# Wastewater Treatment by Natural Polymer

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Water pollution caused by heavy metal ions and dyes is causing serious environmental problems. Heavy metal ions and dyes such as chromium ion (Cr(VI)) and methylene blue (MB) used in various industries are soluble in aquatic conditions. In an aquatic environment, they can be easily consumed and can cause severe health problems, including carcinogenicity and mutagenicity. Natural polymers such as lignin, cellulose, or chitosan are often used, or synthetic microspheres are modified using a bio-based polymer such as vanillin. Natural polymers meet one of the requirements to minimize the secondary pollution in that they are mostly eco-friendly and biodegradable. Besides this, natural polymers also exhibit great performance as adsorbents.

Keywords: polymeric wastewater ; wastewater ; natural polymer

#### 1. Cellulose

Cellulose is abundant in nature, has strong mechanical strength and abundant surface functional groups (hydroxyl groups), and is easy to modify. It is also biodegradable, being non-toxic (as are most natural polymers). Due to its beneficial properties, it is an adequate candidate for adsorbent of MB. The efficiency of its use as adsorbents and their functional groups is summarized in **Table 1**.

S. No	Polymer	Adsorbate	Adsorbent Capacity	Functional Group	Reference
1	CMC-AI@PEI-1.75	MB dye	235 mg/g	Amino	[1]
2	Pd NP/cellulose	MB dye	99.8%	Hydroxyl	[2]
3	CNC/MnO <sub>2</sub> /SA	MB dye	95.4%, 114 mg/g	Carboxyl	[3]

 Table 1. Summary efficiency of cellulose as adsorbent.

CMC: carboxymethyl cellulose, NP: nano particle, CNC: cellulose nanocrystal.

Millimeter-size hollow microspheres were fabricated from carboxymethyl cellulose microspheres (CMC) and PEI with glutaraldehyde as a crosslinking agent <sup>[1]</sup>.

The hydroxide ion in PEI in aqueous solution forms precipitate with Al(III), which can break the coordination bonds between the carboxyl and Al(III) in carboxymethyl cellulose microspheres, forming the hollow structures. SEM analysis was used to investigate the effect of usage and treatment time of PEI, and the results showed that they can make difference in shell thickness and size. The original spherical structure was completely deviated to form a powder-like structure when the PEI usage exceeded 3% and the internal network of composites were loosened as PEI treatment time increased. Thus, the adsorption of CMC-Al@PEI-1.75 was studied. The obtained hollow microsphere showed a superior performance in adsorption of MB of 235 mg/g. The large accessible amount of -NH2 groups and its unique hollow structure allowed the obtained microsphere to be applied in the treatment of wastewater. Another cellulose microsphere, palladium nanoparticles/cellulose microspheres (Pd NPs/CMs) were fabricated as catalyst for MB degradation [2]. The microsphere was prepared by in-situ reduction method based on the cellulosed microspheres. Pd nanoparticles grew on cellulose microspheres, with a Pd conversion rate of 33%. The spherical structure helped the cellulose microspheres function as suitable carriers for catalysts. The rate of decolorization was determined by UV-vis spectrophotometer. The decolorization efficiency of MB in presence of NaBH<sub>4</sub> was over 99.8% and the microsphere showed excellent reusability for five cycles. The decolorization was conducted through the destruction of the chromophores of MB. Zeta potential was measured to investigate the effect of pH. Solutions below pH 3.5 showed a low decolorization rate. The catalytic performance was better under an alkaline condition than in an acidic condition. First, the reactants were adsorbed on the surface of the catalyst ahead of the reaction, then the BH-4 transferred to metal from the surface of the catalyst. The

reactions continuously relayed to destroy the chromophores of MB, consequently decolorizing it. A cellulose nanocrystal (CNC)/MnO<sub>2</sub>-based porous microsphere is also used for MB decolorization. It was fabricated to solve the problem of CNC-based microsphere, namely its low porosity and specific surface area that limits the adsorption ability in wastewater treatment despite its beneficial properties such as simultaneous adsorption, degradation ability, facile separation, and recyclability <sup>[3]</sup>. SEM imaging showed its porous, honeycomb-like structure which was formed by freeze-drying the air bubble templated emulsion and ionic crosslinking method that used SA as a crosslinked matrix. SA added carboxyl groups that provided negative charge for interaction with cationic MB dye. The CNC/MnO<sub>2</sub>/SA microsphere showed low density of 0.027 g cm<sup>3</sup> and high porosity of 98.23%. The removal efficiency was measured through UV-vis spectrometry. The high porosity enhanced the adsorption effect, the decolorization of MB was conducted within 10 min up to 95.4%, and the equilibrium decolorization reached 114.5 mg/g. The great recycling ability and its green and simple fabrication process proved to be a great application prospect in the removal of dye on wastewater treatment. Three cellulose microspheres are all used for removal of MB dyes, but their removal mechanisms differ along their different functional groups.

## 2. Alginate

Algae that adsorb heavy metal ions are mostly used in the form of SA as adsorbents. Alginate is naturally abundant, can be obtained from seaweed, and is biodegradable and hydrophilic. It is modified in various ways; for instance, it can be mixed with zeolite and made into bead form. The efficiency of alginate as an adsorbent is summarized in **Table 2**.

S. No	Polymer	Adsorbate	Adsorbent Capacity	Kinetic Model	Isotherm Model	Reference
1	Fe <sub>3</sub> O <sub>4</sub> @HCO in SA microbead	Sb(III)	15.368 mg/g	PSO	Langmuir	[ <u>4</u> ]
2	HA@SA	Sb(III)	195.7 mg/g	PSO	Langmuir	[5]
3	zeolite/alginate	Ni(II)	98%	PFO	Freundlich	[6]
4	CSM/SA hybrid bead	Pb(II), Cr(VI)	189, 16 mg/g	PFO, PSO	Langmuir	[Z]
5	PAM/SA	MB dye	1070.54 mg/g	PFO	Langmuir	[8]
6	NRGO/SA/PVA	ANT, 2-MAQ	0.72, 0.70 mg/g	PSO	Freundlich, D-R	[9]

 Table 2. Summary efficiency of alginate as adsorbent.

HCO: hydrous cerium oxide, HA: hyperbranched polyamide, CM, CSM: chitosan microsphere, NRGO: N-doped reduced graphene oxide, ANT: anthracene, 2-MAQ: 2-methyllanthraquinone, D-R: Dubinin–Radushkevich.

Ferriferous oxide@hydrous cerium oxide (Fe<sub>3</sub>O<sub>4</sub>@HCO) was encapsulated into sodium alginate microbead (SAB) by an improved co-precipitation method to remove antimony (Sb(III)) ions within a concentration range of 5–60 mg/L <sup>[4]</sup>. The magnetic microsphere can be easily retrieved from aqueous solution by a magnetic separation. The introduction of SA resolves the poor precipitation and easy hardening issues of prior Fe<sub>3</sub>O<sub>4</sub>@HCO adsorbent as SA easily complexes with divalent cations, which can make gel forms. The adsorption kinetics followed the PSO model and the adsorption isotherm followed the Langmuir model, indicating that the mechanism was the result of cooperation of chemisorption (ion exchange) and physisorption (diffusion reaction). Surface hydroxyl groups of SAB whose presence was confirmed by FTIR results were the major source for the adsorption. Initial and pH and temperature had an influence on adsorption performance, and microbeads did not collapse within a pH range of 3–7. The environmentally friendly and cost-effective main components (Fe<sub>3</sub>O<sub>4</sub> and HCO) and the facile preparation of SAB show the potential of the microsphere as adsorbent for Sb(III) in large scale.

Similarly, a hyperbranched polyamide-functionalized sodium alginate (HA@SA) microsphere was prepared for the removal of Sb(III) and followed the PSO and the Langmuir models <sup>[5]</sup>. A HA@SA microsphere was fabricated by grafting 1.0 g of HA on the surface of SA microsphere. SEM image showed that the microsphere had average diameter of 3.0 nm and surface roughness increased after the adsorption of Sb(III). The optimal adsorption was conducted at pH 5.0. and the maximum Sb(III) adsorption capacity was 195.7 mg/g, which was 1.16 times higher than SA microspheres without HA. The adsorption process was a homogeneous single-layer adsorption which was controlled by chemisorption and was an exothermic and spontaneous reaction. The HA@SA microsphere maintained its adsorption capacity of 90% after recycling for eight adsorption-desorption cycles, even at low flow rate and concentration in practical usage. A zeolite/alginate microsphere was fabricated for Ni ions removal from aqueous solution <sup>[6]</sup>. The SA microsphere improves the adsorption of zeolite adsorbent by immobilizing the zeolite powder due to its hydrophilic property. The adsorption ability of the SA-modified microsphere is supported by many characterizations. The FT-IR results shows that Zeolite particles reacted with

alginate polymer through hydrogen bonding. XRD pattern show the crystalline phase is the same as that of zeolite, but in a lower intensity due to the amorphous phase. SEM micrographs shows the folds and groves of the microsphere that enhance its adsorption capacity. The microsphere showed a removal efficiency of 98% within 150 min. The kinetic study showed that the adsorption followed the PSO model, indicating that the metal ion removal rate is dependent on the number of free active sites. An isotherm study shows the sorption process follows the Freundlich model, indicating a heterogeneous surface. The Dubinin–Kaganer–Radushkevich (DKR) model study proves that removal reaction is endothermic and the sorption process is chemical. The Zeolite/alginate microspheres can be reused five times without deformation and with the same efficacy. SA can improve adsorbent in other ways; for instance, it can be used as matrix for different microsphere to produce hybrid beads. Chitosan microsphere/sodium alginate hybrid beads (CSM/SA) were fabricated for the removal of heavy metal ions from aqueous solution <sup>[7]</sup>.

The microsphere was applied in the removal of Cr(VI) and Pb(II). The properties of the hybrid beads were enhanced via mutual interaction between original chitosan microspheres and SA. Additionally, the effects of different metal concentrations, pH solutions, and contact times were evaluated. The maximum adsorption capacity obtained from atomic absorption spectrophotometer was 180 mg/g for Pb(II) and 16 mg/g for Cr(VI). EDX results confirmed that the amount of adsorbate is proportionate to the quantity of Ca<sup>2+</sup> on the surface of CSM/SA hybrid beads, but Cr retention is dependent on electrostatic attraction. TGA-DTA analysis showed the high thermal stability of the CSM/SA. The first step of the four thermal degradation was from 25 to 240 °C and showed a 9.7 wt% loss. The adsorption kinetics were evaluated using the PFO and PSO models. The sorption of both Pb(II) and Cr(VI) fit the Langmuir model, indicating that it was monolayer adsorption.

A PAM/SA adsorbent with double network structure was prepared for adsorption of MB dye, while the MB concentration was determined using a UV-vis spectrophotometer [8]. The PAM/SA microsphere was prepared via emulsion polymerization of acrylamide and SA. The double network structure was formed from the entanglements between PAM and SA molecular chains. TGA results revealed that adding SA decreases the thermal stability and crystallinity of PAM, but the adsorption capacity of microsphere increased. The microsphere had a smooth surface, the particle size was in range of 1-10 µm, the pore size was in range of 0-200 nm, the mesoporous structure was uniform, and the ion crosslinking point was uniformly distributed. At pH 6, 25 °C, and 0.1 g adsorbent dosage, the maximum adsorption capacity reached 75 mg/g.  $-COO^{-}$  on SA has hydrogen bond with -OH and  $-NH_{2}$  and has electrostatic interaction with  $-C=N^{+}$  of MB, which is beneficial for MB molecule to agglomerate and be adsorbed on the surface of SA/PAM composite microspheres. The adsorption followed PFO kinetics and the Langmuir isotherm model, indicating that it was physical adsorption and that the maximum capacity was 1070.54 mg/g. The adsorption force decreased with rising temperatures. SA microspheres can also adsorb organic pollutants <sup>[9]</sup>. An N-doped reduced graphene oxide/sodium alginate/polyvinyl alcohol (NRGO/SA/PVA) microsphere was fabricated to remove anthracene (ANT), its oxygenated-polycyclic aromatic hydrocarbon (OPAH), and 2methylanthroaquinone (2-MAQ) and reduce the risk of the application of nanomaterials in a water environment. It was prepared with 2.0 wt% SA, 1 wt% PVA, and 3.22 wt% NRGO through a simple embed method. NRGO was embedded instead of GO because it has a higher affinity for hydrophobic organic pollutants than GO. TGA and DTG analysis showed that among three steps of thermal degradation, the second stage showed the greatest weight loss of 42.7% at 275-600 °C due to the degradation of PVA and calcium alginate. The residual polycyclic aromatic hydrocarbons (PAHs) concentration was measured using a gas chromatograph-mass spectrometer. The sorption kinetics followed the PSO model and equilibrium data followed the Freundlich and D-R isotherm model, indicating that the adsorption was chemical adsorption. Hydrogen bonding and  $\pi$ - $\pi$  interactions mainly attributed to the adsorption mechanism.

### 3. Chitosan

Chitosan is obtained by treating chitin, obtained from living organisms. Ascribed to its eco-friendly and abundant functional groups such as amino and hydroxyl groups, it is used as adsorbents for pollutants. Additionally, modification into magnetic microsphere is possible due to its nano particle encapsulation property. Its performances as adsorbents are summarized in **Table 3**.

 Table 3. Summary efficiency of chitosan as adsorbent.

S. No	Polymer	Adsorbate	Adsorbent Capacity	Kinetic Model	Isotherm Model	Reference
1	(CYCTS/Span80)-@PEI	DS	572.28 mg/g	PSO	Langmuir, Freundlich	[10]

S. No	Polymer	Adsorbate	Adsorbent Capacity	Kinetic Model	Isotherm Model	Reference
2	BSCM-CM	CR dye degradation efficiency	85%	first order	-	[11]
3	ZBiSe-CM	CR dye degradation efficiency	99.63%	PFO	-	[12]
4	ССФМ	CR, MO dye, Cu(II), Fe(II)	1500, 179.4, 687.6, 398.8 5 mg/g	PSO	Langmuir	[13]
5	chitosan-activated carbon composite	MO dye	35.64 mg/g	PSO	Freundlich	[14]
6	CTA-CSM	MO dye	131.9 mg/g, 98.8%	PSO	Langmuir	[15]
7	CS-PSSS	MB dye	854 mg/g	PSO	Langmuir	[ <u>16]</u>
8	CS	Cr(VI)	945.2 mg/g	PSO		[17]
9	CS-MA-DETA	Pb(II), Cd(II)	239.2, 201.6 mg/g	PSO	Langmuir	[18]
10	CM with PHEMA brushes	Cu(II)	299 mg/g	PSO	Langmuir	[ <u>19]</u>

CYCTS: carboxylated chitosan, DS: diclofenac sodium, BSCM: bismuth cobalt selenide, CM, CSM: chitosan microsphere, CR: Congo red, CCQM: quaternized chitosan@chitosan cationic microsphere, CTA: trimethyl ammonium chloride, PSSS: poly(sodium 4-styrene sulfonate, CS: chitosan, PHEMA: poly(hydroxyethyl methacrylate), MA: methyl acrylate, DETA: diethylenetriamine.

Polyethyleneimine-functionalized chitosan/Span80 microspheres ((CYCTS/Span80)-@-PEI) were fabricated to remove diclofenac sodium (DS) from wastewater effectively <sup>[10]</sup>.

Carboxylated chitosan (CYCTS) was added dropwise into cross-linking agent Zr<sup>4+</sup> solution to spherical structure. PEI was grafted on to its surface, and nonionic surfactant Span80 was dissolute from microsphere using an organic solvent for formation of pores. The surface of microsphere, examined through SEM image, had substantial number of NH<sup>3+</sup> and a dense pore structure, which was useful for adsorption of DS. The DS adsorption was measured via UV-vis spectrophotometer, and the maximum adsorption was 572.28 mg/g at pH 5.00 and 27 °C with adsorbent loading of 15 mg. The adsorption process followed the PSO kinetic model, Langmuir isotherm model, and Freundlich isotherm model, indicating that the adsorption was a multi-layer process.

A chitosan-bismuth cobalt selenide hybrid microsphere (BSCM-CM) was made to remove organic pollutants from aqueous environment [11]. Bismuth cobalt selenide (BSCN) tri-composite nanoparticles with crystalline structures and a narrow bandgap of 2.48 eV were prepared and were embedded in chitosan microspheres via a solvothermal process to prevent the leaching of the photocatalyst and to enhance the recovery and reuse of the composite. The SEM image, FT-IR, and XRD results confirmed that the obtained BSCM-CM had smooth face morphology with an average nanoparticle size of 30 nm, an average microsphere size of 734 µm, and a crystallite size of 21.3 nm. In sunlight radiation, the degradation efficiency for CR dye was 85% of the 90 ppm solution at catalyst amount of 0.6 g, pH 8, for 100 min. The adsorption was well described by first order kinetics, with a constant rate of  $1.50 \times 10^{-2}$  min<sup>-1</sup>. The microsphere could be regenerated and reused for up to five cycles. Similarly, other CMs with BiSe, zinc-bismuth-selenide-chitosan microspheres (ZBiSe-CM), were fabricated as catalysts for photocatalytic degradation of CR dye [12]. First, ZBiSe nanoparticles were synthesized via a solvothermal process and then crosslinked with chitosan for support and to prevent leaching of the catalyst. SEM imaging showed that the average size was 30.9 nm for each nanoparticle and 812 µm for the spherical and porous microsphere, and XRD analysis confirmed that crystallite size was 27.04 nm for the nanoparticles. The degradation efficiency of the ZBiSe-NP reached 99.63% for 40 ppm concentration of CR at catalyst dosage 0.225 g, pH 8.0, and 36-38 °C for 2 h of solar light illumination. The photodegradation of microsphere followed PFO kinetics, and the microsphere remained its high decontamination efficiency for five cycles. Both BSCM-CM and ZBiSe-CM shows high potential for photocatalytic degradation of CR dye using clean and renewable energy of solar light irradiation sources, while ZBiSe-CM showed higher degradation efficiency than BSCM-CM. The effects of several factors for the absorption and the relationship between the factors were investigated using response surface methodology (RSM) modeling. A quaternized chitosan@chitosan cationic polyelectrolyte antibacterial microsphere (CCQM) was fabricated via the chemical crosslinking and emulsification method for removal of dyes and heavy metal ions [13].

CCQM has a higher specific surface area, pore volume, and surface charges, lower crystallinity, and displayed higher adsorption capacities than did pristine chitosan microspheres. Through DTG analysis, it was found that the highest decomposition rate was at a lower temperature than pristine chitosan and that the addition of quaternized chitosan increased the thermal stability. The adsorption followed the Langmuir and PSO models and Fickian diffusion laws' equation, indicating that the adsorption was primarily monolayer chemisorption and pore diffusion mainly determined the adsorption rate. The adsorption reached equilibrium within 4 min, and the adsorption capacity was 1500 mg/g for CR, 179.4 mg/g for MO, and 687.6 mg/g for Cu(II), and 398.8 mg/g for Fe(III). The effective absorbance of  $Cu^{2+}$  is due to its smaller steric hindrance. Cation exchange, chelating effect, proton exchange, and complex formation facilitated effective heavy metal ion removal, and electrostatic interaction and hydrogen bonding facilitated the removal of dyes. CCQM can be used as a filler in adsorption columns to purify wastewater, as it has superb recyclability, antibacterial viability for sterilizing, and biodegradability within 165 days. Other CMs made using the emulsion cross-linking method is chitosanactivated carbon composite microspheres, which were prepared for adsorption of MO <sup>[14]</sup>. A chitosan solution was mixed with activated carbon powder and then chitosan was cross-linked by epichlorohydrin under microwave irradiation, which effectively shortens the cross-linking time. SEM imaging displayed that the obtained microsphere had a diameter of 200-400 µm and activated carbon powder was dispersed on the surface of chitosan composite microsphere. The maximum adsorption of MO was obtained when the mass ratio of chitosan to activated carbon was 10:4, labeled CA4, and the capacity was 35.4 mg/g. TG curves showed that CA4 loses weight rapidly in the temperature range 200-350 °C due to the decomposition of chitosan. The adsorption was dependent on temperature, and maximum adsorption occurred at 30 °C. The adsorption followed the PSO model and the Freundlich isotherm model. The microsphere retained 94.49% of its adsorption capacity for MO after it was reused for three cycles. A quaternary ammonium salt-modified chitosan microsphere (CTA-CSM) was prepared for the treatment of dye in wastewater [15]. The CTA-CSM was fabricated through an emulsion cross-linking reaction between 3-chloro-2-hydroxypropyl trimethyl ammonium chloride (CTA) and chitosan. SEM imaging confirmed that the microsphere had smooth surface and was well dispersed. Through laser light scattering particle size analyzer, it was discovered that particle size was distributed in the range of 5 to 125 µm. The grafting of CTA on the CS microsphere enhanced the adsorption capacity for MO dye from previous reports, as the maximum removal rate was 98.8% and adsorption capacity was 131.9 mg/g under optimal condition. The MO adsorption process well fitted by the Langmuir isotherm model and followed the PSO kinetic model. Additionally, the CTA-CSM retained its high removal rate after it was reused for five cycles over 87.4%. Thus, CTA-CSM is a promising adsorbent for treating wastewater that contains MO dye for its cost-effective, sustainable, and highly reusable properties. For the removal of cationic dyes and MB, a MCS-g-PSSS microsphere was made by grafting poly(sodium 4-styrene sulfonate) onto magnetic chitosan microspheres [16].

Chitosan microspheres are also used as adsorbents of heavy metal ions. A porous chitosan microsphere was produced without other polymers using the freezing-lyophilization drying method for the removal of hexavalent chromium, Cr(VI) <sup>[127]</sup>. The optimal chitosan microsphere was produced by freezing chitosan hydrogel beads at -20 °C and subsequently lyophilizing the frozen structure, which allowed for the easy obtaining of some beneficial structures of the chitosan microspheres for efficient removal, rough surfaces, and large pores. The microsphere was characterized using porosity analysis. Microspheres with good sphericity, thinner pore walls, and small pore sizes made with an initial chitosan solution concentration of 3% (*w*/*v*), a syringe diameter of 500 µm, a pH range from 3.0 to 5.0, a temperature of -20 °C, and 72 h freezing time showed a maximum adsorption capacity of 945.2 mg/g for Cr(VI). The adsorption capacity increased as freezing time increased. The adsorption rate was governed by multiple steps, and the adsorption was primarily attributed to amine and hydroxy groups of chitosan microspheres. In optimal conditions, the equilibrium adsorption rate was  $1.83 \times 10^{-5}$  g/mg-min and the adsorption amount at equilibrium was 107.05 mg/g. Cross-linking of CS improves mechanical property, but it consumes the functional groups that are beneficial for adsorption. Thus, a chitosan-methyl acrylate-diethylenetriamine microsphere was made without any cross-linking agent to uptake Pb(II) and Cd(II), from wastewater [18].

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