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Modern Trends in Using Marine Algae for Treatment of Aquatic Pollution

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Abstract: Aquatic pollution became a worldwide problem. Pollutants may cause primary damage, with direct identifiable impact on the environment, or secondary damage in the form of minor perturbations in the delicate balance of the biological food web. Many chemical contaminants, including organochlorine compounds, herbicides, domestic and municipal wastes, petroleum products and heavy metals are now recognized to have adverse affects on aquatic environments, even when released at low levels. Marine algae could be used in different methods as by using native dried algal biomass without any pretreatments, by using chemical reinforced biomass, immobilized algal biomass, by drying the algal biomass either by pyrolysis or by using concentrated acids or by using algal polysaccharides such as sodium alginate and carrageenan for preparing hydrogels (xerogels rather than aerogels. The using of marine algae and algal polysaccharides hydrogels and nanocomposites showed an efficient loading ability to pollutants in aqueous ecosystem, good stability responded to external stimuli as well as fast loading process render them potentially applicable as environmental friendly candidate for the treatment of water pollution.

Key Words: marine algae, aquatic pollution, heavy metals, hydrocarbon, dyes.

Introduction

1. Marine algae

The algae are a ubiquitous group of photosynthetic organisms responsible for the majority of photosynthesis in most sunlit streams. Benthic algae are dominant members of the periphyton community living on submerged substrata in the photic zone of most aquatic ecosystems including both marine and fresh water. Although algae are usually studied as a group of organisms that are closely related at a functional level, they are very diverse on an evolutionary level and have been assigned to several different kingdoms based on morphological, chemical, and ecological parameters. An alga (singular) or algae (plural) are organisms lacking true tissues and multicellular gametangia and containing chlorophyll a, and their colorless relatives¹.

1.1. Algal Systematic and Classification

As early as 1866, Haeckel suggested the term Protista for unicellular microorganisms - bacteria, algae, fungi, and protozoa. Bacteria were referred

to as lower protists and the rest were the higher protists. The researches on algae revealed great diversity in pigments, food reserves, number of flagella,

and algal cell wall composition. These characteristics have since then formed the basis for algal classification. Fritsch² gave one of the earliest and widely accepted classifications, where eleven classes were identified, which are given as follows: (i) Cyanophyceae, (ii) Chlorophyceae, (iii) Xanthophyceae, (iv) Chrysophyceae, (v) Bacillariophyceae, (vi) Cryptophyceae, (vii) Dinophyceae, (viii) Chloromonadineae, (ix) Euglenineae, (x) Phaeophyceae, and (xi) Rhodophyceae. For long, the Cyanophyceae were the only prokaryotic algae; but later in early 1980s, a green prokaryotic alga - *Prochloron* - was discovered. In the light of Whittaker's work on classification of living organisms, it was suggested that the blue green algae be placed under Kingdom Monera with archaebacteria and eubacteria as two groups³. Eubacteria included two phyla or divisions - Cyanophyta (= Cyanobacteria)) and Prochlorophyta (= Chloroxybacteria)). The latter was constituted to include *Prochloron*. In 1977, Stainer proposed a new name for blue green algae (BGA)⁴. This new name - Cyanobacteria - emphasizes two aspects of BGA better than the traditional name Cyanophyta, namely the prokaryotic nature of blue green algal cell and the fairly close relationship between BGA and Eubacteria.

Algae exhibit a remarkable diversity of form and size, ranging from flagellated swimming green cells as minute as 1 micron in diameter to brown kelps up to meters in length. These have a long fossil history, some possibly extending back to the time of origin of photosynthetic cellular plants. Algae are generally considered to be the group from which all the more complex cryptogams and, ultimately, the seed-bearing plants arose. These appear as rose-red feathery fronds in deep clear marine coastal waters (Rhodophyceae), green scum on a quiet pond (Chlorophyceae), Sargasso weed in the massive Atlantic gyre (Phaeophyceae) and as organisms responsible for colouration on mountain snow.

1.1. 1. Green algae

Green algae form the phylum *Chlorophyta* and are named for their chloroplasts, which are similar in composition to the chloroplasts found in land plants. More than 500 genera and 8000 species of green algae have been identified.



Fig. 1. marine green algae, Ulva lactuca

1.1.2. Red Algae

Red algae form the phylum *Rhodophyta* with approximately 500 genera and 6000 species. Found in warm coastal waters and in water as deep as 260 m (850 ft), red algae species adapt to varied water depths by having different proportions of pigments. Their red color is due to a red pigment, *phycoerythrin*, which is well suited to absorb the blue light that penetrates deeper into water than the other colors of light.



Fig.2. Marine red algae, Chondrus crispus

1.1.3. Phaeophyceae: Brown Algae

Golden-brown algae, brown algae, and diatoms form the large and complex phylum *Heterokontophyta*, with organisms ranging in size from a fraction of a millimeter to more than 100 m (300 ft) long. Heterokontophyta have carotenoid secondary pigments that tend to mask the green of the primary chlorophyll pigment, giving them a golden or golden-brown appearance. The golden-brown algae, also known as the yellow-brown algae, include about 200 genera and 1000 species that receive their characteristic coloring from the carotenoid pigment *fucoxanthin* Examples: *Laminaria* and *Saccharina*, *Fucus*, *Sargassum muticum*.



Fig.3. Marine brown algae,(a): Sargassum muticum, (b): Laminaria sp.

2. Environmental Pollution

Environmental pollution is any discharge of material or energy into water, land, or air that causes or may cause acute (short-term) or chronic (long-term) detriment to the Earth's ecological balance or that lowers the quality of life. Pollutants may cause primary damage, with direct identifiable impact on the environment, or secondary damage in the form of minor perturbations in the delicate balance of the biological food web that are detectable only over long time periods.

Until relatively recently in humanity's history, where pollution has existed, it has been primarily a local problem. The industrialization of society, the introduction of motorized vehicles, and the explosion of the human population, however, have caused an exponential growth in the production of goods and services. Coupled with this growth has been a tremendous increase in waste by-products. The indiscriminate discharge of untreated industrial and domestic wastes into waterways, the spewing of thousands of tons of particulates and airborne gases into the atmosphere, the "throwaway" attitude toward solid wastes, and the use of newly developed chemicals without considering potential consequences have resulted in major environmental disasters, including the formation of smog in the Los Angeles area since the late 1940s and the pollution of large areas of the Mediterranean Sea. Technology has begun to solve some pollution problems and public awareness of the extent of pollution will eventually force governments to undertake more effective environmental planning and adopt more effective antipollution measures.

3. Aquatic pollution: a global concern

Globally, more than 3 billion people live in proximity to the marine coast. Wastes from both industrial and domestic sources as well as habitat destruction have a substantial impact on the coastal environments⁵. Internationally accepted procedures for environmental/ecological impact and risk assessment have been established to manage human impact on coastal environments⁶. The oceans were previously considered to be a vast reservoir for the safe disposal of pollutants. Many chemical contaminants, including organochlorine compounds, herbicides, domestic and municipal wastes, petroleum products and heavy metals are now recognized to have adverse affects on ocean environments, even when released at low levels^{7,8}. Little attention has been given to this problem until shortly before the 19th century. The adverse effects of environmental pollution have been well documented^{9,10}.

The primary sources of heavy metals pollution are the burning of fossil fuels, mining and smelting of metalliferous ores, municipal wastes, fertilizers, pesticides, and sewage. Metals with specific gravity higher than 5 g.cm 3, defined as heavy metals, have generated enormous concern amongst

environmentalists. A variety of heavy metals are found naturally in freshwater and seawater environments due to weathering of rocks. Certainothers are, however, added through unmindful anthropogenic activities. Heavy metals, such as iron (Fe), manganese (Mn), zinc (Zn), copper (Cu), molybdenum (Mo), nickel (Ni), cobalt (Co), and vanadium (V) are considered to be essential for plants, but may cause harm if available in excess. Other metals are categorized as non-essential, e.g., lead (Pb), cadmium (Cd), aluminium (A1), chromium (Cr), mercury (Hg), silver (Ag), arsenic (As), and tin (Sn). Those, which do not enter into the primary metabolism, are detrimental to plant growth and development even in traces. Metals in aquatic environment may exist in dissolved or particulate forms. These may be dissolved as free hydrated ions, complex ions, chelated with inorganic ligands, such as OH⁻, CI⁻ or CO_3^{2-} , or complexed with organic ligands, such as amines, humic acid, fulvic acid, and proteins. Certain chemicals, that cannot be degraded, can accumulate in the environment to levels that threaten human health or environmental quality. Deleterious effects of some metals have been studied in detail. The biological effects of metals are complicated by their interactions with other metals. Cadmium has received widespread attention because of its accelerated release into the environment as a result of industrial utilization and the resulting pollution¹¹. Cadmium is a relatively rare element with no known biological function. It is ranked amongst the most hazardous heavy elements in the environment and is highly toxic to all components of aquatic communities¹².

4. Removal of heavy metals by marine algae

4.1. Removal of heavy metals by native marine algae

Algae as biosorbents of heavy metals offer a cost effective, potential and alternative to conventional methods for decontamination of water bodies at global, regional, and local levels. Microalgae (green and cyanobacteria) have been used to remove heavy metals from aqueous system, since they have a high capacity to accumulate dissolved metals¹³. It is also known that phytoplanktons affect trace metal chemistry in natural waters, not only by surface reactions, but also by metal uptake and by production of extracellular organic matter with metal complexing properties. The exudates of these algae may be important in keeping the free metal ion concentrations at low levels in natural waters, thus decreasing the toxic effects. It has been observed that polyhydroxamate siderophores, which are strong metal complexing agents, are released by cyanophytes under certain conditions¹⁴. These are also discharged by some species of eukaryotic algae^{15,16}. With respect to macro marine algae, there has been a particular interest because of their biomass. The adsorption of Cu(II) by Ulva fasciata sp. was investigated as a function of pH, contact time, initial Cu(II) and adsorbent concentrations and adsorbent size. About 0.1 g of Ulva fasciata sp. was found to be enough to remove 95% of 20 mg/L copper from 30mL aqueous solution in 20 min¹⁷. Also the native algae U. reticulata exhibited very high copper, cobalt and nickel biosorption capacities in packed column compared to most of the biosorbents reported in the literature. This alga showed unique ability to remove all three heavy metal ions and retain its uptake capacity in three regeneration cycles¹⁸. Brown algae are considered efficient and cheap material for biosorption, e.g., Sargassum and Ascophyllum. Thus, various groups of algae have potentials of bioremediation.

Recent applications of metal-algae interactions reported include the use of algae as biosorbents for recovery of metals from industrial solutions, either to sequester toxic metals or to recover precious metals. And algae have also been proposed as monitoring organisms for Cu and Hg in estuaries. The popularity of algal based systems lies in the fact that these systems have several advantages over currently available chemical technologies. These are:

(i) Versatility and flexibility for a wide range of applications.

(ii) Robustness.

(iii) Selectivity for heavy metals over alkaline earth metals.

(iv) Ability in some cases to reduce metal concentration to drinking water

standards (through biosorption).

(v) Cost-effectiveness.

(vi) Sustainability

(vii) Ability to remove the pollutants without themselves contributing any

harmful substances to water bodies.

(viii) Easy to filter out.

4.1.1. Important features of the algal biosorption process

(i) Algal biosorption techniques/processes can be used to remove toxic metals and/or radionuclides from liquid effluent before its discharge into water bodies. In addition, the algal biomass can be harvested and utilized for metals of value.

(ii) Biosorption is a rapid phenomenon involving passive metal sequesteration by the non-growing biomass.

(iii) Biosorption mainly involves adsorption, cell surface complexation, ion

exchange and/or microprecipitation. The physio-chemical phenomena, besides being rapid, are reversible.

(iv) Biosorption is a growth-independent phenomenon.

(v) The sorption technology has advantages of low operating cost, effectiveness in dilute solutions, and in generating minimum effluent.

4.1.2. Functional groups related to the biosorption

According to the metal classification by Pearson, 1963^{19} as well as by Nieboer and Richardson, 1980^{20}], metal affinity for ligands is supposed and illustrated in Table 1²¹. The symbol R represents an alkyl radical such as CH₂-, CH₃CH₂-, etc. Class A metal ions preferred to bind I type of ligands through oxygen. Class B metal ions show high affinity for III types of ligands, but also form strong binding with the ligands with II types of ligands. Borderline metal ions could bind these three types of ligands with different preferences.



Table 1. The representative functional groups and classes of organic compounds in biomass

4.1.3. Role of cell wall

The mechanism of biosorption is based on a number of metal-binding processes taking place with components of the cell wall. Various types of interactions occur between metals and cell wall biomolecules. Electrostatic attraction (ion exchange phenomena are based on such attraction) occurs with some metals (e.g., Ca, Na), covalent type bonding with others (Cu) and

redox reactions with certain noble metals (Au). The algal cell wall can reversibly biosorb metals and, thus, functions in a way similar to an ion exchange resin²². Thus, the biosorption mechanism can be considered as being dependent on the composition of the algal cell wall. Mostly, algal cell walls are made up of cellulose, polysaccharides, such as mannans, xylans, and chitin. These components, along with the proteins present, can provide acid-binding sites, such as amino, amine, hydroxyl, imidiazole, phosphate, carboxylates, thiols, and thioesters and sulphate groups. Fucoidin and alginic acid of brown algal walls offer anionic sites to which metals bind readily. Carboxylic and sulphate groups have been identified as the main metals equestering functional ionic groups in marine algal cell wall^{23,24}.

4.1.4. Factors affecting biosorption

Certain factors, that affect biosorption, are cell size and morphology, pH of the medium, and physiological state of algal biomass. Greater the cell surface area to dry weight ratio, more is the amount of metal biosorbed by a cell surface per unit weight. The pH of the external medium also affects biosorption of

metals. The solution pH affects the solution chemistry of the metals, the activity of functional groups in the biomass as well as the competition of metallic ions for binding sites. Since the pH is related to the net charge on the cell surface, which determines the extent of the cellular sites occupied by protons and other ions of the medium³⁵, the competition

between heavy metals and H for same cellular binding sites can result in a decrease or an increase in cellular heavy metal uptake and toxicity, depending on pH.

4.1.5. Desorption-sorption cycles

Processes in which the algal biosorbent can be stripped of metal cheaply and the biosorbent reused, are considered to be more viable as commercial metal removal systems. This part of the process would be similar to ion exchange, where metals are eluted from the biosorbent by an appropriate solution to give a small concentrated volume of metal-containing solution. However, such recovery of metals must be non-destructive so that the regenerated biomass can be reused in multiple biosorption-desorption cycles³⁶.

4.2. Removal of heavy metals by chemically-reinforced biomass

Since biomass is the basis of bioremediation, its quality needs to be maintained, if one is expecting good results. Studies have been carried out where marine algal raw biomass has been chemically processed in order to reinforce it for sorption process applications and also to enhance the sorption

process³⁷. Metal sorption was observed to be related to the particle size. In general, big particles had a higher metal uptake than small particles. Algal biomass material can be chemically modified in many different ways, in order to reinforce it and provide for its improved mechanical stability and pressure resistance required for sorption column applications.

Biomass chemical modification

The biomass may be subjected to:

- (i) formaldehyde cross-linking (FA),
- (ii) glutaraldehyde cross-linking (GA),
- (iii) polyethylene imine embedding (PEI).
- (iv) NH₄Cl pretreatment³⁸
- (v) Acidification³⁹
- (vi) Epichlorohydrine cross-linking and potassium permenganate oxidation⁴⁰.

4.3. Drying algal biomass to activated carbon

A new activated carbon obtained from *Pterocladia capillacea*, a red marine macroalgae, via acid dehydration was also investigated as an adsorbent for toxic chromium. The dried red algal (DRA) biomass of *P. capillacea* treated with 98% H_2SO_4 and the resulting reaction mixture was kept for 1 h at room temperature followed by refluxing for 5 h in an efficient fume hood. After cooling to room temperature, the reaction mixture was poured onto cold water (4 L) and filtered⁴¹. The proposed sorbents are efficient, environment friendly and can reduce the huge amount of indiscriminate effluent discharges around the small industry concerns.





The morphology of this material can facilitate the sorption of metals, due to the irregular surface of the alga, thus makes the sorption of metal possible on different parts of this material. So, based on the morphology, as well as on the fact that high amounts of silicate which concentrated on the alga and its carbon, it can be concluded that this material presents an adequate morphological profile to adsorb metal ions.

4.4. Pyrolysis of algal biomass

The adsorptive removal capacities of highly available *Turbinaria turbinata* alga and its derived carbonaceous products (i.e. pyrolyzed, physically and chemically activated carbons) were investigated⁴².

For physical activation, algal biomass pyrolyzed in a Barnstead/Thermolyne furnace F-21100 under nitrogen atmosphere at 800 C for 1 h. Charcoals thus prepared "turb-pyr", were then activated with steam under a nitrogen atmosphere at 800 C for 8 h with a heating rate of 10 C/min in the same furnace giving sample "turb-H₂O" ⁴³.

For chemical activation, *T. turbinata* were impregnated in phosphoric acid (H₃PO₄) 85% for 24 h, in order to facilitate the access of the acid inside the particles⁴⁴. Impregnation ratio; XP (g H₃PO₄/g precursor) 1:1 is used producing the sample "turb-P1". After impregnation, the sample is dried for 4 h at 105 C in a drying oven. The sample thus dried is pyrolyzed under nitrogen flow at 600 C for 1 h.⁴⁵.Several textural and chemical characterizations were performed on the alga and its activated carbons (ACs). Besides, kinetics and isotherms assays were performed and modeled in order to monitor the sorption capacities and dynamic behaviors. The main results showed that the raw *Turbinaria* biomass has a non porous structure. Then, after thermo-chemical treatments, a porous matrix starts to develop and the total pore volume drastically increased from 0.001 cm3/g for the algal precursor (turb-raw) to 1.316 cm³/g for its derived chemically AC (turb-P1). As well, the specific surface area improved from m²/g for (turb-raw) to 1307 m²/g for (turb-P1). Consequently, the maximum sorption capacity went from 63 mg/g for the algal biomass up to 411 mg/g for the chemically ACs. Moreover, the removal rate was taken into consideration in order to set a more reliable and realistic approach to figure out the most efficient *AC*. Thus, based on those criteria, it was found that the chemically activated carbon "turb-P1" is the most efficient *Turbinaria*-derived sorbent to adsorb and remove methylene blue (MB) molecules from aqueous solutions with 169 g of the dye using 1 kg of raw alga (considering an AC production yield of 49%).



Fig. 5. SEM images of raw *Turbinaria* "turb-raw" (A), chemically activated carbon "turb-P1" (B), pyrolyzed *Turbinaria* "turb-pyr" (C) and physically activated carbon "turb-H₂O"(D)⁴².

Indeed, as shown in Fig. 5, the surface structure of the biomass changes from a non-porous one, with a star-like pattern (cf. Fig. 5A), into a rough surface after the pyrolysis step (cf. Fig. 5C). Then, the carbonaceous material started to develop a kind of porous structure (from a surface view) after the activation. In this case, the chemical activation seems to be more drastic on the surface structure than the physical one. Actually, as shown in Fig. 5, the steam activation was soft enough not to destroy the surface. Indeed, it is clear that the star-like pattern, distinctive of the raw biomass, is still perceptible in the physically activated carbon "turb-H₂O"(cf. Fig. 5D). However, after the chemical activation, the surface of "turb-P1" (cf. Fig. 5B) seems to lose the star-like shape and develop a porous structure with what seems to be from the surface view as macropores.

5. Removal of heavy metals by Immobilized biomass (living/dead)

5.1. Immobilization of marine algae by alginate:

Alginates constitute a family of linear binary copolymers, consisting of (1/4) linked b-D-mannuronic acid (M) and a-L-guluronic acid (G) residues (see Fig. 6a, b and c). Chemical composition and sequence may vary widely between algae species and even between different parts of the algae and the time of year when it is harvested. Alginate with a very high content of guluronic acid, which is of importance for the mechanical properties of the alginate gel, can be prepared from special algal tissues such as the outer cortex of old stipes of *Laminaria hyperborea*. Alginates with more extreme compositions containing up to 100% mannuronate can be isolated from bacteria⁴⁶. Alginates may also be sequentially modified by post-polymerisation enzymatic modification applying mannuronan C-5 epimerases from Azotobacter vinelandii⁴⁷, which convert M to G within the polymer chain.



Fig.6. Structural characteristics of alginates: (a) alginate monomers, (b) chain conformation, (c) block distribution⁴⁶.



Fig. 7. Alginate beads with encapsulated cells manufactured by the diffusion setting method⁴⁸.



Fig. 8. In an alginate gel, the G blocks on different polymer chains form ionic crosslinks through Ca²⁺ (red circles).

Brown alga, *Fucus vesiculosus*, immobilized on alginate showed a good results showed how these types of gels could be influenced in biosorption. and the success of bioremediation for the in situ removal of heavy metals⁴⁹. Also *Turbinaria decurrens* immobilized in sodium alginate showed increasing intraparticular diffusion of lead, stability of the metal binding, and affinity for lead. Equilibrium lead concentrations were attained after 9 h. The maximum lead uptakes were 1.14, 1.35, and 1.79 mmol g^{-1} , respectively, for alginate xerogels, free alga, and immobilized alga.⁵⁰



Fig.9. SEM micrograph of immobilized biomass surface before (a1) and after lead uptake (b1) and alginate xerogel before (a2) and after (b2) lead uptake. The interior of immobilized biomass (c1) and alginate xerogel (c2)⁵⁰

Figure 9a shows SEM micrographs of immobilized biomass and alginate xerogel surfaces before lead uptake, whereas Fig. 9b shows micrographs after binding of lead with the functional groups of the external surfaces of the beads and the channels. The interior surface of immobilized biomass (Fig. 9c1) shows the presence of algal tissue inside the beads, whereas Fig. 9c2 shows the smooth interior surface of alginate xerogel beads; both before lead uptake.



Fig. 10. EDX monograph of alginate xerogel bead after lead uptake (a) EDX monograph of immobilized biomass bead after lead uptake (b)⁵⁰.

After lead uptake the presence and mapping of lead distribution inside the beads were determined using EPMA–EDX (electron probe X-ray microanalysis in EDX mode) micrographs. Figures 10 show the EDX micrographs of the cross section of alginate xerogel beads and the immobilized biomass beads after lead uptake at pH 5, respectively. The distribution pattern of lead was measured on a unit surface area of 20 μ m of beads. In the case of alginate xerogel (Fig. 10 a) the functional groups are homogeneously distributed in the alginate structure. In the case of immobilized biomass (Fig. 10 b) the distribution of lead ions on the algal tissue in the middle of the beads is homogeneous and of higher intensity than on the margins of the beads, where the alginate layer is present. This homogeneous distribution indicated that Pb²⁺ ions are capable of penetrating into the beads and reacting with functional groups. Therefore, both the alginate xerogels and immobilized biomass beads can be considered as porous ion exchangers having high permeability.

6. Algal polysaccharides for preparation of hydrogels

6.1. Alginate Hydrogels for water treatment

Compared with traditional adsorbents, the structure of hydrogel can be flexibly designed, and the properties can be adjusted by altering the type and number of functional groups according to the usage requirement. For this purpose, various petroleum-based monomers were copolymerized and crosslinked to derive the hydrogel adsorbents with different functional groups⁵¹⁻⁵⁴. With the growing global environmental concerns, the petroleum-based hydrogel adsorbents highlighted their non-renewable, expensive and nonbiodegradable disadvantages. To overcome these drawbacks, the eco-friendly nanocomposite adsorbents based on renewable natural polymers and the abundant, low-cost, non-toxic natural nano-clays

were greatly concerned and such materials have been honored as the materials of "in greening the 21st century materials words"⁵⁵. Thus far, many natural polysaccharides (i.e. chitosan⁵⁶, alginate⁵⁷, and carrageenan⁵⁸ were introduced to derive the nanocomposite hydrogel with improved network structure and properties

6.1.1. (Sodium Alginate / Itaconic Acid) Hydrogel Prepared By Gamma Radiation

6.1.1. 1. For removal of lead

Alginate hydrogels are prone to enzymatic degradation and suffer from limitations in fabrication, which limits its application in some fields, for example, in controlled-release technology. To overcome this problem,

efforts have been made to develop chemically modified matrices by grafting. Grafting is a well-established and powerful method for the development of natural-synthetic polymer hybrid materials. Itaconic acid (IA) is one of the monomers, which is readily available at low cost. It is obtained from renewable resources by fermentation with *Aspergillus terrus* using carbohydrate materials as molasses and hydrolyzed starch⁵⁹⁻⁶⁰. Poly itaconic acid (PIA) is interesting as a polyelectrolyte having two ionizable groups, with different pKa values, which can form H bonds. These groups bring additional capability of chelate formation under certain cases.

pH-sensitive hydrogel based on (NaAlg), (IA) as a sorbent for removal of Pb⁺² ions from aqueous solution was investigated⁶¹. The novelty of this work is to identify applicability of NaAlg/ IA hydrogel and also to identify various important parameters on the removal of Pb metal ions from its aqueous solution.

The study demonstrated that the NaAlg/IA hydrogel may be an extremely viable adsorption for application in the treatment of water and industrial waste water contaminated with Pb^{2+} . The adsorption capacity of Pb^{2+} ions nearly linearly increased with the increase in the initial concentrations of Pb^{2+} ions, then reached surface saturation at concentrations around 1.23 mmol/l. This indicated that at lower initial concentrations, the adsorption sites on the hydrogel were sufficient, increase in Pb^{2+} concentration can accelerate the diffusion of Pb^{2+} ion into the polymeric networks as a result of an increase in the driving force of concentration gradient. However, at higher initial concentrations, the adsorption sites on the surfaces of the hydrogel reached saturation, and the adsorption of Pb^{2+} achieved equilibrium. Judging from the correlation coefficients, R2, the pseudo-second-order model have higher correlation coefficients (*R*2 0.97) compared to the correlation coefficient for both pseudo-first-order (*R*2 0.95) and intra-particle diffusion model (*R*2 0.86). Obviously, the adsorption of Pb^{2+} ions on NaAlg/ IA can be well described by the pseudo-second-order adsorption mechanism. The values of correlation coefficients of Freundlich equation were higher than the other two isotherm values, which indicated the Freundlich isotherm correctly fitted the equilibrium data, confirming the multilayer coverage of Pb^{2+} onto the hydrogel. In addition, Freundlich parameter, (n=1.84) meant that adsorption intensity was favorable at high concentration but much less at lower concentration



Fig. 11: SEM micrograph of the hydrogel surface before (a) and after lead uptake (a))¹⁶



Fig. 12: EDX monograph of hydrogel after lead uptake⁶¹

6.1.1.2. For removal of methylene blue

Sodium alginate poly itaconic acid (NaAlg/ IA), prepared by free radical polymerization using gamma radiation, used in removal of methylene blue from waste water⁶². The hydrogel swelling in water increases with time till reached equilibrium swelling value after 5 hours. The maximum extent of the equilibrium swelling was at pH 8. The thermogravimetric analysis showed that a little increase of thermal resistance for dye loaded NaAlg/IA hydrogel than the free one. The results showed that the percentage of dye adsorbed increases with the increase in the initial dye concentration, but the time required to reach equilibrium is independent of the initial MB concentration. The kinetic studies showed that, the pseudo-second- order reaction is better than pseudo-first-order reaction for low concentrations of MB and Vice Versa. It was shown also that the composition of the hydrogel has a great effect on the adsorption. As increasing the sodium alginate percentage in the hydrogel the adsorption process also increased. Studying the thermal effect showed that, the behavior indicates that the sorption process is exothermic process and more favorable at low temperatures.

6.1.2. Alginate/polyaspartate hydrogels

Poly(aspartic acid), PASP, is one of the synthetic water soluble polymers with a carboxylic acid pendant, which can be produced from the hydrolysis of polysuccinimide (PSI), a thermal condensation polymer of L-aspartic acid monomer⁶³⁻⁶⁵. PASP has been commercialized as a biodegradable polymeric dispersant, and has also been widely investigated as a polymeric drug carrier⁶⁶. In addition, several different PASP-based hydrogels have been prepared by chemical crosslinking, and the swelling property was investigated⁶⁷⁻⁶⁸. It is interesting to investigate the potential industrial application of crosslinked gels from high molecular weight PASP with its beneficial biodegradable characteristics of material and the easy separation in their use for the dye removal from contaminated water.

Biodegradable Alg/PASP hydrogel beads were prepared and the dye adsorption behavior was investigated⁶⁹. The hydrogels significantly absorbed as much as 300–700 mg per g of gel of basic dyes, such as Methylene Blue and Malachite Green.



Fig. 13. Chemical structure of dyes

The ionic polar interaction between the dye and hydrogel matrix appears to be responsible for the observed adsorption phenomena. A type-S adsorption isotherm was found, which is characteristic of a weak solute–solid interaction. The adsorption of the dye decreased slightly with increasing $CaCl_2$ concentration but was enhanced significantly by treating the beads with an acid solution. Crosslinked Alg/PASP composite hydrogels can be used as an effective adsorbent for the removal of cationic dyes, and has potential applications in the related industrial and environmental areas.



Fig.14. Cross-section SEM micrographs of gel beads; (a) 5:5 Alg/PASP and (b) pure Alg⁶⁹.

The relative amount of the dyes sorbed onto the hydrogels increased in the following order: MB > MG > MO. The level of adsorption on sample C-3, which is a composite gel without the acid treatment, was lower than the other gel samples. Since these hydrogels containing carboxylic acid groups in the structure can be anionic in character, the hydrogel can interact with the cationic group of the dyes efficiently, and adsorb MB or MG dye better through an electrostatic interaction between the gel matrix and the cationic functional groups of the dyes. On the other hand, there will be little attractive interaction with molecules containing anionic groups, as in case of MO with a sulfonate group in its structure. From the adsorption behavior of the different dyes, the electrostatic interaction between the gel matrix and dye molecules was found to be very important. Moreover, these Alg/PASP gels were quite effective in removing the cationic dyes in the aqueous solution. Another important type of interaction between the amine group on the dye molecules, and the amide and carboxylic group of the matrix polymer. However, the electrostatic interaction between the dye molecules and gel matrix appears to be the major intermolecular interaction in this system.

6.1.3. Alginate aerogels rather than xerogel for removal of heavy metals

Calcium alginate porous aerogel beads were prepared by sc-CO₂ drying, characterized and for the first time⁷⁰ evaluated for their performance on metal ion sorption in comparison with their non-porous xerogel analogues. The aerogels were mainly mesoporous, also containing micropores and macropores with BET surface area of 419 m² g⁻¹. The material exhibited enhanced sorption capacity with 20% higher degree of active site saturation after sorption compared to the xerogel beads and sorption values reaching 126.82 mg g⁻¹ for Cu²⁺ and 244.55 mg g⁻¹ for Cd²⁺. The sorption kinetics exhibited a significant decrease in sorption time, with 99% removal achieved 600–800 min earlier than for xerogel beads. This behaviour indicates increased functional groups accessibility combined with increased flexibility due to the effect of porosity, facilitating chain rearrangement during ion exchange.



Fig.15. SEM micrographs of the alginate aerogels⁷⁰.

The alginate aerogels form a rather loose 3D network of interconnected fibrils retaining the structure of the precursor hydrogel⁷¹. This textural feature is representative of most freeze-dried or supercritically dried polysaccharide gels as well as other semi-crystalline polymers⁷²⁻⁷³. The fibril diameter ranges from 4 to 15 nm, while the average network openings seemed to be between 50 and 200 nm, revealing that macropores are also present in the sample. The most frequent contact between fibrils is at nodes connecting the ends of three or more fibrils. The structure of well separated polymer fibrils in the aerogel is closely related to the structure of the precursor hydrogels⁷⁴. Indeed, Small Angle X-ray Scattering experiments suggested that ethanol exchange and CO_2 supercritical drying do not affect the spatial organization of the secondary structures of the gel and that characterization of the aerogel can provide information on the organization of the parent hydrogel⁷¹. In order to obtain alginate aerogels, supercritical drying is essential, as the solids formed by evaporative drying of polysaccharide hydrogels usually present no porosity at all⁷⁵⁻⁷⁶.

Water absorption and swelling measurements

Equilibrium water absorption of the Medium viscosity (MV)-alginate aerogel reached a maximum of 120 g/g in 24 h in saline solution, whereas the absorption of DI water only reaches a maximum of 20 g/g.⁷⁷ It is interesting that the water absorption of MV-alginate aerogels is higher when immersed in saline solution as compared to immersion in DI water, which is a promising feature for the practical applications of superabsorbent materials. In contradistinction, a typical synthetic or biopolymer based superabsorbent material absorbs much less saline solution (40–50 g saline/g material) compared to DI water (400–500 g water/g material)⁷⁸⁻⁸⁰. The super absorbents water absorbency primarily depends on the osmotic pressure, electrostatic repulsion and the elasticity of the polymer network. In this instance a possible reason for the increase in saline absorbency of the alginate aerogels is the increased ion-ion repulsions due to the enhanced availability of COO- groups in the highly porous aerogel network. The observed behavior of an ionic polymer in a salt solution is typically attributed to either salting-out or salting-in phenomena⁸¹. Salting-out occurs when the charges on the polymer are discharged in the presence of salt ions and, therefore, the interactions are decreased between the polymer and water, which leads to reduced water absorbency. Salting-out is expected to occur when a superabsorbent ionic polymer is put into saline solution. Salting in occurs when the polymer increases its charge in the presence of salt ions and favorable interactions are increased between the polymer and water, which leads to increased absorbency. Salting in is expected to occur when an alginate aerogel is put into saline solution. The increased saline absorption of the alignate aerogel beads is also accompanied by the swelling of the beads. Fig. 16 shows that the swelling of the MV-alginate aerogel beads in saline is significantly higher than the swelling in DI water. This swelling behavior of the alginate aerogel beads is in agreement with the higher water absorbency of alginate aerogel beads in saline as compared to DI water.



Fig. 16. Scanning electron micrographs of Ca-low viscosity (LV)-alginate aerogel (A) Ba-LV-alginate aerogel (B), Zn-LV-alginate aerogel (C), and Ca-MV-alginate aerogel (D)⁷⁷

6.2. Alginate fiber as photocatalysts for dye photodegradation

 TiO_2 photocatalysts can be effectively dispersed and stabilized into the matrix of Ca alginate porous hollow fibers, to develop pre-, or post-treatment photocatalytically active elements for membrane filtration. The photodegradation rate for a typical pollutant like methyl orange was much higher for TiO_2/Ca alginate fibers compared to bulk TiO_2 powder due to their high surface area and their MO adsorption capacity combined with the excellent dispersion and stability of the TiO_2 nanoparticles into the biopolymer matrix. In the hybrid photocatalytic/ ultrafiltration process proposed in this work, the presence of the prepared TiO_2/Ca alginate fibers as a pre-treatment stage to the membrane process led to a three folds enhancement of the MO removal efficiency and to dilution rather than condensation in the membrane retentate as commonly observed in filtration processes. This is very important especially in cases of highly toxic pollutants. The addition of fibers in the process increased the permeability of the photocatalytic membrane leading to an increased recovery rate at steady

state. The enhancements described above, are achieved by relatively low membrane and stabilized photocatalyst surfaces (26 cm² and 31 cm² respectively). In this context, upscaling would lead to much higher water yields without adding significant cost to the proposed water treatment process as the methods applied for the development of the involved materials (CVD and dry-wet phase inversion in a spinning setup) are easily upscalable⁸².



Fig. 17. TiO₂ nanoparticles deposited on the ultrafiltration membrane during the CVD, (a, b) externally, (c) internally (def) Ca alginate/TiO₂ hollow fibers⁸²

6.3. Alginate/chitosan micro-shells for removal of organic pollutants

layer-by-layer (LbL) assembled hydrogel films or films containing micro-gel components have received particular attention because of their high loading capability of guest materials in films, good biocompatibility and stimulus-responsive behavior of the films⁸³⁻⁹⁰. This LbL technology has been extensively utilized in three-dimensional geometry to produced hollow polymeric microcapsules/ micro-shells with various hydrogel components⁹¹⁻⁹³.

Natural polyelectrolyte micro-shells were constructed⁹⁴ through layer-by-layer (LbL) assembling of alginate sodium (ALG) and chitosan (CHI) onto weakly cross-linked melamine formaldehyde (MF) colloidal particles and subsequent removal of core. The assembled materials presented good film formation ability. It was found that under moderate conditions (room temperature, pure water solution) the ALG/CHI microshells can effectively load organic pollutants such as 2,4-dichlorophenol (DCP) and salicylic acid (SA). SEM and AFM images confirmed that the loading behavior of pollutants in the shells occurred and displayed that the feature of shell architecture changes before and after loading. The loading amount of pollutants into shell system was calculated and characterized through HPLC. The loading kinetics analysis showed that the loading process can

reach an equilibrium state after approximately 4 h. Compared to the conventional polyelectrolyte $(PSS/PAH)_5$ shells, the $(ALG/CHI)_5$ shells had stronger adsorption capacity and faster adsorption rate for pollutant loading. The adsorption isotherm result of organics in the ALG/CHI micro-shells can be well described by Langmuir equation. Advantages of the assembled natural microshells composed of ALG/CHI i.e. efficient loading ability to pollutants in aqueous ecosystem, good stability responded to external stimuli as well as fast loading process render them potentially applicable as environmental-friendly micro-container for the treatment of organic pollutants from aqueous solution.



Fig. 18. SEM images of the (ALG/CHI)₅ hollow shells (a) and shells upon incubating the preformed shells in various organic solutions in pure water medium: (b) DCP;
(c) SA. Scale bars are 5 mm for a, 5 mm for b and 3 mm for c.⁹⁴

As shown in Fig. 18(a), the assembled hollow ALG/CHI shells with a size of ca. 4 mm at the dry state exhibited many folds and creases owing to air-drying. When the obtained shells were loaded with organic compounds i.e. DCP, SA, apparent changes in the morphology of the filled shells appeared (see Fig. 18(b) and (c)). The empty shells look like folded thin shells, but the loaded shells look like filled balloons. All above images provided strong evidence that organic molecules including DCP and SA can migrate across the shell walls and then stay in the interior of the shells. Besides, the profile of each loaded shell is discerned as a spherical shape and this means that the ALG/CHI shells in external environments possess good stability. It is worth mentioning that the diameter of organics-loaded shells at the dry state is approximately 2.3 mm for DCP and 2.0 mm for SA, which is significantly smaller than the original template size of 3 mm. Furthermore, the surface of the DCP- or SA-loaded shells looks like smooth and rigid. This difference in the size and morphology of the shells loaded with organics could be explained by considering the shell wall components and molecular architecture of organic pollutants chosen. In the ALG/CHI shell walls, there should exist some residual charges originated from the carboxylic groups of ALG chains and amino groups of CHI that allow producing hydrogen bonds with organic substrates having suitable functional radicals such as hydroxyl groups and carboxylic groups. In addition, DCP and SA also facilitate forming hydrogen bonds in shell walls in view of their chemical structure. As a result, the interaction of the network structure composed of ALG/CHI and DCP or SA might cause the contraction of shell wall architecture and thus eventually make the framework of shell walls look like rigid and smooth. The changes of morphology and texture of the ALG/CHI films or ALG/ CHI beads have been observed by addition of ionic, rigid particles or phenolic derivatives⁹⁵⁻⁹⁷. All these observations suggest that the ALG/CHI shells just like an elastomer possess loading capacity and strong mechanical property.

6.4. Entrapment for nanoparticles

6.4.1. Entrapment of iron nanoparticles in calcium alginate beads

In recent years, zero-valent iron (Feo) nanoparticles (nZVI) have been used for the removal of various groundwater contaminants including chlorinated compounds⁹⁸⁻⁹⁹, pesticides¹⁰⁰⁻¹⁰², heavy metals^{103,104}, and explosives¹⁰⁵⁻¹⁰⁶ in water. Advantages of nZVI over other zero-valent iron (ZVI) such as microparticles (mZVI) and iron filings include higher reactive surface area (25–54 m² g⁻¹ for nZVI^{102,107,108} and 1m² g⁻¹ for mZVI¹⁰²), faster and more complete reactions, and injectability into the aquifer¹⁰⁹.

Because of smaller particle size and relatively higher dispersibility (as compared to other ZVI materials), nZVI becomes mobile in the aquifer¹¹⁰⁻¹¹¹. Further, if present in higher concentration, nZVI tend to agglomerate due to magnetic and van der Waals forces and form larger particles that settle into aquifer media pores. Agglomerated particles have decreased specific surface and hence lose the very advantage individual nZVI has. The higher mobility, agglomeration, and oxidation by non-target compounds in groundwater remain as major challenges for nZVI use for groundwater remediation. To overcome these problems Zero-valent iron nanoparticles (nZVI) have been successfully entrapped in biopolymer, calcium (Ca)- alginate beads¹¹². The study has demonstrated the potential use of this technique in environmental remediation using nitrate as a model contaminant. Ca-alginate beads show promise as an entrapment medium for nZVI for possible use in groundwater remediation. Based on scanning electron microscopy images it can be inferred that the alginate gel cluster acts as a bridge that binds the nZVI particles together. Kinetic experiments with 100, 60, and 20mg NO₃ -N L⁻¹ indicate that 50–73% nitrate-N removal was achieved with entrapped nZVI as compared to 55–73% with bare nZVI over a 2-h period. The controls ran simultaneously show little NO3 -N removal. Statistical analysis indicates that there was no significant difference between the reaction rates of bare and entrapped nZVI. The authors have shown for the first time that nZVI can be effectively entrapped in Ca-alginate beads and no significant decrease in the reactivity of nZVI toward the model contaminant (nitrate here) was observed after the entrapment.



Fig. 19. (a) An alginate bead with entrapped nZVI, (b) SEM image of alginate bead. The section was taken through the center of the bead, (c) SEM image of alginate bead surface after nZVI entrapment, (d) higher magnification of SEM image (b) bead interior with entrapped nZVI, (e) TEM image of Ca-alginate bead section shown in (d). Agglomeration/ concentration of nZVI can be observed. Non-uniform crosslinking within the Ca-alginate bead had led to cluster formation and high agglomeration/concentration of nZVI, (f) blow-up image of the circled area in (e). Nanoparticles are agglomerated/concentrated more in certain area rather than being uniformly distributed throughout the bead¹¹²

6.4.2. Dye adsorption by biocompatible composite (alginate/titania nanoparticle)

The preparation, characterization and dye adsorption properties of novel biocompatible composite (Sodium Alginate/titania nanoparticle) (SA/n-TiO₂) was investigated¹¹³. Titania (Degussa P25) was utilized. Its main physical data are as follows: average primary particle size 30 nm, purity above 97% and with 80:20 anatase to rutile.

Preparation of SA/n-TiO₂

3 g of SA were mixed with 1.5 g of $n-TiO_2$ powders in 300 mL of aqueous solution. The viscous solution was stirred continuously for 12 h. The slurry was stirred continuously for 24 h to obtain the final transparent solution. The dye adsorption measurements were conducted by mixing various amounts of SA/n-

 TiO_2 (0.15–1 g/L) for DR80 and AG25 in jars containing 200 mL of a dye solution (50 mg/L) at various pH (2–10).



Fig. 20. Chemical structure of Direct Red 80 (DR80) and Acid Green 25 (AG25).



Fig. 21. SEM images of (a) SA, (b) SA/n-TiO₂, (c) n-TiO₂, (d) AG25 adsorbed SA/n-TiO₂ and e) DR80 adsorbed SA/n-TiO₂.

The direct evidence of the formation of nanoparticles on the surface of SA was given by SEM (Fig. 21). SEM images of the SA/n-TiO₂ novel composite show that titania nanoparticles exist on the SA.

SA/n-TiO₂ were studied using FT-IR, SEM and WDX. Equilibrium and kinetic studies were done for the adsorption of Direct Red 80 (DR80) and Acid Green 25 (AG25) from aqueous solutions onto SA/n-TiO₂. Results showed that titanium oxide nanoparticles were immobilized onto SA. Adsorption studies showed that SA/n-TiO₂ could be effectively used as a biocompatible composite adsorbent for the removal of anionic dyes. The equilibrium data showed that data for DR80 and AG25 followed with Langmuir isotherm. The kinetics data indicated that the adsorption kinetics of dyes on SA/n-TiO₂ followed the pseudo-second order. The results showed that the SA/n-TiO₂ being a biocompatible, eco-friendly and low-cost adsorbent with relatively large adsorption capacity might be a suitable alternative for elimination of dyes from colored aqueous solutions.



Fig. 22. WDX images of (a) SA, (b) n-TiO₂ and (c) SA/n-TiO₂. WDX images of SA/n-TiO₂ novel composite showed the content of titanium at different samples (Fig. 22). Results show that titania nanoparticles exist on the SA.

6.4.3. Alginate gel beads filled with halloysite nanotubes

Novel hybrid gel beads with a well defined and controlled size formed by alginate biopolymer and halloysite (Hal) nanotubes were designed, prepared and characterized for removal of crystal violet from aqueous solutions¹¹⁴.

Halloysite (Hal) nanotubes are natural occurring clay minerals. The tubular structure shows typically the inner diameter from 15 to 100 nm, and the length from 500 to 700 nm¹¹⁵. Hal presents inner and outer hydroxyl groups, which are located between layers and on the surface of the nanotubes, respectively. These nanomaterials have hydrophilic character but, due to their size, they do not form kinetically stable dispersions in water. Recently, a large range of new exciting applications for these cheap and abundantly available natural clay minerals with nanoscale lumens were discovered and developed¹¹⁶⁻¹²¹.

These arguments straightforwardly prove the versatility and the potential use of Hal within several fields. The Hal encapsulation into matrices with dimensions of the order of millimeters may represent an advancement towards a multidisciplinary impact on many fields, like the environmental one, where new adsorbent materials are required to make efficient, effective and quantitative the removal of contaminants. Biopolymers as well as gel beads composed of polymers or polymer mixtures with sequestrant capabilities were proposed to capture contaminants from the aqueous phase¹²²⁻¹²⁵.

The formation of alginate gel beads occurs also in the presence of Hal. The gel beads' size is not significantly influenced by the Hal content while the transparency is reduced upon the addition of the clay mineral amount (Fig. 23).



Fig. 23. Optical images for hybrid gel beads at variable Hal content: a, PHal =0 mass%; b, PHal =33.2 mass%; c, PHal =48.5 mass%; d, PHal =60.2 mass%. The bar is 1 cm.

Gel beads present several advantages for controlled adsorption and release of substances (contaminants, drugs, and so on) thanks to the fact that they are easy to prepare, to collect and to dispose. With this in mind they loaded the alginate gel beads with efficient adsorbent nanotubes with the aim of obtaining new environmental friendly nanomaterials, which on one side have improved adsorption ability and on the other side make easy and practical the removal process.



Fig. 24. Scanning electron microscopy images of gel beads loaded with Hal at PHal =33.2 mass%. a, b, c refer to the surface; d, e, f refer to the core.

The SEM micrographs show that the dried bead possesses a rough surface with pores in the micrometer range (Fig. 24a–c) that is similar to what was observed in the absence of Hal¹²⁵. In addition, the nanotubes appear at the bead surface even if they are well incorporated into the polymer network. Investigating the core structure of the dried gel bead (Fig. 24 d–f), the Hal particles are more numerous than those at the surface

The thermogravimetry made it possible to determine the water content, the total as well as the local compositions of Hal into the gel beads. Dielectric spectroscopy evidenced that Hal reduced the fluctuation of ions. The performance of these materials was verified with the specific purpose of adsorbing crystal violet from aqueous phase. The alginate gel beads populated by Hal improved their ability to capture the dye so that they can have important implications in the enhancement of controlled adsorptions.

6.4.4. Alginate-g- poly(sodium acrylate-co-styrene) (NaAlg-g-p(AA-co-St) illite/smectite clay (I/S) nanocomposites for <u>adsorption of methylene blue</u>.

The mixed-layer illite/smectite clay (I/S) was organified and compounded with the sodium alginate-g-poly(sodium acrylate-co-styrene) (NaAlg-g-p(AA-co-St)) matrix to prepare a NaAlg-g-p(AA-co-St)/organo-I/S nanocomposite for adsorbing methylene blue (MB)¹²⁶.

Illite/smectite mixed-layer clay (I/S) is traditionally thought of as a mixture of crystallites that contain illite and smectite as two distinct, interstratified mineral entitles¹²⁷. It is produced from the illitization of smectite, which is one of the most frequent mineral reactions occurring in deeply buried sedimentary environments, and so it has the dual characteristics of illite and smectite¹²⁸. The mixed-layer structure characteristics make I/S clay is easily to be organized by cetyltrimethylammonium bromide (CTAB) through an ion-exchange process. The organo-I/S can be exfoliated as nano-sheet during polymerization more easily than the raw I/S. Thus, it is desired that the organification of I/S can further improve the comprehensive properties of composite hydrogel. There is rare report on the usage of I/S or organo-illite/smectite mixed-layer clay (organo-I/S) for the preparation of nanocomposite hydrogel. Sodium alginate -g-poly (sodiumbacrylate-co-styrene)/organo-illite/smectite mixedlayer clay (NaAlg-g-p(AA-co-St)/organo-I/S) nanocomposite hydrogels was prepared¹²⁷ by introduced organo-I/S with different organification degree.

NaAlg-g-p(AA-co-St)/organo- I/S nanocomposite was tested for adsorbing methylene blue (MB)¹²⁷. Fourier transform infrared spectroscopy, Xray diffraction and scanning electron microscope analyses confirmed the organification of I/S and the formation of the nanocomposite. The adsorption properties of the nanocomposite for MB was systematically investigated by optimizing the influence parameters, such as the organification degree of I/S, the pH of MB solution, contact time, initial concentration of MB and temperature. It was found that the nanocomposite can rapidly adsorb MB with a higher adsorption capacity (1843.46 mg/g), and the adsorption isotherm and kinetics were described well by Langmuir isotherm model and Ho's pseudo-second-order model, respectively. The moderate organification (0.25 E) (**0.25 folds of** (cation-exchange capacity) **CEC of I/S**), of I/S contributes to enhance the adsorption capacity of the nanocomposite for MB, which renders the nanocomposite promising for the efficient removal of cationic dyes.

Conclusion

In summary we have demonstrated that marine algae as biosorbents offer a cost effective potential and alternative to conventional methods for decontamination of water bodies at global, regional and local levels. Marine algae could be used in different methods as by using native dried algal biomass, rather than the fresh algae, without any pretreatments, by using chemical reinforced biomass, immobilization of algal biomass and by drying the algal biomass either by pyrolysis or by using concentrated acids or by using algal polysaccharides such as sodium alginate and carrageenan for preparing hydrogels (xerogels rather than aerogels), alginate fibers, alginate micro shells and alginate nanocomposites. The using of marine algae and algal polysaccharides hydrogels and nanocomposites showed an efficient loading ability to pollutants in aqueous ecosystem, good stability responded to external stimuli as well as fast loading process render them potentially applicable as environmental friendly candidate for the treatment of water pollution.

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