

Agro-Waste Valorization for Green Nanocellulose Synthesis and Quinone-Based Functionalization toward Heavy Metal Remediation: A Review

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ABSTRACT

Heavy metals such as lead (Pb²⁺), mercury (Hg²⁺), cadmium (Cd²⁺), and hexavalent chromium (Cr (VI)) continue to find their way into rivers, groundwater, and drinking-water supplies, and they do not go away easily once they arrive: they resist biodegradation, accumulate in tissue, and remain toxic at trace levels. The materials conventionally used to remove them, activated carbon, ion-exchange resins, membrane systems, work, but they tend to be expensive, chemically intensive, or wasteful in their own right. Nanocellulose pulled from agricultural waste offers a different kind of answer. It is cheap, renewable, biodegradable, and, once its surface hydroxyl groups are functionalized, genuinely good at binding metal ions. This review pulls together what is currently known about nanocellulose extraction from underused agro-waste streams, with a particular focus on *Borassus flabellifer* (palmyra palm) flower waste, and pairs it with what is known about neem (*Azadirachta indica*) as a source of redox-active, quinone-rich phytochemicals. Along the way it looks at how nanocellulose is typically functionalized for metal capture, how quinone chemistry underlies colorimetric and electrochemical metal sensing, and the isotherm and kinetic models used to judge whether an adsorbent actually performs. The picture that emerges points to a gap nobody seems to have filled yet: grafting neem-derived quinones onto *Borassus flabellifer* nanocellulose through green esterification, to make a material that both captures heavy metals and signals their presence. The review closes with the characterization and evaluation benchmarks such a study would need to meet.

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1. Introduction

Industrial growth has a water problem it has never quite solved. As factories, refineries, and urban centers have expanded, so has the quantity of heavy metal discharged into rivers and groundwater, and metals like Pb²⁺, Hg²⁺, Cd²⁺, and Cr(VI) are especially unforgiving: they do not break down, they build up in living tissue, and they stay harmful even in very small amounts. The tools available for dealing with this, chemical precipitation, ion exchange, membrane filtration, activated-carbon adsorption, do the job, but usually at a price: high running costs, sludge that itself needs disposing of, or a dependence on non-renewable, energy-hungry inputs. That trade-off is what has pushed researchers toward adsorbents made from renewable, cheap, and biodegradable starting materials instead.

Nanocellulose fits that description well. Its enormous surface-area-to-volume ratio, dense coating of modifiable hydroxyl groups, low toxicity, and mechanical strength make it a natural scaffold for both trapping pollutants and, once functionalized, detecting

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them. A separate but related strand of research has been looking at plant phytochemicals, quinones in particular, for their ability to chelate or reduce heavy metal ions while producing a visible colour change in the process. Put the two together, a renewable cellulose scaffold carrying a renewable quinone functional group, and you get something that is green on both counts and useful in two ways at once: it can pull metals out of water and tell you they were there. This review works through the literature behind both halves of that idea, agro-waste nanocellulose (with a close look at underused *Borassus flabellifer* flower biomass) and neem tissues as a quinone source, along with the functionalization approaches already used for nanocellulose-based metal remediation and sensing, to map out where the field currently stands and where it does not yet reach.

2. Nanocellulose from Agro-Waste Biomass: Sources and Extraction

Crop and food-processing residues are, chemically speaking, mostly lignocellulose, a mix of cellulose, hemicellulose, and lignin, which makes them a large

and cheap, if still underused, reservoir of nanocellulose (Padhi, Singh, & Routray, 2023). Getting from raw biomass to nanocellulose usually takes two stages: a pretreatment step that strips away everything that is not cellulose, lignin, hemicellulose, waxes, pectin, followed by a size-reduction step where acid hydrolysis, enzymatic digestion, or mechanical shearing breaks the purified fibers down into cellulose nanocrystals (CNCs) or cellulose nanofibers (CNFs). Reviews covering non-woody and agro-waste sources have surveyed an unusually wide range of raw materials, from fruit and vegetable peels to cereal husks to palm residues, and one point comes up again and again: the crystallinity, morphology, thermal behaviour, and surface charge of the final nanocellulose depend heavily on which plant it came from and which extraction chemistry was used.

Where crystallinity is the priority, acid hydrolysis tends to be the method of choice, producing highly ordered CNCs, whereas TEMPO-mediated oxidation and enzymatic routes are gaining ground where the goal is a smaller environmental footprint and less acidic wastewater to deal with afterward. Three things stand out across this literature: agro-waste valorization genuinely compares favourably with virgin wood pulp on both cost and environmental grounds; the pretreatment chemistry chosen has downstream consequences for how well the resulting nanocellulose can later be functionalized; and, despite how much agro-waste exists, only a small fraction of it has actually been characterized this way, which leaves plenty of regionally available feedstocks still waiting to be looked at.

3. *Borassus flabellifer* Flower Waste as an Emerging Nanocellulose Feedstock

Borassus flabellifer, better known as the palmyra palm, grows across South and Southeast Asia, and almost every part of it, fruit fibers, leaf stalks, flowers, has been looked at as a possible cellulose source at one point or another. Fruit fiber compositional studies put cellulose content somewhere between 45% and 70%, with hemicellulose and lignin making up the rest, though the exact numbers shift depending on the specific plant part and where it was grown. Leaf-stalk fiber tells a similar story, cellulose-dominant, with hemicellulose and lignin present but modest. What is easy to overlook is the flower: every flowering season produces a sizeable amount of *Borassus* flower biomass, and right now almost all of it is discarded as low-value waste, despite carrying a cellulose content perfectly capable of supporting real biopolymer production.

A handful of recent studies have started to change that. Microcrystalline cellulose pulled from *Borassus flabellifer* flower (BFF) waste has been used as a reinforcing filler in banana-fiber composites, where it measurably improved tensile and flexural strength and pushed up the temperature at which the material starts to thermally degrade, all confirmed through FTIR, XRD, TGA, and SEM. A separate study swapped the matrix for polylactic acid, making BFF-filled biofilms and again confirming, via FTIR, that the chemical modification had actually taken, while also reporting

crystallinity and moisture-related data relevant to how the material might behave in the field. Nanofibrillated cellulose from *Borassus flabellifer* has also passed biocompatibility testing, which hints at applications beyond just structural reinforcement (Athinarayanan, Alshatwi, & Periasamy, 2020). Most recently, and most interestingly for green functionalization work, BFF waste has been converted into hydroxypropyl methyl cellulose through etherification, with a yield around 69% and a fairly low crystallinity index near 28%, FTIR confirming the expected hydroxyl, methyl, and ether signatures. Put together, these studies make a solid case that *Borassus flabellifer* flower waste is a real, working nanocellulose feedstock. What nobody has done yet is take that same material and functionalize it specifically for heavy-metal capture.

4. *Neem (Azadirachta indica)* as a Source of Quinone-Rich Phytochemicals

Neem is not a shy plant, chemically. More than 300 bioactive compounds have been catalogued across its leaves, bark, seeds, and flowers, ranging from limonoids like azadirachtin and nimbin to a long list of flavonoids, phenolics, and terpenoids. How those compounds get extracted varies, maceration and Soxhlet extraction remain common, but ultrasound-assisted and deep-eutectic-solvent methods are increasingly the preferred green alternatives, and several reviews have gone through these techniques in detail. Neem bark specifically keeps coming up as a rich source of phenolic and quinonoid compounds with well-documented antioxidant and free-radical-scavenging activity, which is exactly the kind of chemistry a heavy-metal-binding ligand would need.

That redox activity is not just incidental; it is the mechanism that makes quinones useful for both chelating metal ions and detecting them. Synthetic aminoanthraquinone chemosensors, close structural relatives of neem's own quinonoids, are known to change colour visibly when they bind Cu^{2+} or Pb^{2+} in water, the shift coming from how complexation with the metal alters the quinone's UV-Vis absorption. That gives a plausible, literature-backed reason to expect that neem-derived quinones, once anchored to a nanocellulose scaffold, could behave the same way, functioning as a built-in chromophore for metal detection. Nobody appears to have actually tried this combination, though, a plant-derived quinone grafted onto a plant-derived cellulose carrier, so for now it remains a reasonable extrapolation rather than a demonstrated result.

5. Functionalization Strategies for Heavy-Metal-Targeted Nanocellulose

Plain, unmodified nanocellulose is not a particularly strong metal adsorbent on its own. It only starts to perform well once metal-binding groups, amino, carboxyl, aldehyde, sulfhydryl, or a chelating aromatic ring, are attached to its hydroxyl-covered surface. The routes for doing this, according to reviews of nanocellulose-based heavy-metal adsorbents, fall into three broad categories: direct chemical modification, surface grafting via free-radical polymerization, and physical activation, and amino-functionalized cellulose in particular shows a substantial jump in uptake of cationic metals like Cu^{2+} , Cd^{2+} , Hg^{2+} , and Pb^{2+}

compared with the unmodified starting material. One concrete example: nanocellulose grafted with acrylamide and then cross-linked with graphene oxide reached maximum adsorption capacities of about 46 mg/g for Cu^{2+} and 187 mg/g for Pb^{2+} at neutral pH and room temperature, removing more than half the metal present in solution.

Conjugated polymers work well too, especially for metals that are themselves redox-active. A polypyrrole-nanocellulose composite reached a Langmuir maximum of roughly 560 mg/g for Cr(VI) , with pseudo-second-order kinetics pointing to a chemisorption-driven process, and the removal itself happened through a combination of reducing the more toxic Cr(VI) down to the less toxic Cr(III) and electrostatic pull between the protonated polymer and the chromium oxyanion. Whatever the functionalization route, the field has settled on a fairly consistent way of judging performance: Langmuir and Freundlich isotherms, pseudo-first- and pseudo-second-order kinetics, and close attention to pH, contact time, starting concentration, and interference from competing ions. That shared framework is useful here, because it gives a ready-made template against which a neem-quinone-functionalized *Borassus* nanocellulose could eventually be measured.

None of this requires harsh chemistry, either. Esterification with bio-based anhydrides or acids, citric acid and succinic anhydride are common choices, carried out solvent-free or in water, has already been used to load carboxyl groups onto cellulose surfaces without resorting to the toxic solvents that many older grafting methods depend on. That is essentially the same green-chemistry logic behind the esterification step proposed for attaching neem quinones to *Borassus flabellifer* nanocellulose.

6. Quinone-Based Mechanisms for Colorimetric and Electrochemical Heavy Metal Sensing

Adsorption is only half of what quinone chemistry offers. Quinones and related aromatic chelators have a long track record as colorimetric chemosensors in their own right. Aminoanthraquinone chemosensors carrying polyamine arms, for instance, visibly change colour and show a measurable shift in UV-Vis absorption when they bind Cu^{2+} , and in some derivatives Pb^{2+} , and the shift is large enough that the two metals can be told apart just by looking at the colour. Schiff-base sensors built on benzothiazole, thiophene, and quinoline backbones do something similar for Cu^{2+} , Hg^{2+} , and Cd^{2+} , with the binding confirmed by UV-Vis, FTIR, and NMR, and the strength of binding quantified using the Benesi-Hildebrand method.

What is happening chemically in all these cases is fairly consistent: the metal ion coordinates at an electron-rich site on the quinone or heteroaromatic ring, which disrupts the ring's conjugation and shifts where it absorbs light, and in some systems this is amplified further by the ligand losing a proton in the process. Whole-cell and pigment-based biosensors add another layer of supporting evidence, showing that biologically derived colour-producing systems really can give a

measurable, dose-dependent response to Cu^{2+} , Cd^{2+} , Hg^{2+} , and Pb^{2+} at concentrations that actually matter environmentally. All of this makes it reasonable to expect that neem-derived quinonoids, once fixed onto a nanocellulose carrier, would behave as a working chromogenic sensor for heavy metals. Reasonable is not the same as proven, though; the actual spectral response, selectivity, and detection limit would still need to be measured rather than assumed.

7. Research Gaps and Future Directions

A few gaps stand out clearly once all of this is laid side by side. *Borassus flabellifer* flower waste has been proven out as a nanocellulose source for structural and composite uses, but nobody has yet pushed it toward environmental remediation through surface functionalization, that door is still open. Neem's antioxidant and antimicrobial chemistry is well documented, but how its quinonoid compounds actually behave once grafted onto a solid cellulose support, chelating heavy metals, resisting leaching, holding up under repeated use, has simply not been studied. And the specific pairing this review has been building toward, ultrasound-extracted neem quinones coupled to *Borassus flabellifer* nanocellulose through green esterification, has no precedent in the literature at all.

Turning that gap into a real study would mean working through the same checklist this field already uses elsewhere: FTIR and XRD to confirm grafting and crystallinity, SEM/TEM for morphology, TGA for thermal stability, zeta potential for surface charge, and adsorption data fitted against Langmuir/Freundlich isotherms and pseudo-first/second-order kinetics.

A sensing protocol, colorimetric or electrochemical, would need its own detection mechanism, linear range, and limit of detection spelled out. And weighing the results against WHO and Bureau of Indian Standards limits for drinking water would help ground the whole thing in something practically meaningful, rather than leaving it as a purely academic exercise. None of this is exotic; it is the standard bar this kind of material is held to. What is missing is simply someone doing the work.

8. Conclusion

Neither half of this idea is new on its own. Agro-waste nanocellulose is well established as a green remediation material, and plant-derived quinones are well established as sensing chemistry, each with its own solid body of literature behind it. *Borassus flabellifer* flower biomass has already proven itself as a usable, if underexploited, nanocellulose source, and neem's quinonoid compounds share enough structural similarity with synthetic quinone chemosensors to make their sensing behaviour a reasonable bet.

What has not happened yet is putting the two together in one material that both adsorbs and signals. That gap is real, it is well motivated by the literature surveyed here, and the characterization techniques and evaluation benchmarks already used across this field give a fairly clear roadmap for anyone willing to actually run the experiments.

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