CELLULOSE CHEMISTRY AND TECHNOLOGY

CLADOPHORA CELLULOSE–POLYANILINE COMPOSITE FOR REMEDIATION OF TOXIC CHROMIUM (VI)

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This paper describes the fabrication of a composite material consisting of *Cladophora* cellulose and polyaniline (PANI). Cellulose extracted from environmentally polluting green algae *Cladophora rupestris* was used as a matrix and conducting polyaniline coating was applied on its surface. The characterization of the composite revealed the presence of a nano-layer of PANI coating on the cellulose fibers, thus preserving the high surface area of the cellulose. The cellulose/PANI composite was used effectively as a reducing agent in the remediation of toxic hexavalent chromium. The efficiency of the reduction activity of metals can be attributed to the high surface area of the cellulose/PANI composite. This study provides alternative ways to solve an environmental issue and maximize the use readily available resources.

Keywords: polyaniline, *Cladophora* cellulose, composites, chromium (VI) reduction

INTRODUCTION

Eutrophication of bodies of water is a serious environmental problem.[1] The excessive bloom of green algae results in severe reduction in water quality particularly in lakes.[2] This algal biomass lingers for a long time despite nutrient erosion and depletion.[3] Maria Stromme correctly asked the question: "What are we to do with all these Algae?"[4] The utilization of these abundant, yet unwanted materials is an obvious answer.

The cellulose derived from the environmentally polluting green algae (*Cladophora* sp.) is an appealing material and has been studied for its application to functional materials.[5] However, most studies conducted on algal cellulose are done using the marine pollutant *Cladophora* species. In this study, we collected *Cladophora* green algae not from the sea, but from lake water, particularly in Taal Lake (Batangas, Philippines), where the active Taal Volcano lies. The environment in which the *Cladophora* grows in Taal Lake with an active volcano differs from the salt water condition for marine algae. The water chemistry may impart some physiological changes on algal growth or morphological changes in the cellulose chains. The alga grows on rocks, but seasonally, it floats heavily on water affecting the ecological balance of the lake, making it an undesirable occurrence. Local folks usually spend time, effort and money just to gather and burn these algal blooms. Thus, it is highly desirable to find technological use for these pollutants.

The general structure of the cellulose extracted from *Cladophora sp.*, as compared to plant-derived microcrystalline cellulose, usually shows a higher degree of crystallinity (95% vs. 82%; X-ray diffraction), a larger surface area (63-95 m^2/g vs. 1 m^2/g via N_2 gas adsorption) and a higher pore volume (0.554 cm^3/g vs. 0.003 cm^3/g; BET N_2 adsorption).[6-7] The large surface area of algal cellulose offers high potential for the adsorption of liquid drugs,[8] pharmaceutical and food dispersible ingredients[9] and pyrrole monomers.[10] The adsorbed monomers in the latter have been demonstrated to undergo polymerization to obtain a cellulose-polypyrrole composite.

Cellulose infused with conductive polymers has received significant attention recently. The cellulose provides the matrix to reinforce mechanically brittle conductive polymers, supporting their unique electrical, conductive and redox activities. These composite materials have been shown to be highly suitable for use in acidity-sensing,[11] heating devices,[12] design of actuators,[13,14] flame retardation,[15] electromagnetic interference shielding,[16] electrochemically controlled ion-exchange,[17,18,19] ultrafast polymer battery[20] and reduction of metals.[21]

Composite materials based on cellulose, whether derived from land plants or bacterial cellulose,[22] and conducting polyaniline (PANI) can be prepared by mixing the cellulose, aniline monomer and oxidizing agent in a one-pot process to allow *in situ* polymerization on cellulose fibrils[21,22,23,24] or by dipping the cellulose in a toluene solution of PANI.[25] A layer-by-layer approach has likewise been described for a conductive paper made from wood microfibers, carbon nanotubes and poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT-PSS). In most of these techniques, thick layers of the conducting polymers are generally achieved.

To obtain a thin layer, a unique approach based on chemical polymerization-induced adsorption process has been demonstrated on commercial filter paper[26] and more recently on *Cladophora* cellulose,[10] where nano-layers of polypyrrole coating is applied uniformly on the cellulose fibers. The formation of thin coating is particularly significant where efficiency of ion exchange is desired because ions are capable of penetrating only on short distances into the polymer matrix. Thus, thin coating of conducting polymer distributed uniformly over a large internal surface area exhibited more efficient ion exchange than thick coating on a non-porous substrate.[17,18]

In the application of the conductive polymer for metal reduction, PANI is well studied because of the ease of preparation, good conductivity and excellent stability. Composites of electrically conductive polymers are highly sought because they exhibit conductivity close to that of the conducting polymer, yet with the potential for more useful flexible film applications. We report herein the fabrication of a composite consisting of thin layers of conducting PANI applied on high surface area *Cladophora* cellulose and its use in the remediation of toxic chromium.

EXPERIMENTAL

Materials

The aniline (Sigma-Aldrich), ammonium peroxodisulfate (Merck), tween-20 (Asia Pacific Specialty Chemicals Ltd.), $NaOCl_2$, acetic buffer, HCl, NaOH, potassium dichromate (UNIVAR Ajax Chemicals) were used as received. Unless otherwise specified, deionized (0.006 μS) water was used.

Aniline-HCl salt was prepared by adding concentrated HCl dropwise to 100 mL aniline under constant stirring at room temperature and in the dark. The completion of the reaction was monitored when the drops turned green, by testing the mixture on a methyl violet-soaked filter paper. The salt was precipitated by placing the solution in a salt-ice bath, filtered and washed with ice-cold water. A 2.60 g of aniline-HCl was dissolved in 50 mL deionized water. A drop of tween-20 was added to the solution. The solution was stored for one hour prior to use. The oxidant was prepared by dissolving ammonium peroxodisulfate (5.73 g) in 50 mL deionized water. This solution was allowed to stand for at least an hour prior to use.

The green *Cladophora* algae were collected from the shores of Taal Lake in Barangay Balas, Talisay, Batangas, Philippines. The algae growing around rocks were collected and identified at the Philippine National Museum as *Cladophora rupestris*. The washed and air-dried algae were bleached by soaking with 70% $NaOCl_2$ solution in acetic acid buffer. The mixture was kept at 60 ºC in a water bath for 4 hours. After bleaching, the mixture was filtered and washed with distilled water until a neutral pH was reached. The algae were then soaked in 0.5M NaOH, maintaining a temperature of 60 ºC overnight. The resulting pulp was washed to neutrality with distilled water. The cellulose obtained was ground in a blender then soaked in 1 L of 5% HCl. The suspension was boiled for 20 minutes then allowed to stand overnight. The product was filtered, washed to neutrality then air-dried. The cellulose was further dried using a freeze-drier (LABCONC Freeze Dryer System/Freezone) and then ground using a coffee grinder (Dowell).

The preparation of the composite was achieved by preparing a 300 mg sample of *Cladophora* cellulose, dispersed in 150 mL deionized water using ultrasonication (KLN Ultraschall-GMBH 6148 at a frequency of 39 KHz) for 20 minutes. The cellulose was collected through filtration then added into a prepared aniline-HCl solution in a beaker and dispersed again using the ultrasonicator for 3 minutes to allow the anilinium chloride to adsorb onto the cellulose fibers. The cellulose slurry was then collected in a filter paper using the Buchner funnel and the ammonium peroxodisulfate solution was allowed to pass through the filter cake to induce polymerization of the adsorbed aniline. The formation of polyaniline was observable through a blue/green coloration of the filter cake. The polyaniline-coated cellulose was rinsed with HCl solution (0.2M) by allowing the acid to run through the cellulose composite in the same Buchner filtration set-up. The treatment by HCl ensures the formation of the emeraldine salt (ES) form of PANI. After washing with deionized water until neutrality, the free polyaniline was removed from the composite using ultrasonication with acetone for 20 minutes and rinsing with acetone through a filter paper. The process was repeated until the acetone washing obtained was opaque. The cellulose-polyaniline composite was then collected through a filter paper, rinsed with acetone, air-dried and stored in a dessicator.

Characterization methods

The freeze-dried composite was measured using the Nicolet Nexus 6700 FTIR instrument using the KBr pellet method. The FTIR of the cellulose and polyaniline were likewise measured using the KBr pellet method. The surface morphology of the cellulose/PANI composite was analyzed using the JEOL JSM 5310 Scanning microscope. Energy dispersive X-ray spectroscopy (EDX) analyses were likewise done on the same samples. TGA analysis was done using TGA Q500 v6.7. The conductivity of the cellulose/PANI composite was done using the four-point probe Van der Pauw technique using pelletized samples of the dried composite.

Reduction of toxic chromium (VI) using *Cladophora* cellulose-polyaniline composite

The chromium solution was prepared using potassium dichromate (50 mg) and 1 L of deionized water. The pH was adjusted to pH 2 by adding freshly prepared 1N H_2SO_4 solution.

The *Cladophora* cellulose/PANI salt composite was soaked in freshly prepared 1M NH_4OH for 30 minutes to facilitate the formation of the emeraldine base (EB) form of polyaniline. After the deprotonation process, the resulting blue-black composite was washed with water, rinsed with acetone and air-dried.

The remediation of chromium (VI) was achieved by soaking the cellulose/polyaniline composite (0.515 g) in 200 mL of the 50 mg/L Cr(VI) solution. The mixture was stirred using a magnetic stirrer. An aliquot sampling was done by drawing out 6 mL of the mixture using a pipette at 5, 10, 20, 30 and 60 minutes, respectively. Three trials for every time exposure were carried out. Each of the suspensions was then filtered and the filtrates were tested for hexavalent chromium [Cr(VI)] concentrations using UV-Vis. The absorption spectra of each sample were recorded between 200 and 800 nm and the concentration of the remaining Cr(VI) in each of the samples was determined by measuring the absorption of each at ~355 nm.[27] The same procedure was carried out for pure *Cladophora* samples, to serve as controls.

RESULTS AND DISCUSSION

The cellulose extracted from the cell walls of green *Cladophora* algae is insoluble in water, but contrary to cellulose from common paper, it does not swell much, suggesting less capacity to absorb much water. This observation indicates the highly crystalline nature of the *Cladophora* cellulose derived from the lake. Despite the presence of many hydroxyl groups in the chain, water cannot easily penetrate through the chains, if the cellulose has a high degree of crystallinity. This observation supports the report of Mihranyan *et al.*,[28] according to which moisture absorption by cellulose decreases as the degree of crystallinity increases. The ability of water to penetrate the structure and cause swelling depends largely on the number of available hydroxyl groups or, in other words, degree of crystallinity.[29] The degree of crystallinity of cellulosic materials can be determined quantitatively from FTIR spectrum by measuring the ratio of intensities of preselected absorption bands.[30] The infrared peak ratios between 1429 cm^{-1} and 897 cm^{-1} (H_{1429}/H_{897})[31] and between 1372 cm^{-1} and 2900 cm^{-1} (H_{1372}/H_{2900})[32] are a measure of crystallinity in cellulosic material. The peak intensity ratio H_{1429}/H_{897} is a measure of lateral order crystalline packing of the cellulose chains. Table 1 shows the observed IR peak ratios as compared to published data. The IR peak ratios of the *Cladophora* cellulose from Taal Lake shows consistent IR peak ratios and thus comparable % crystallinity with that reported in literature for marine *Cladophora* cellulose, which differs significantly from wood cellulose.

The high degree of crystallinity for the *Cladophora* sample indicates a higher order of the polymer chains and thus higher surface area, compared to wood cellulose. Cellulose of type I, which is the native cellulose found in terrestrial plants and commonly used in paper industry, has a relatively small specific area, of the order of 1 m^2/g.[7] On the other hand, cellulose extracted from the cell walls of *Cladophora* sp. green algae is highly crystalline[6] and has a uniquely high surface texture composed of numerous intertwined strings, producing an aggregate web-like structure of high porosity and large surface area.[7]

Cellulose fibers are known to be well wetted by polymers, like polypyrrole, making the homogeneous coating of individual cellulose fibers possible. Composites of cellulose with conductive polymers are attractive since these are fully recyclable, lightweight, mechanically robust, and can be manufactured at low costs.[16,17]

The polymerization of aniline, with formation of thin coating on cellulose fibers was achieved by allowing the aniline monomers to adsorb onto the surface of the cellulose fibers before allowing the polymerization agent to pass through. Cellulose fiber in contact with the reaction mixture becomes coated with a thin layer of PANI via H-bonding between aniline N-H groups and oxygen moieties in cellulose. By this technique, a nano-layer of polyaniline (PANI) is developed on the cellulose fibers compared to the micro- and milli-layers that can be formed by mixing the monomer, polymerization agent and the cellulose in one pot. A nano-layer of PANI coating will maintain the high surface area of the cellulose.

The blue coloration observed after allowing the polymerization agent to pass through the cellulose with adsorbed aniline indicates a successful polymerization. After sonicating the residue with acetone to remove the free PANI and washing several times in acetone, the obtained cellulose-PANI composite remains blue in color, which is indicative of PANI being still locked in the cellulose fibers. The FTIR spectrum of the composite in the fingerprint region distinguishes the presence of PANI: a) the peaks at 1560 cm^{-1} and a shoulder band at 1480 cm^{-1} observed in the FTIR spectrum of the composite refers to the quinine and benzene ring stretching deformations; b) the band at 1306 cm^{-1} corresponds to π-electron delocalization induced in the polymer by protonation;[33] c) the band at 1232 cm^{-1} is characteristic of the conducting protonated form of PANI; d) the band at 1147 cm^{-1} is assignable to a vibration mode of the $–\mathrm{NH}^{\bullet+}–$ structure in the spectrum of PANI hydrochloride.

The SEM images (Figure 1) of the pure *Cladophora* cellulose indicate intertwining fibers with smooth surfaces, while those of the *Cladophora* cellulose coated with PANI show all fiber surfaces coated with amorphous/granular-like coating, indicative of uniform morphological modification. Nano-layers (~50 nm) of PANI coatings are formed on the cellulose fibers maintaining its high surface area. EDX data of the cellulose/PANI composite confirm the presence of the conducting polymer coating as indicated by high levels of N (32.64%). The detection of chlorine also shows that the PANI is in the emeraldine salt form, which is the conducting form of PANI.

The presence of PANI as coating in cellulose is also manifested in the thermogravimetric analysis (TGA), as shown in Figure 2. TGA measures the amount and weight change in a material as a function of increasing temperature in a controlled atmosphere. About 87% of the original *Cladophora* cellulose material is lost at 318 ºC, while at 446 ºC, the material is almost degraded. The initial losses are due to the moisture, followed by evaporation of volatiles as a result of cellulose backbone degradation. In the PANI-coated cellulose on the other hand, 48.40% of the composite mass is reduced at 288 ºC, leaving mostly the PANI. The gradual loss of material starting at 300 ºC is attributed to PANI loosing an acid due to the deprotonation of protonated PANI to PANI base.[34] The thermal stability of the resulting PANI base is higher than that of pure cellulose, thus the composite residue above 446 ºC is higher compared with that of neat cellulose fibers. The same observations have been reported by Stejskal.[35]

The presence of PANI coating on the cellulose fibers is further confirmed by measuring the electrical resistivity profile and conductivity of the composite, as compared to those of pure *Cladophora* cellulose. The measurement was done using the four-point probe Van der Pauw technique, where the conductivity of the composite (0.670 S/cm) increased significantly, compared to that of pure cellulose (0.091 S/cm). The improvement of the conductivity is due to the presence of the conductive polymer coating. The specific conductivity of PANI is of approximately 5 S/cm and PANI polymer blends with wood cellulose have been reported to exhibit around 0.4 S/cm.[35]

Table 1
Infrared peak ratios of *Cladophora* cellulose sample

Sample	H_{1429}/H_{897}	H_{1372}/H_{2900}	Ref.
Cladophora cellulose sample from Taal Lake	37	0.96	---
Marine *Cladophora* cellulose	39	1.0	41
Wood cellulose	3.5	0.6	41

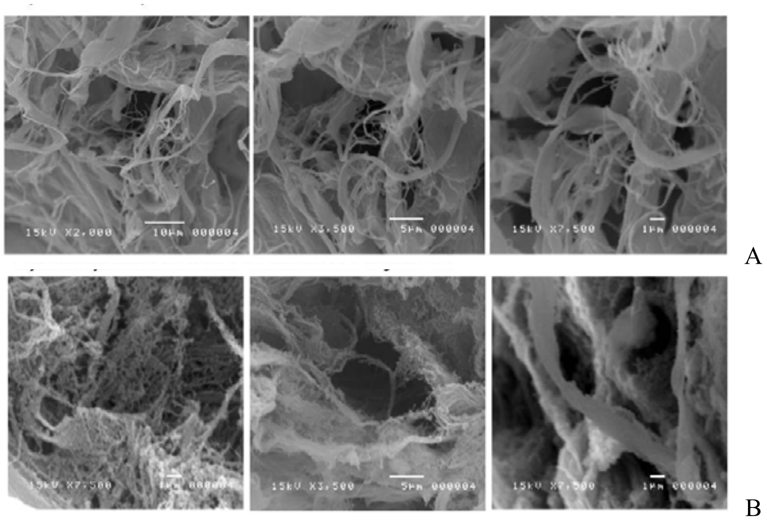

Figure 1: SEM images of A) pure *Cladophora* cellulose and B) *Cladophora* cellulose coated with polyaniline

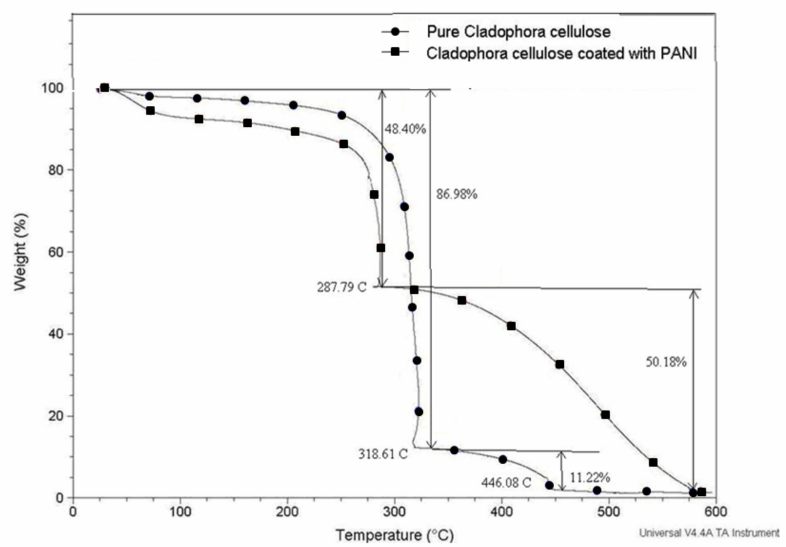

Figure 2: Thermogravimetric analysis of *Cladophora* cellulose fibers in their pure form and after coating with PANI

The conductivity measured in this study shows better performance and can be attributed to the higher surface area of PANI on *Cladophora* cellulose. This means that highly conducting composites can be prepared with nano-layers of the conducting component. The fabricated cellulose/PANI composite was applied for the remediation of toxic metals. Chromium is an industrial commodity, particularly in tanning and plating industry. Once used, chromium ions are often dumped along with wastewater into the river system. Chromium exists in two oxidation states, Cr(VI) and Cr(III). The hexavalent chromium is extremely toxic and mobile in the environment. The trivalent form however is significantly less toxic. The standard industrial technique for the removal of Cr(VI) involves the formation of chromium hydroxide sludge, which is also hazardous.[36] Direct electrochemical reduction of Cr(VI) to Cr(III) is not practical due to poor electron transfer kinetics. Hence there is a need to develop a cheap and efficient process to reduce Cr(VI) to Cr(III).

Conducting polymers offer an alternative approach for the remediation of Cr(VI) due to their unique redox activity.[37] The use of conducting polymers for the reduction of very toxic Cr(VI) to less toxic Cr(III) has been reported using pure polypyrrole,[38] then pure polyaniline films.[39] For polyaniline, the PANI in its reduced form (emeraldine base, EB) will act as a reducing agent upon exposure to hexavalent chromium. The PANI will in turn be oxidized to pernigraniline as the Cr(VI) is reduced to Cr(III).

In this work, PANI is prepared as coating for *Cladophora* cellulose. The emeraldine salt (ES) form of polyaniline in the cellulose composite was first treated with ammonia solution to obtain the reductant emeraldine base (EB) form of polyaniline. A weighed sample of the *Cladophora* cellulose-PANI$_{(EB)}$ was stirred in 200 mL of 50 mg/L solution potassium dichromate at pH 2. The exposure was performed at different times followed by filtration and the filtrates were used for the determination of hexavalent chromium [Cr(VI)] concentrations using UV-Vis spectroscopy. The concentration of Cr(VI) in solution was determined for different times of exposure to the cellulose-PANI composite and to the pure cellulose for comparison. Figure 3 shows the % absorbance of Cr(VI) recorded between 200 and 800 nm. The λ_{max} at 355 nm was used to monitor the decrease in Cr(VI) concentration. As the exposure time to 0.515 g of *Cladophora* cellulose-PANI composite increases, a decreasing trend of % absorbance can be observed. In contrast, no decrease in % absorbance was observed when Cr(VI) was exposed to the same amount and time of neat *Cladophora* cellulose. A plot showing the comparison of the change in concentration of Cr(VI) versus its initial concentration (C_t/C_0) against time (Fig. 4) shows that Cr(VI) was reduced over time using the cellulose/PANI composite, which is in contrast to the cellulose-only set-up, where the average Cr(VI) concentration did not change after the same time of exposure to pure *Cladophora* cellulose without PANI coating. This indicates that the reduction of the hexavalent chromium is due to the reducing capability of the PANI$_{(EB)}$ coating on cellulose and that the cellulose by itself is unable to reduce Cr(VI).

The removal mechanism of chromium in the presence of cellulose/PANI composite may be due to the combination of redox activity and surface adsorption. The drop of Cr(VI) concentration in the solution indicates that the cellulose-PANI composite is responsible for the reduction of Cr(VI) to Cr(III) at acidic pH, as shown in the following equation:[40]

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow Cr^{3+} + 7H_2O \quad E\text{o} = 1.33V$$

$$3PANI_{(Emeraldine)} + 6\ HSO_4^- - 6e^- \rightarrow 3PANI(HSO_4)_2\ _{(Pernigraniline)}$$

where PANI has been converted to its pernigraniline oxidized form. Although not a metal, the reduction potential of PANI (emeraldine form) is comparable to that of silver, thus it is able to reduce chromium efficiently.

Another mechanism might be also plausible via surface adsorption. The nitrogen atoms in cellulose/PANI composite form coordinate bonds with the positive charge of Cr through the lone pair electron of nitrogen. Moreover, electrostatic attraction may occur between solution anions (chromate and dichromate) and the protonated form of nitrogen atoms in PANI under acidic conditions.

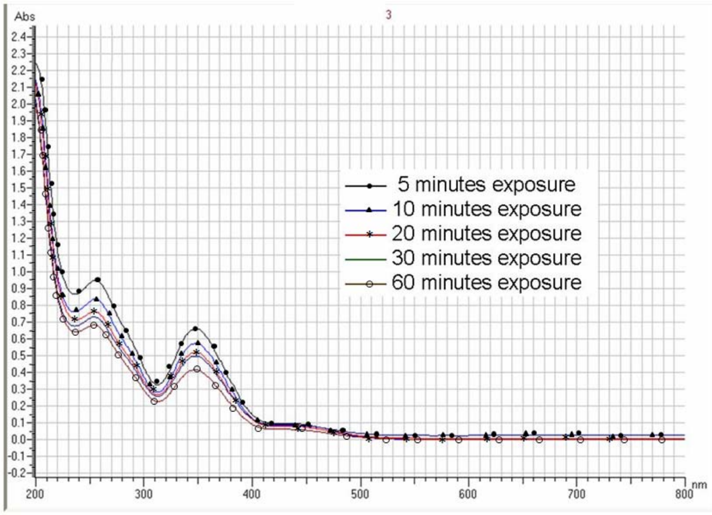

Figure 3: Absorbance peaks of Cr(VI) at different times of exposure to *Cladophora* cellulose-PANI composite, measured from 200 nm to 800 nm

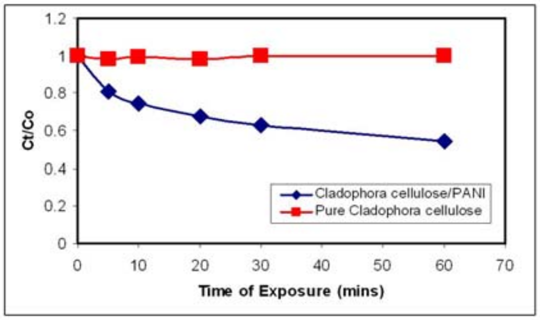

Figure 4: Plot of Cr(VI) reduction at different times of exposure to *Cladophora* cellulose-PANI composite (♦) and pure *Cladophora* cellulose (■)

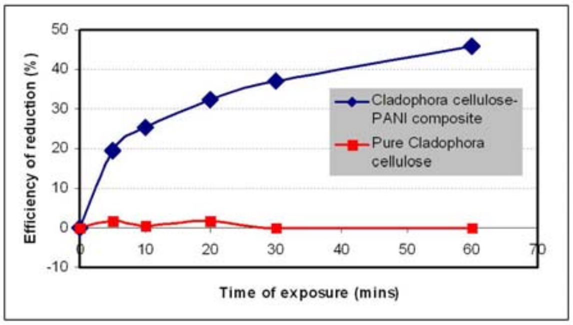

Figure 5: Efficiency of Cr(VI) reduction at different times of exposure to *Cladophora* cellulose-PANI composite (♦) and pure *Cladophora* cellulose (■)

Regardless of the mechanism, the toxic hexavalent chromium can be removed from wastewater using cheap *Cladophora* cellulose coated with nano-layers of PANI. The efficiency of chromium (VI) reduction was determined as calculated using the equation:

$R=100(C_0-C_t)/C_0$

where C_0 = initial concentration of Cr(VI) in the solution, and C_t = concentration of Cr(VI) after Clad/PANI composite exposure.

The efficiency of reduction reaches 46% (Figure 5) after 1 hour exposure to the cellulose/PANI composite, while no change occurs when using the pure *Cladophora* cellulose. As compared to the pure PANI powder, where the efficiency reaches 99% within 16 minutes,[27] the composite in this study although less efficient, still fares well considering that the amount of the expensive PANI in the cellulose/PANI composite is minimal. At the initial concentration of 50 mg/L Cr(VI), the 0.515 g composite still actively removes Cr(VI) from the solution within 1 hour exposure. This is in contrast to the system developed by Kumar,[40] where PANI was synthesized on Jute fiber: adsorption/reduction equilibrium of Cr(VI) was achieved within 40 minutes and no more significant activity could be observed beyond 40 minutes. The observed higher activity of the *Cladophora* cellulose/PANI system indicates rapid reduction and/or adsorption, suggesting a more readily available large surface area.

The results presented show that the *Cladophora* coated with thin layers of polyaniline is effective in removing the toxic hexavalent chromium from industrial wastewater.

CONCLUSION

Cellulose with high crystallinity and high surface area has been extracted from abundant and yet unwanted green algae, *Cladophora rupestris*. The *Cladophora* cellulose fiber served as a matrix and the conducting polyaniline (PANI) was efficiently synthesized on its surface. The characterization of the composite showed a thin layer of PANI coating, thus preserving the high surface area of the cellulose. The cellulose/PANI composite was used effectively in the remediation of toxic hexavalent chromium. The efficiency of the reduction activity of metals can be attributed to the high surface area of the cellulose/PANI composite. Further studies are underway to determine the kinetics of the reduction of chromium.

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