method of synthesis is that this approach does not use any organic solvent, and it is compatible with current industrial polymer extrusion and blending processes. However, some disadvantages presented by intercalation in molten state are that forms microcomposites at higher clay loading as a consequence of clay agglomeration. Moreover, this technique uses thermoplastic polymers, which are normally hydrophobic, and this restricts the application of nanocomposites in water treatment.

Environmental Applications of Polymer-Clay Nanocomposites

Possibly, one of the most intensely studied applications of PCN's is the removal of inorganic contaminants from aqueous solutions. However, PCN's have also been intensively used for the removal of organic pollutants from water. For instance, dyes and pigments, pharmaceuticals and personal care products, surfactants, pesticides, herbicides, different industrial additives and several chemicals, claimed to be endocrine disrupter, are not metabolized and discharged into drains and wastewater treatment plants. For most organic

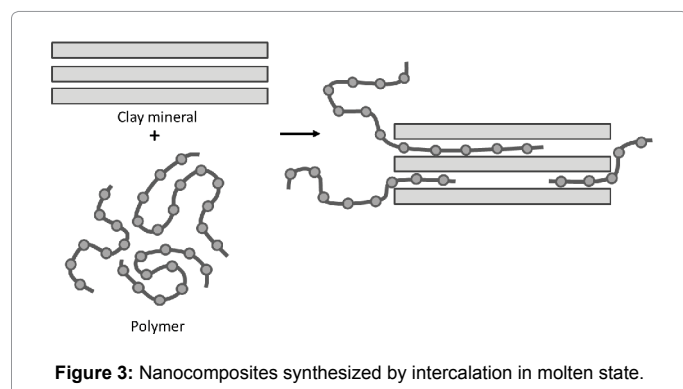**Figure 3:** Nanocomposites synthesized by intercalation in molten state.

contaminants, incidence, risk assessment and ecological-toxicological data are not available, and it is hard to predict their fate in the aquatic environment. The reason for this is a lack of analytical methods for their determination at trace concentrations. Analysis of organic contaminants is a real analytical challenge, not only because of the variety of chemical properties of these compounds, but also because of their low concentrations (usually at part per billion (ppb) or part per trillion (ppt) levels). In addition, these compounds have received little attention because they are not on regulatory lists as environmental pollutants. However, today analytical methodologies for different groups of organic contaminants are being developed, and a rising number of methods are reported in the literature. Recent studies have demonstrated the great amount of research made in the field of water treatment on three main types of pollutants: organic dyes and pigments, phenolic compounds, and emerging organic contaminants such as herbicides, pesticides, pharmaceuticals and endocrine disruptor compounds.

Mainly, we are citing three types of water pollution: 1) contamination due to the discharge of untreated or partially treated industrial dye wastewaters into the ecosystem. This problem has been reported by Akar and Uysal [27]. Furthermore, in several industry processes, such as textiles [28,29], leather, rubber, paper [30], plastic and so on, the incorporation of dyes are one of the most polluting industrial processes because they produce enormous quantities of colored wastewaters. As it has been previously reported by Rafatullah et al. [31], in addition to their color, some of these dyes could degrade to highly toxic products: carcinogenic, mutagenic and allergenic for exposed organisms even at low concentrations (less than 1 ppm). They contaminate not only the environment, but also the entire food chain, leading to biomagnifications.

Phenolic compounds: These pollutants have been found as byproducts from diverse industrial processes, such as in the synthesis of dyes, aspirin, paper, etc. Even in low concentration, phenol causes toxicity and foul odor to the water. This is due to its reactivity with chlorine (Cl) and nitrate (NO_2) in the soil to form chlorophenol and nitrophenol, respectively. Most countries specify a maximum allowable concentration of phenol in wastewater to be less than 1 ppm [32,33]. The exposure of phenol and its derivative compounds to human and animals causes liver and kidney damage, central nervous system impairment, diarrhea, and excretion of dark urine [34,35]. Therefore, it is necessary to develop methods that allow one to detect, quantify and remove phenol from wastewater [36].

Emerging contaminants: These pollutants have been detected in wastewater treatment plant effluents, in shallow waters, seawater, subterranean waters and in some drinking waters. Their concentration in the effluents varies depending on the country and the consumption; these substances are bioaccumulative, so they pose a great danger for the environment and humans [37-40]. Some examples of these kinds of contaminants are pesticides and herbicides, pharmaceutical products, such as antibiotics and microbial agents, personal hygiene products, like shampoo, detergents, and so on.

In addition, although activated carbon remains one of the most widely used adsorbent, its relatively high cost limits its use. However, adsorptive properties and availability are important criteria when choosing an adsorbent for contaminant removal, thereby encouraging research into materials that are not only efficient but also cheap. Many non-conventional low-cost adsorbents, including natural materials, biosorbents, and waste materials from agriculture and industry have been proposed by Namasivayam et al. [41-44]. As mentioned before, considering low cost, abundance and high sorption properties, clay

minerals are interesting materials for use as adsorbents, since they can be easily obtained and regenerated, as it has been demonstrated by Gil et al. [45].

Organic Compounds Removal from Water with Polymer-Clay Nanocomposites

Nowadays, the conventional water treatment technology involves different processes such as coagulation, chlorination, flocculation, filtration, ozonation and sedimentation. Coagulation and flocculation processes are used to remove suspended particles, such as bacteria, clay, silts and organic matter from the contaminated water; however, it also leads to the removal of minerals from water, resulting in a decrease of its quality. Sedimentation and filtration processes could be used for the removal of floc and sludge; but, it is necessary to check the condition of the sedimentation bed, which increases the cost of water purification. Finally, chlorination and ozonation could remove microbes present in water, since both chlorine and ozone are well-known oxidizing agents that can react with organic matter to generate disinfectant byproducts such as bromate, chlorite, haloacetic acids and trihalomethanes. All of the mentioned disadvantages in the former processes have created the need for a new type of technology that can overcome the problems and allow easy access to pure water.

Nanotechnology has arisen as a possibility to the conventional water treatment technologies for effective removal of chemical and microbial contaminations due to their large surface-area-to-volume ratio, enhanced catalytic properties, high conductivity, antimicrobial properties and self-assembly on surfaces. Currently, nanotechnology-enabled water treatment technology principally focuses on two major areas to improve its quality:

a) Degradations of organic pollutants, and

b) Removal of pollutants by adsorption process.

Adsorption is a surface phenomenon in which adsorbate molecules (liquid or gas) are concentrated on the surface of a solid (adsorbent). Gupta and Suhas [46] defined this process as physisorption or chemisorption depending on how the adsorbate species get adsorbed onto the adsorbent surface. Kumar et al. [47,48] explained that dyes molecules may be adsorbed on the surface of an adsorbent through several forces such as hydrogen bonding, electrostatic interaction, van der Waals forces, hydrophobic interaction etc. Usually, adsorbents possess porous structures, which increase the total exposed surface area and allow fluid to pass through faster.

Meanwhile, Kyzas et al. [49] described adsorption as a simple and economical method for dye-pollutants removal from water and wastewater. It has high treatment efficiency and adsorbents can be regenerated for multiple purposes. Initial pollutant concentration, temperature, solution pH, adsorbent dosage and contact time are the main aspects that control the performance of most of the adsorption process.

In the case of organic compounds, adsorption has been extensively studied with different porous materials such as clay minerals. That is why the search for new types of materials, such as PCC's and PCN's, has been developed. Specifically they have been synthesized for the removal of highly pollutant organic substances, e.g., dyes; some byproducts of phenolic compounds and a new kind of pollutant known as "emerging pollutants", among which can be counted some pharmaceuticals, steroids, pesticides, endocrine disruptive compounds and so on.

Dyes removal

Wastewater discharges from dyeing or finishes of textile industries, as well as of some food, pharmaceutical or chemical industries contain various types of dyes, many of which are mutagenic or cancerogenous for humans [45]. They are important because they are used to give color to other materials and are absorbed when applied. Dyes discharge in bodies of water is an important environmental problem, since there is no norm to limit it in Mexico, and they could change when exposed to sunlight, to acids, excessive heat, etc. Dye dissemination into water bodies leads to colored water, which is a visible concern. These dispersed dye molecules block sunlight from reaching the bulk of affected water system, and therefore, reduce the dissolved oxygen (DO) level in water. Dyes may also increase the biochemical oxygen demand (BOD) of the contaminated water body.

Among the reported treatments for the removal of dyes are: separation membranes [50-54], coagulation-flocculation [48,51,52,55], biological degradation [56] or advanced oxidation [57,58], and among which stands out adsorption [45,59-68].

Dye-adsorption with nanocomposites and composites acquires relevance because of the potential it offers, as shown on Table 1.

Phenolic compounds removal

Phenol and its byproducts are some of the most extensively studied organic pollutants due to their toxicity to living beings and the environment. Phenolic pollutants discharged from different kind of industries, such as pesticides, paints, polymer resins, paper, and petrochemistry have been found in their effluents [69,70]. There are two main treatment technologies for phenolic compounds: the first consists of chemical oxygenation processes with reagents such as hydrogen peroxide [71,72], and the second of adsorption and extraction processes [73-75]. Chemical adsorbents such as clays and clay minerals, and even polymers play an important role in the removal of these compounds [76-79]. Clay minerals, in particular, received a great deal of attention due to their large specific surface area and cation exchange capacity on the one hand, and low cost and toxicity on the other [80,81]. The adsorption of organic molecules to these minerals is affected by various parameters, such as the exchangeable cations, the distance between the clay mineral layers, and the existence of water molecules between the layers [80].

Also, adsorption onto a polymeric sorbent, (SP206, a polystyrene matrix crosslinked with divinyl benzene) by Moon et al. [82] showed that phenol, p-chlorophenol, and p-nitrophenol adsorption data had a maximum adsorption capacity of 0.0626, 0.736 and 0.815 mg·g^{-1} respectively. They also reported that phenolic compounds on SP206 were desorbed very quickly with a 0.05 N sodium hydroxide solution within a few minutes.

Also, the adsorption of o-nitrophenol onto nano-iron oxide loaded with calcium alginate beads was studied by Soni et al. [83]. It was observed that the optimum pH for the adsorption was 2. Similarly, the equilibrium time was 4 hours with percentage removal of 96%. Besides, Chen et al. [84] studied the adsorption of phenol and 4-nitrophenol on Mg/Al oxide derived from Mg/Al-layered double hydroxide (Mg/Al-LDH). They observed that it took 10-12 h for the adsorption of 4-nitrophenol to reach equilibrium, in comparison with that of phenol which was 24 h. The kinetic process followed the Lagergren's first-order model for 4-nitrophenol and the pseudo-second order model in the case of phenol. They also noted that the adsorption capacity for 4-nitrophenol could be as high as 367.8 mg·g^{-1}, while that of phenol was

PCN or PCC system	Dye	Enhancement action of PCN or PCC system	Authors
Poly(acrylamide)/Laponite Clay (PAAm/ Lap) hydrogel nanocomposite	Basic Blue 12 (BB12), Basic Blue 9 (BB9) and Basic Violet 1 (BV1)	Dye uptake speed and equilibrium amount increases significantly with increasing of clay content up to 40%	Li et al. [58]
Poly(acrylic acid)/Bentonite/FeCo particles (PAAc-B-FeCo) hybrid hydrogel nanocomposite	Crystal Violet (CV)	Exfoliated bentonite clay and Fe–Co particles increased the strength and stability of hydrogel and assisted the adsorption of CV	Shirsath et al. [90]
Poly(acrylamide-co-sodium acrylate-co-Carrageenin)/Sodium-Montmorillonite P(AAm-Na-AA-NaMMT) clay nanocomposite	Crystal Violet (CV)	Enhancement in CV adsorption speed was observed when the AAm amount in AAm/Na-AA ratios increased up to 50 wt-%.	Reza-Mahdavinia et al. [91]
PAAm/Lap Clay hydrogel nanocomposite	Basic Fuchsin (Basic Violet 14)	Increases of AAm and Lap content in PAAm/Lap nanocomposite hydrogel, the pH and temperature of the dye solution increased the adsorption of basic fuchsin dye.	Zhang et al. [92]
Poly(Acrylamide)/κ-Carrageenin/Sodium Alginate Sodium Montmorillonite (MMT) Clay hydrogel nanocomposite	Crystal Violet (CV)	Dye adsorption capacity of hydrogels was influenced by both, clay content and biopolymers weight ratio. At acidic media, the dye adsorption capacity of nanocomposites was enhanced as the carrageenan and clay content were increased.	Reza-Mahdavinia et al. [93]
Chitosan/Modified Ball (MBC-CH) Clay composite	Methylene Blue (MB)	Adsorption of MB on MBC–CH was found to increase as the initial concentration, solution pH and temperation of the process were increased.	Auta and Hameed [94]
Poly(acrylamide-co-acrylic acid)/Kaolinite P(AAm-AAc/Kao) Clay composite	Bromophenol Blue (BPB)	An increase in temperature resulted in increase in the amount of BPB dye adsorbed per unit mass of sorbents	El-Zahhar et al. [95]
Poly(kappa-carrageenin-co-PVA)/Fe$_3$O$_4$ magnetic nanocomposite hydrogels	Crystal Violet (CV)	Removal of CV decreased by the incorporation of magnetite particles, and was improved by increasing the ratio of kappa-carrageenan. CV adsorption capacity of hydrogels decreased with increasing the ion strength of CV solution.	Reza et al. [96]
Poly(N-isopropylacrylamide)/ lithium magnesium silicate hydrate (LMSH) hydrogel nanocomposite P(NIPAAm/LMSH)	Crystal Violet (CV)	The adsorption capacity of hydrogel increase 2–4 times when CV concentration was added from 10 to 30 mg/L, and increase 1–1.5 times as pH value increases from 3.0 to 8.9.	Zhang et al. [97]
Polystyrene(PS)/LDH Mg-Al and PS/MMT Clay nanocomposites	Methyl Orange (MO) and Methylene Blue (MB)	Clays can be employed to adsorb the organic dyes (MO and MB), and improve the thermal stability and smoke suppression properties of polymer nanocomposites.	Zhou et al. [98]
Poly(ethylene glycol-co-acrylic acid)/Bentonite Clay nanocomposite semi-IPN type hydrogel	Congo Red (CR) and Methyl Violet (MV)	The nanocomposites showed high adsorption capacity and removal-% of CR and MV for low and high concentrations of them at a solution pH of 7	Bhattacharyya and Kumar [99]
Amino-functionalized attapulgite clay nanoparticle adsorbent (ATP@CCS) onto hydrothermal carbonized chitosan	Methylene Blue (MB)	The MB adsorption could achieve a quickly equilibrium (<120 min) with maximum adsorption capacity of 215.73 mg g^{-1} and the removal of MB kept above 80% for five consecutive cycles	Zhou et al. [53,54]

Table 1: Dye removal with polymer-clay composites or nanocomposites.

25.5 mg·g^{-1} at room temperature. In Table 2, other results on phenolic compound adsorption with different nanocomposites are shown.

Emerging pollutants

Emerging pollutants (pharmaceutical products, pesticides, herbicides and personal hygiene products) are compounds of which relatively little is known; as far as their presence, impact and treatment, they are mostly non-regulated pollutants [85].

Antibiotic and antimicrobial agents are between the most widely investigated pharmaceuticals due to their direct effect on the natural microbiota and the formation of resistant strains [86,87], particularly alkylphenol ethoxylates, natural and synthetic hormones and diphenyls, have been addressed.

Putra et al. [88] investigated the removal of amoxicillin from aqueous solutions by adsorption on bentonite. A high value of initial amoxicillin concentration (300 mg·L^{-1}) was chosen to represent pharmaceutical wastewater. Adsorption of amoxicillin was strongly affected by pH because it can alter the charge of amoxicillin molecule.

In this study, adsorption capacity of bentonite was compared with a commercial granulated activated carbon (GAC). Both adsorbents were found to be quite effective because removal percentage as high as 88% was accomplished. q$_e$ value was comparable (around 20 mg·g^{-1} for bentonite and 25 mg·g^{-1} for commercial activated carbon), but adsorption equilibrium time for activated carbon was only 35 min compared to 8 h of bentonite. The main reason could be the different surface area of the two adsorbents: 92 m^2·g^{-1} for bentonite and 1,093 m^2·g^{-1} for GAC.

Bekçi et al. [89] studied montmorillonite as adsorbent in the removal of trimethoprim, one of the main antibacterial agents used in human and veterinary medicine worldwide. As a consequence of thermodynamic studies, the authors verified that physisorption was the chief mechanism of adsorption. Another parameter that affected adsorption of trimethoprim was pH. At low pH conditions (in an aqueous solution montmorillonite has a pH value of 3.31), trimethoprim is in the protonated form, so it was adsorbed to the negatively charged surface of the montmorillonite. In the best conditions, the amount of

PCN or PCC system	Phenolic Compound	Enhancement action of PCN or PCC system	Authors
Triblock copolymers composites based on ethylene oxide (EO) and propylene oxide (PO) units with Laponite (Lap) clay	Phenol (PhOH)	The copolymer replaces PhOH from the water/Laponite clay interface; moreover, the lateral copolymer-phenol interactions enhance the anchoring of PhOH to the solid surface and they are more effective for a composite structure PO-EO-PO than for a EO-PO-EO.	De Lisi et al. [100]
Na-montmorillonite/alginate composites microcapsules	4-nitrophenol (4NP)	The 4NP adsorption increases with the proportion of montmorillonite in the composite materials, and its adsorption capacity is strongly affected by the encapsulation.	Ely et al. [101]
Nanocomposites of Poly(4-vinylpyridine-*co*-styrene) and polydiallyl dimethylammonium chloride (PDADMAC) with MMT and Sepiolite (Sep) Clays	Trichlorophenol (TCP) and Trinitrophenol (TNP)	The adsorption of PDADMAC and PVPcoS to MMT was faster for both polymers than their adsorption to the porous SEP. Also, both pollutants showed higher affinity towards PVPcoS–MMT nanocomposite.	Ganigar et al. [102]
Chitosan- coated-Perlite (CCP) beads composites	Phenol, 2-chlorophenol and 4-chlorophenol	CCP beads show higher adsorption capacity for chlorophenols than phenol. Moreover, the highest adsorption of phenolic compounds occurred at pH 7.0 for all species	Kumar et al. [47]
Sodium Alginate-Aluminum pillared clay (Al-MMT-PILC) or surfactant-modified pillared clay (CTAB-Al-Mont-PILC) and divalent cation (Ca^{2+}), gel-like beads	Pentachlorophenol (PCP)	Modification of the biopolymers by introduction of pillared clays resulted in an enhancement of the adsorption capacity.	Lezehari et al. [103]
Poly(acrylamide)/Bentonite-modified with cethyltrimethyl ammonium (CTMA) composite	Phenol (PhOH)	The sorption capacity of the organobentonites towards phenol demonstrated to increase until the maximum, and then began to decrease as the saturated cationic exchange capacity (CEC) further increased.	[73]
Composite beads of Mauritanian clays (R3, NKCO4, ZS26, ZS23) encapsulated with sodium alginate (SA)	4-nitrophenol (4NP)	Adsorption of 4NP was favorized onto activated carbon and the order was Activated Carbon (AC)>AC/SA>Sodium montmorillonite (Na-MMT)>Na-ZS26/SA, Na-mont/SA.	Ely et al. [104]
Poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate) functionalized with diethylenetriamine (DETA) and acid modified bentonite composite	4-nitrophenol (4NP)	The incorporation of the acid modified clay into the copolymer matrix lead to the increase of porosity, total pore volume, specific surface area, and sorption efficiency of the 4NP	Marinović et al. [105]
Composite beads of aluminum-pillared clay (Al-Mont-PILC) and surfactant-modified pillared clay (CTAB-Al-Mont-PILC) onto Alginate	Pentachlorophenol (PCP)	Higher values of removal were obtained for the encapsulated surfactant-modified aluminum-pillared clay compared with the encapsulated aluminum-pillared clay.	Lezehari et al. [106]
Wheat straw/Palygorskite Clay/Phenolic Resin Woodceramic composite	Phenol (PhOH)	Palygorskite clay modified woodceramics had the highest adsorption rate; in addition, the higher the phenol solution concentration and pH, the lower the adsorption efficiency was.	Wu et al. [107]
Poly(glycidyl methacrylate-*co*-ethylene glycol dimethacrylate) functionalized with diethylenetriamine (DETA) and acid modified bentonite nanocomposite	2-nitrophenol (2NP), 4-nitrophenol (4NP) and 2-chloro-4-dinitrophenol (2Cl4NP)	Affinity of nanocomposite toward phenol derivatives increases in the following order 2NP <4NP <2Cl4NP, probably attributed to the hydrogen bonds that they could form with the sorbent.	Marinović et al. [108]

Table 2: Phenol and its derivatives removal with polymer-clay nanocomposites or composites.

drug adsorbed was 60 mg·g⁻¹ for 1 h of contact time (initial compound concentration was 290.3 mg·L⁻¹).

Some other investigations related to the use of nanocomposites for the removal of emerging pollutants are reported and discussed on Table 3.

Conclusions and Perspectives

As it has been stated in this review, PCN's have significant advantages of established adsorbents for water treatment, for example their easy production, their good performance, and their enhanced. Furthermore, with the data reported here, it is important to mention that polymer nanocomposites are not only studied with the objective of reinforcing the polymer matrix, but also to find improvements in their properties. The advantages of nanoscale clay bonding lead to a number of applications, for instance in barrier properties, in separation membranes, in flame resistance and as polymer compatibilizer, to mention a few.

In the case of polymer matrices of organic origin, the most widely used is chitosan, due to the high removal values found and reported in the tables, while among those of synthetic origin are acrylates, mainly due to the properties they present when external conditions such as pH, temperature, vary. Despite this, PCN's have not reached their total development and currently, from laboratory research to large-scale engineering projects, it is necessary to encourage it, to have an idea of these versatile materials' complete potential and their applications in environmental remediation, specifically for the removal of organic compounds from water.

Acknowledgements

PNC or PCC system	Emerging Compound	Enhancement action of PCN or PCC system	Authors
Chitosan/MMT composite	Tannic Acid	The polycation chitosan and montmorillonite is an adsorbent of relatively high stability and at low concentrations where tannic acid is completely dissociated, its adsorption arises electrostatically and is unaffected by pH.	An and Dultz [109]
Nanocomposites of Poly(4-vinylpyridine-*co*-styrene) and polydiallyl dimethylammonium chloride (PDADMAC) with MMT Clay	Atrazine (pesticide)	The polymer–clay composite filter, consisting of poly(4-vinylpyridine-*co*-styrene) succeeded in reducing atrazine concentrations below the current EPA standard.	Zadaka et al. [110]
Montmorillonite (SWy-2)–chitosan bionanocomposites (SW–CH)	3,6-dichloropyridine-2-carboxylic acid (Clopyralid)	The removal of clopyralid from aqueous solution was greater for bionanocomposites with higher chitosan contents	Celis et al. [111]
Composite of Magnetite/Bentonite Clay composite	Amoxicilin	The adsorbent mixture was efficient, chemically inert, and had a removal rate of 50% of amoxicillin in water. The adsorption process was physical and activated depending on the temperature.	[112]
Poly(4-vinylpyridine-*co*-styrene)/MMT clay composite	Triazine, simazine and terbuthylazine pesticides	Herbicide binding affinity increased with a decrease in herbicide molecular size due to enhanced accessibility of the small herbicide to the binding sites of the polymer.	Gardi et al. [113]

Table 3: Examples of emerging compounds removed through polymer-clay nanocomposites or composites.

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