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Novel nano cellulosic fibers for remediation of heavy metals from synthetic water

ABSTRACT

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The increased surface area-to-volume ratio of nanoparticles, quantum size effects and the ability to tune surface properties through molecular modification make nanostructures ideal for environmental remediation. The present piece of work reports the preparation and characterization of nano cellulosic fibers (NCFs) with further polymeric reinforcement using vinyl sulphonic acid for the remediation of cationic toxic metals from water bodies. The modified NCFs exhibited enhancement in sorption efficiency (more than 90 %) and stability in terms of increased (3 to 5) regeneration cycles for Cd (II), Pb (II), Ni (II) and Cr (III) ions in single and multi metal solutions. Novel NCFs were also characterized on the basis of FTIR and TGA techniques and found to have enough potential for environmental remediation.

Keywords: *Polymerized; Nano cellulosic fibers; Vinyl sulphonic acid; Remediation; Heavy metals.*

INTRODUCTION

Recent advances in nano scale science and engineering suggest that many of the current problems involving water quality could be greatly diminished by using nano- particles [1]. Nano particles exhibit good adsorption efficiency especially due to the higher surface area and greater active sites for interaction with metallic species [2-4]. However, there is also a wide debate about the safety of nanoparticles and their potential impact on environment and biota [5- 8]. Especially the new field of nano toxicology has received a lot of attention in recent years [9, 10]. The variety of inorganic nano structured materials has been explored for remediation of metallic ions but they are found to be associated with toxicity issues [11-13]. One way to address such issues related to sustainability is to incorporate renewable materials of miniaturized elements of plant origin.

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Nature is gifted with several nanomaterials which could be easily prepared from plants. Cellulose and starch are abundant, natural, renewable and biodegradable polymers. By intelligent processing techniques they could be used as classical nano reinforcing elements in polymers. The increasing interest in nanomaterials of plant origin and their unique properties have led to intensive research in the area of nano cellulosic materials [14-16].

Graft copolymerization of different monomers onto cellulose regarded as one of the best methods of producing materials with modified properties such as, hydrophilic or hydrophobic character, improved elasticity, water absorption and ion-exchange capabilities. Although a large number of studies have been carried out with grafting of acidic monomers such as acrylic [17, 18] and itaconic acid [19, 20] containing weak acid group (COOH), only limited work has been concerned with grafting of vinyl sulphonic acid having strong acid group (SO₃H). In continuation of our work on biosorption of toxic metals using agricultural wastes [21-23], the present paper communicates the preparation, characterization and graft copolymerization of vinyl sulphonic acid onto

NCFs for improved decontamination of toxic metals from water bodies.

EXPERIMENTAL

Extraction & Preparation of NCFs

The native rice straw was collected from Dayalbagh agricultural farms, Agra and washed with distilled water several times, dried in an oven at 50°C for 24 h. They were chopped to an approximate length of 5–10 mm and finally crushed into small fibers. Fibers were soaked into the sodium hydroxide solution (0.5 M) for 2 h and washed with distilled water. Bleaching treatment with a sodium chlorite solution (pH 4) for 1 h at 50°C was carried out to remove the remained lignin and washed again with distilled water. The pre-treated pulp was hydrolyzed for 3 h at 70°C and then washed with distilled water repeatedly. The acid treatment hydrolyzed the hemicelluloses and pectin by breaking down the polysaccharides to simple sugars and released NCFs (Figure 1). These fibers were ultra sonicated, dried and finally subjected for microscopic analysis (SEM and TEM).

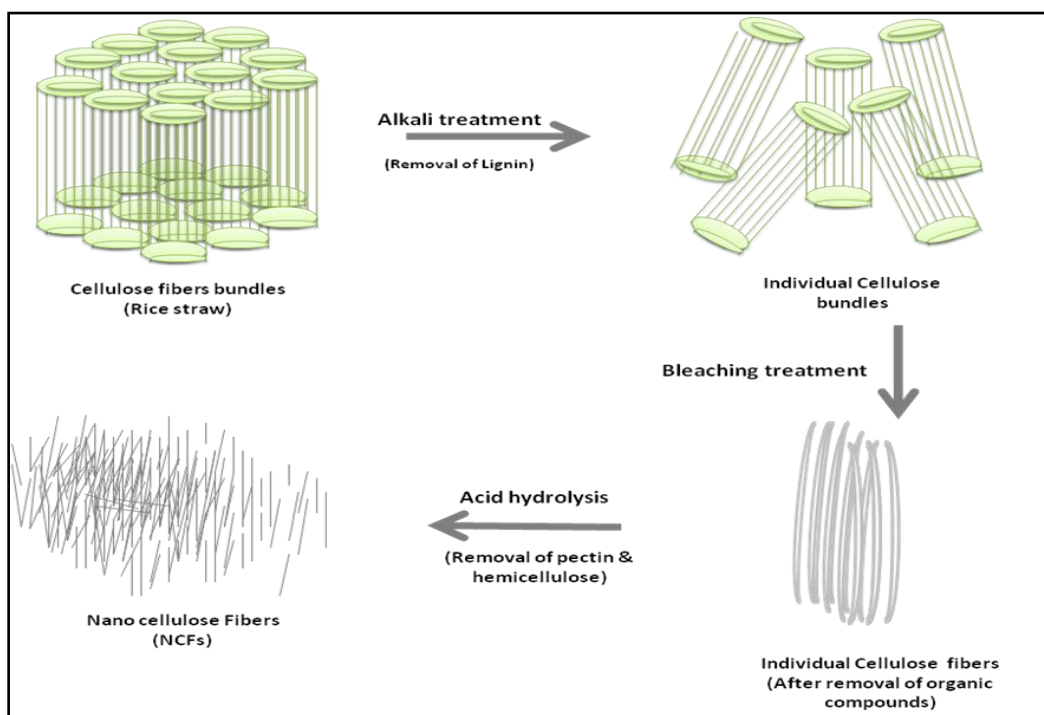


Fig. 1. Schematic chart showing the preparation of nano cellulosic fibers (NCFs) from native rice straw fibers.

Sorption Studies

Batch experiments (triplicates) were performed in clean air-conditioned environmental laboratory with Cd (II), Cr (III), Pb (II) and Ni (II) in single as well as multi-metal cationic solution. After proper pH adjustments [pH 6.5], NCFs (0.5 g) was added and metal-bearing suspension was kept under stirring until the equilibrium conditions are reached. After shaking, suspension was allowed to settle down. The residual NCFs sorbed with metal ions were filtered. Filtrate was collected and subjected for metal ions estimation using flame atomic absorption spectrometer [Perkin Elmer-2380]. Percent metal sorption by the sorbent was computed using the equation: $(C_o - C_e)/C_o \times 100$ where 'C_o' and 'C_e' are the initial and final concentration of metal ions in the solution.

Desorption studies

Desorption studies were conducted to restore the NCFs as a function of concentration of different desorption reagents (hard acid 0.05 M nitric). Metal loaded NCFs obtained from sorption experiments, were transferred to Erlenmeyer flasks and shaken with 50 ml of each desorption reagents as a function of time: 20 - 80 min at room temperature. At the end of each time interval the suspension was stirred for 5 min. The suspension was filtered using Whatman 42 filter paper and in filtrate estimation of metal ion concentration was carried out.

Graft co-polymerization onto NCFs

NCFs (0.5 g) were dispersed in water (50 ml). Potassium per sulfate (0.1 g) was added slowly to the reaction mixture. Vinyl sulphonic acid (1.0 ml) was added drop wise to the reaction mixture. The reaction flask was placed in a water bath at 10–85°C for pre standardized time (1 h) under stirring. The reaction mixture was filtered and the homopolymer was removed with excess water. The grafted sample was dried to a constant weight and used for sorption studies.

Characterization

FTIR analysis in solid phase in KBr was performed using a fourier transform infrared spectrometer (FTIR-8400, Shimadzu). Spectra of the native and polymerized sorbent were recorded.

TGA was performed using thermo gravimetric analyzer (DTG-60, Shimadzu). The

comparison of final decomposition temperature (FDT) of native and polymerized sorbent was evaluated. Sorption efficiency and number of regeneration cycles of the native and polymerized sorbent were carried out in single as well as multi-metal solution using procedure mentioned above.

RESULTS AND DISCUSSION

Figure 2 shows SEM micrograph of native rice straw bundle of fibers (a), after alkali treatment the surface of native fiber is cleaned due to partial removal of lignin, pectin and other non-cellulosic components (b) and bleaching treatment resulting into micro fibrillated individual cellulose fibers (c).

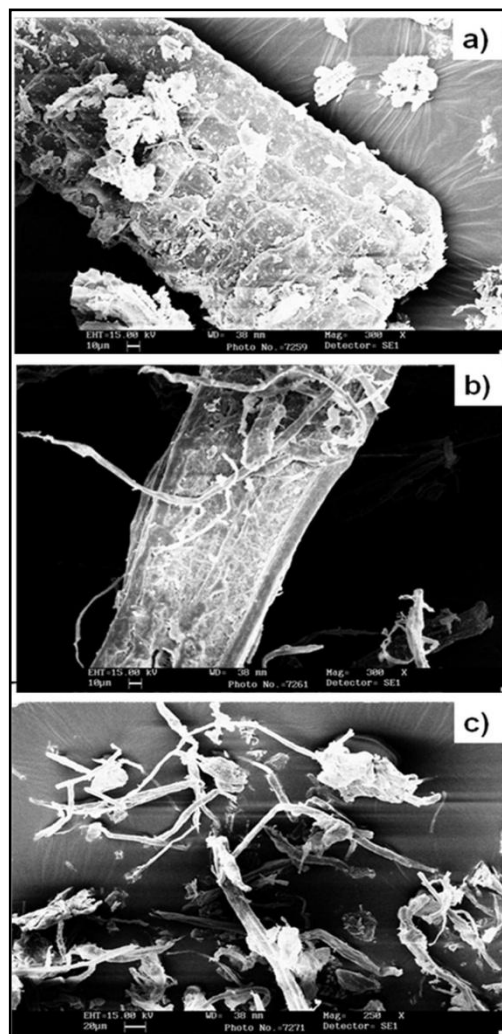


Fig. 2. SEM micrograph of native rice straw (a), alkali treated fibers (b) and derived cellulose fibers after bleaching treatment (c).

Figure 3 shows TEM micrograph of nano cellulosic fibers (NCFs). Their morphology looks rod-like nano fibrillated cellulose with high length and low diameter (nm).

Sorption studies result in the standardization of the optimum conditions of dosage: 0.5 g, metal concentration: 25 mg/l, contact time: 40 min and volume: 200 ml at pH 6.5. Maximum sorption for different metal ions in single metal solution: Pb (II): 94.2%, Cd (II): 90.7%, Ni (II): 85.5% and Cr (III): 89.3% and for multi-metal solution: Pb (II): 93.9%, Cd (II): 88.2%, Ni (II): 84.1% and Cr (III): 85.4% was observed.

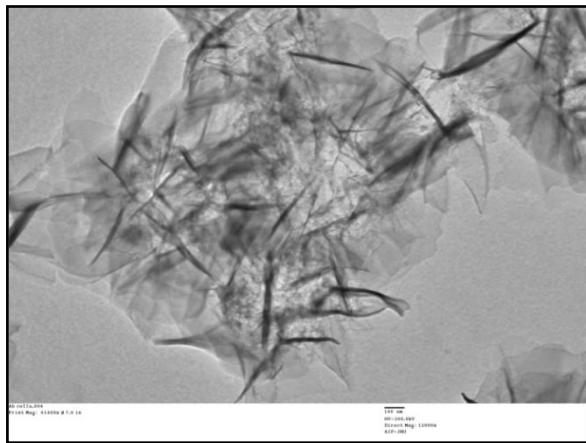


Fig. 3. TEM micrograph of nano cellulosic fibers (NCFs).

Mechanism of metal-NCFs interaction

The percentage sorption of cations (under study) on native NCFs increases with the pH range 4.5- 8.5, showing maximum sorption at pH 6.5. There was no significant difference in sorption behavior with further increase in pH up to 7.5. Investigation on pH variation beyond 7.5 yielded an apparent increase in sorption up to pH 8.5, which might be due to the precipitation carryover of metal ions which starts at pH 7.5 [24]. Metal precipitation interferes and is undistinguishable from sorption phenomenon at pH 7.5 [25]. NCFs-metal ion binding thus appears to be van der Waals forces of attraction and largely ion exchange process between negatively charged COO^- groups of nano cellulosic fibers and metallic cations.

In order to increase the efficiency of biomaterial to attract M^+ ion, strengthening of the sulphonic group for possible metal ion interaction site [26-28] was considered logical. In the present case, graft co-polymerization with vinyl sulphonic acid to increase the number of negatively charged sulphonate groups onto the native NCFs was found successful (Figure 4). Polymerizations onto native NCFs have been characterized on the basis of FTIR and TGA studies. Polymerizations intensify and shift the peak of sulphonic group; $1384.3\text{-}1354.8\text{ cm}^{-1}$ confirming polymerization of native NCFs (Figure 5).

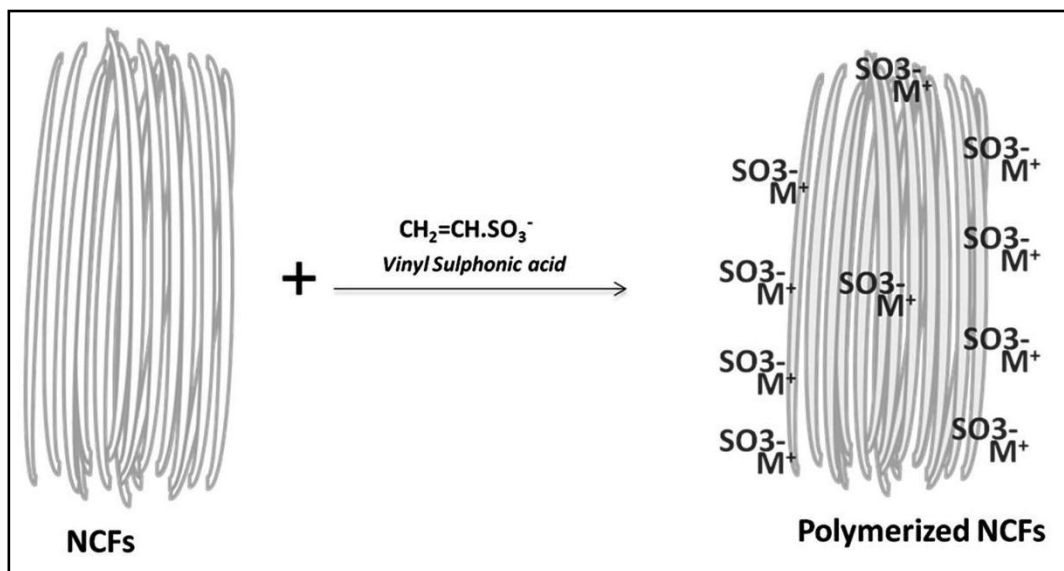


Fig. 4. Graft co-polymerization of NCFs.

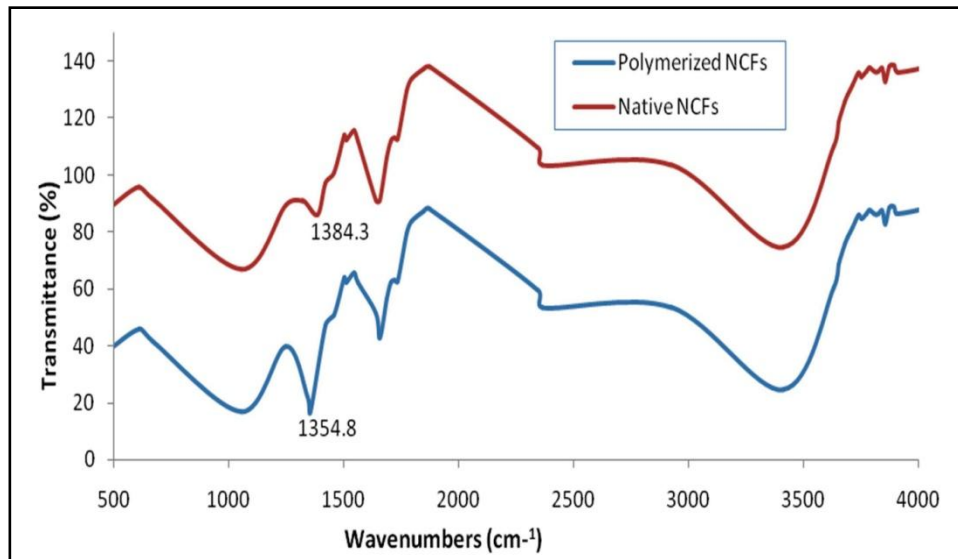


Fig. 5. IR spectra's of native (a) and graft copolymerized (b) NCFs.

Enhancement in sorption and reusability of polymerized NCFs

Polymerized biomaterial was evaluated for the increase in sorption efficiency in single and multi-metal solution under previously standardized optimum conditions. Marked increased in sorption efficiency was observed in the polymerized NCFs under similar experimental conditions (Table 1).

The number of reusability of polymerized NCFs was also found to be increased to 5 cycles, compared to 3 cycles of native NCFs (Figure 6). TGA of polymerized NCFs showed FDT values (893.1°C) compared to FDT value (705.48°C) of native NCFs (Figure 7). The increase in the reusable cycles in the case of polymerized NCFs may be associated with their enhanced stability.

Table 1. Enhancement in sorption efficiency of polymerized NCFs for cationic metals.

Metal ions	% Sorption	
	Native NCFs	Vinyl Sulphonic Polymerized NCFs
Single Metal Solution		
Cd (II)	90.7 ± 1.6	94.1 ± 1.2
Ni (II)	85.5 ± 1.2	91.3 ± 1.3
Pb (II)	94.2 ± 1.9	97.1 ± 1.1
Cr (III)	89.3 ± 1.11	93.1 ± 1.7
Multi Metal Solution		
Cd (II)	88.2 ± 1.3	92.1 ± 1.2
Ni (II)	84.1 ± 1.7	90.3 ± 1.5
Pb (II)	93.9 ± 1.5	95.2 ± 1.4
Cr (III)	85.4 ± 1.12	91.3 ± 1.2

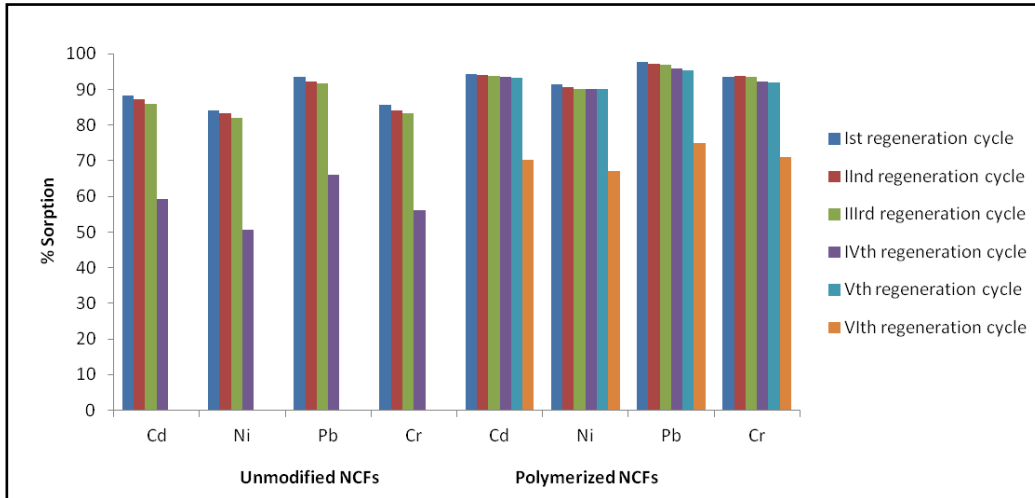


Fig. 6. Enhancement in reusability of polymerized NCFs.

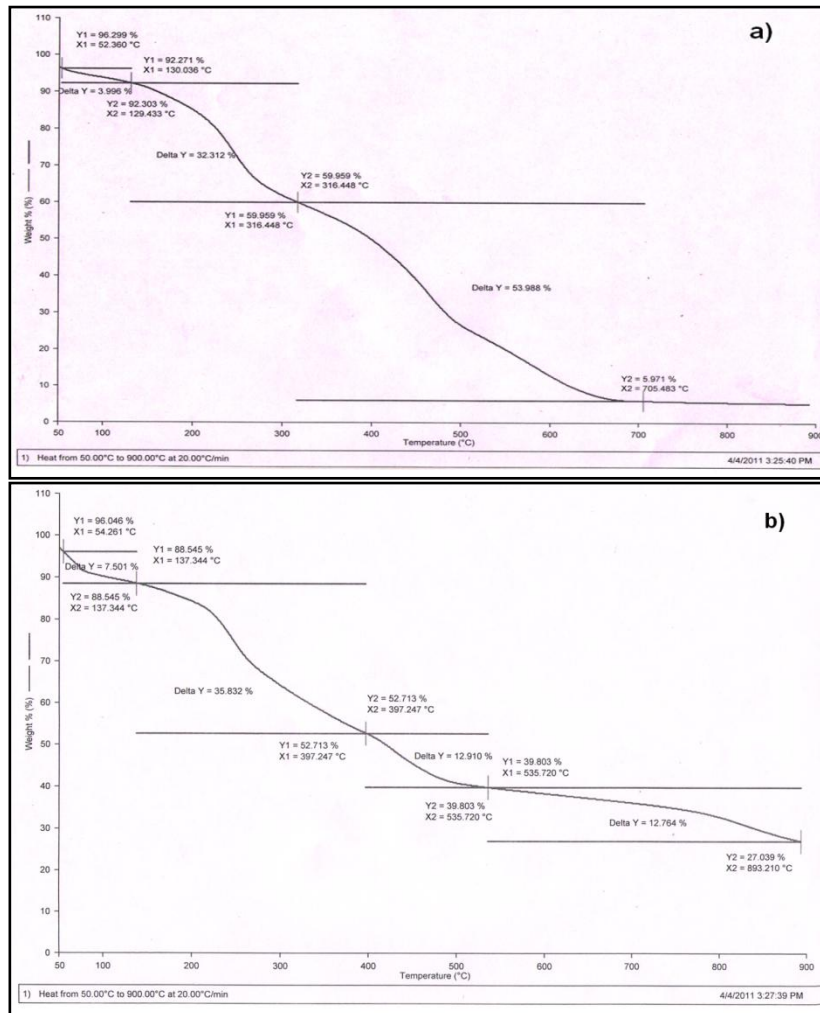


Fig. 7. TGA of native (a) and polymerized (b) NCFs.

CONCLUSION

The present piece of work highlights the successful polymeric reinforcement using graft copolymerization of vinyl sulphonic acid for enhanced sorption efficiency with stability for the remediation of toxic metals from water bodies. Studies are recommended for structuring of filter sheets, pads or candles for environmental remediation or at least as a pretreatment step for industrial effluents before large chemical treatment methods.

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