Optical Sensing of Heavy Metals Using Biomass Derived Nanomaterials: A Mini Review

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Abstract: Heavy metals pollution is a severe threat to the environment and public health. Some heavy metals such as cobalt, zinc, iron and copper are required by living organisms in minute quantities, but their presence in higher concentrations leads to toxic effects. Heavy metals such as cadmium, lead, arsenic, chromium and mercury are fatal even at trace concentrations. Therefore, the development of a sensitive platform for the detection of heavy metals in various point sources is of the utmost importance. Plant biomass derived nanomaterials have provided unique opportunity to invent eco-friendly, sustainable and highly sensitive and selective methods for the sensing of heavy metals. Here we have briefly described several plant biomass derived nanomaterials which have been successfully explored for the optical sensing abilities in the detection of toxic heavy metal ions.

INTRODUCTION

Heavy metals (HMs) is a broad term given to the metals and metalloids which have higher density compared to water. In recent time, an exponential rise in the exposure of these metal to the humans and the living organism has raised ecological and public health concern globally. The unchecked release of HM due to industrial activities, aggressive mining, agricultural practices, pharmaceutical waste, domestic effluents, and atmospheric sources has contributed significantly to environmental pollution. These metals are toxic over a minimal concentration; although their trace quantities are required for several biological activities in living organisms. However, few heavy metals such as Hg, As, Pb, and Cd are highly toxic even at the ppb level. They lead to great risk to environment and human health due to their ability to form bond with the thiol group in proteins, and so upon entering the cell, it modifies the biochemical life cycle. These metals are the most probable causes for most heavy metal related diseases, and are considered as environmental health hazards and are ranked in the top 10 in the list from “Agency for Toxic Substances and Disease Registry Priority List of Hazardous Substances”, based on toxicity of substance and potential exposure to contaminated air, water and soil. HMs are present as ion, elements or as complexes with the density >4 g/cm³. Because of these reasons, it is becoming increasingly crucial to detect heavy metals in trace amounts, and a lot of research is being dedicated on developing versatile sensors that selectively detect trace amounts of heavy metals. On-field determination of these toxic HMs in different environmental sources like drinking water, soil, air and marine is the need of the time.

Standard laboratory techniques of Heavy metal detections which include Liquid chromatography, Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), X-ray Fluorescence Spectroscopy (XFS), and Anodic Stripping Voltammetry (ASV) are highly sophisticated and require tedious sample preparation and state of the art instrumentation facility. This prerequisite makes these techniques a limiting factor in the rapid determination of HMs; therefore, a more robust and user-friendly detection method is required to achieve quick results at the point source. In recent times, the development of various sensing platforms has provided the opportunity for robust and sensitive detection of HMs in various sources. Nanotechnology has given new dimensions to the sensor-based
detection of heavy metals by improving the sensitivity, selectivity, limit of detection and reproducibility of the sensors along with enabling miniaturization of the technology as lab on chip measurements\(^\text{15}\).

Green synthesis of nanoparticles (NPs) has drawn keen attention in recent years due to their sustainable, reliable and eco-friendly synthesis approach. Metal oxide and Carbon derived nanoparticles are commonly produced from plant extracts which are most frequently used for the development of sensing platforms\(^\text{16, 17}\). The current review focuses on the optical sensing strategies of the HM through the biomass driven nanoparticles-based sensors. The optical sensing platforms include but not limited to fluorescent, colorimetric, surface plasmon resonance (SPR), and surface-enhanced Raman scattering (SERS) sensors. Here we put particular emphasis on the plant-derived nanomaterials for the development of optical sensors to detect heavy metals.

**PLANT-DERIVED NANOPARTICLES**

The prerequisite of any nanomaterial to be utilized in sensing application is its good optical and conductive properties. Biological materials like plants, biomass have an abundance of bio-macromolecules which are comprised of essential elements like Carbon and Nitrogen. Conversion of raw materials carrying these elements into nano form is the key to the development of plant-derived nanoparticles. Majority of the nanoparticles synthesized from plants through green synthesis approaches are Carbon-based nanomaterials which are described in details in the following section.

**Carbon quantum Dots (CQDs)**

Carbon dots or Carbon Quantum Dots (CQDs) are ultra-small size (<10nm), zero-dimensional Carbon-based nanomaterial with outstanding optical, fluorescence and photo-electronic properties. CQDs are highly biocompatible and water-soluble, offer high quantum yield and chemical stability along with providing ease of modification. These properties make CQDs a favorable candidate in sensing application. Top-down and bottom-up are the two most common approach for the synthesis of CQDs; among which hydrothermal Carbonization of biomasses and plants (bottom-up approach) has shown a remarkable advantage in terms of ease of synthesis, sustainability and output efficiency. Currently, production of CQDs from various Carbon sources like several plant species, biomass and waste biological materials are immerging as a popular fabrication approach for the manufacturing of sensing platforms. Use of CQDs in developing optical sensors for the detection of heavy metals has gained immense popularity in recent times. Tunable photoluminescence properties of CQDs provide immense support in designing optical sensors. Majority of the detection methods are based on fluorescence quenching properties of heavy metals. CQDs show broad-spectrum fluorescence properties from intense blue to resonant red emission, depending on their size and concentration. The intense blue emission could be produced by an intrinsic bandgap which may lead to confinement of sp\(^2\) Carbon conjugation in the core state of CQDs\(^\text{18}\) or an extrinsic fluorescence due to surface dangling states of the CQDs\(^\text{19}\). Several Heavy metal ions like Ag\(^{2+}\), Cr\(^{6+}\), Pb\(^{2+}\), Fe\(^{2+}\), and Cu\(^{2+}\) are successfully detected using CQDs with a wide range of linearity.

**Nitrogen-Doped Carbon Quantum Dots (NCQDs)**

Nitrogen-doped Carbon quantum dots are a modified form of Carbon quantum dots with Nitrogen element. NCQDs are synthesized using various Nitrogen-rich biomass sources\(^\text{24}\) along with chemical Nitrogen precursors. Presence of Nitrogen in nanoparticles offers better fluorescence quantum yield compare to CQDs, which allow improved sensitivity for heavy metal detection\(^\text{15}\). Highly sensitive detection of Hg\(^{2+}\), Pb\(^{2+}\), and Fe\(^{3+}\) is achieved for a wide range of detection limit using NCQDs.

**Nitrogen and Sulphur Co-Doped Carbon Quantum Dots (NSCQDs)**

Carbon quantum dots are modified by doping of Nitrogen and Sulphur. Doping of these hetero-atoms plays a vital role in tuning the compositions and structure of Carbon quantum dots. Plants and biomass are used as a source of Carbon, while heteroatoms come from Nitrogen or Sulphur-rich plants and biomass sources or an external source of chemical form of these atoms is added during the synthesis process. Nitrogen and Sulphur co doped Carbon dots are sporadic; only a few plant sources are known which have all sources of Nitrogen, Carbon and Sulphur. Garlic,
Onion and scallion leaves are some common plant-based source for the synthesis of NSCQDs. Specific detection of Fe$^{3+}$ and Ag$^{+}$ is achieved through optical sensing abilities of NSCQDs.

**Graphene Quantum Dots (GQDs)**

Graphene Quantum Dots are Carbon-based nanomaterial with tiny fragments of single and multilayer sheets of graphene in diameters less than 20 nm. GQDs have unique physical and chemical properties with high optical stability, adjustable photoluminescence ability, low toxicity, good thermal and electrical conductivity, and solubility in various solvents. Similar to the CQDs, GQDs are synthesized by top-down and bottom-up approaches, although bottom-up approaches of hydrothermal and solvo-thermal methods provide an advantage in green synthesis. GQDs are equally sensitive for the detection of heavy metals as compared to the CQDs. The detection methods are based on fluorescence quenching approaches, GQDs provide immense variety in fluorescence quantum yield depending on the raw material used for the synthesis. Variable Quantum yield of the nanoparticles defines the sensitivity of heavy metal detection. GQDs are successfully used for the detection of Fe$^{3+}$, and Ag$^{+}$ in aqueous solutions.

**DETECTION OF HEAVY METALS USING PLANT-DERIVED NANOPARTICLES**

Plant-derived nanomaterials have unique optical properties which make these materials suitable for the detection of any change in the presence of analytes. The interactions of nanoparticles with the heavy metal ions result in alteration of the intrinsic properties which are specific to heavy metal ions. Several studies are performed so far, using various plant-derived nanoparticles to detect the variable concentration of the heavy metal ions in different sources. In the current section, we have described very recent studies performed for optical sensing to detect heavy metal ions. Singh et al. synthesized highly fluorescent Carbon quantum dots (CQDs) using the one-pot synthesis method from mango (*Mangifera indica*; M. indica) leaves. The developed nanoparticles showed excellent blue emission spectra upon excitation at 435 nm. An intriguing sensitivity of 0.62 ppm for the detection of Fe$^{2+}$ ions in water sample was achieved using photoluminescence quenching mechanism. The particles have shown excellent chemical stability for a prolonged period.

Jing et al. synthesized Carbon quantum dots (average size of 2.4 nm) from biomass using hydrothermal method. The nanoparticles displayed excellent sensitivity for Pb$^{2+}$ detection in a mix population of various heavy metal ions. The limit of detection of Pb$^{2+}$ was reported as low as 1.3 μM with the wide linear range of 106.7 μM. Liu et al. synthesized Nitrogen-doped Carbon quantum dots from grass using the hydrothermal method with increased reaction temperature. The increased reaction temperature leads to a decrease in size with a significant increase in the quantum yield (QY) of the nanodots. The synthesized nanoparticles demonstrate a handy label-free fluorescent sensing platform to detect Cu$^{2+}$ ions in aqueous solution with a minimum detection limit of 1 nM. Issa et al. have developed Nitrogen-doped Carbon quantum dots with an average size of 3.4 nm with graphitic nature from carboxymethylcellulose (CMC) of oil palm empty fruit. The synthesized nanoparticles showed broad pH stability and enhanced blue-green fluorescence emission in an acidic environment, which is mostly dependent upon the solvent polarity. A limit of detection of 0.14 μM was achieved for Fe$^{3+}$ detection in acidic solution.

Tadesse et al. have synthesized Nitrogen doped fluorescent Carbon quantum dots (average size of 3 nm) from citrus lemon juice using hydrothermal method. The nanoparticles selectively detected Hg$^{2+}$ ions from an aqueous solution containing a cocktail of heavy metal ions with a sensitivity (LOD) of 5.3 nM and the limit of quantification of 18.3 nM at a 99% confidence level. Sun et al. synthesized Sulphur and Nitrogen-doped Carbon quantum dots from Garlic with external addition of Ethylenediamine to improve the photoluminescence quantum yield of the nanoparticles. Such synthesized CQDs exhibited excellent salt tolerance and broad pH range stability. The specific fluorescence quenching by Fe$^{3+}$ allows detection of the ion in aqueous solution with a minimum concentration of 0.2μM. One such another latest study for the selective detection of Fe$^{3+}$ with a LOD of 12.4 ppb was done by Adinarayan et al. using silicon NPs. The microwave assisted one pot synthesis was demonstrated successfully by using *Equisetum arvense* (Horsetail) plant extract, which is known to be rich in silicon content. The synthesized silicon nanoparticles exhibited strong fluorescence which was excitation wavelength independent. The adapted schematic illustration representing the fluorescence quenching of SiNPs upon addition of Fe$^{3+}$ ions is shown in Figure 1.
FIGURE 1. The rendered schematic representing the basic methodology behind optical sensing based on the fluorescence quenching mechanism. Here fluorescence quenching of Si NPs upon addition of Fe$^{3+}$ ions is shown (adapted from ref. 38).

Chen et al. used Garlic to synthesized Nitrogen and Sulphur doped Carbon quantum dots by hydrothermal treatment. The prepared fluorescent nanodots displayed strong fluorescence with the quantum yield of 13%, which was efficiently quenched by Fe$^{2+}$ in environmental water. The quenching of fluorescence of nanodots resulted in a susceptible method to detect Fe$^{3+}$ ions in as low as 0.22 nM concentration. Cheng et al. developed Nitrogen and Sulphur doped Carbon quantum dots from cellulose-based bio-waste of willow catkin. The combustion method used for the synthesis of nanoparticles has resulted in the average particle size of 7.3 nm with superior pH stability along with the low cytotoxicity. The synthesized nanoparticles have shown sensitive detection of Fe$^{3+}$ with a fabulous limit of detection of 0.03μM. Wang et al. developed an optical sensing method to detect Fe$^{3+}$ ions using Rice husk driven graphene quantum dots with an average size of 3.9nm. The nanoparticles were synthesized using the one-pot hydrothermal method showed an intense blue light photoluminescence. The quenching of photoluminescence intensity has achieved the limit of detection of 5.8nM for Fe$^{3+}$ ions.

TABLE 1. Summarized table showing work done using Plant-derived nanomaterials for optical sensing of different heavy metal ions.

<table>
<thead>
<tr>
<th>Sr. no.</th>
<th>NPs</th>
<th>Source</th>
<th>HMIs</th>
<th>LOD</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>CQDs</td>
<td><em>Mangiferaindica</em> leaves</td>
<td>Fe$^{2+}$</td>
<td>0.62 ppm</td>
<td>Singh et al. (2020)$^{19}$</td>
</tr>
<tr>
<td>2.</td>
<td>CQDs</td>
<td>Biomass</td>
<td>Pb$^{2+}$</td>
<td>1.3 μM</td>
<td>Jing et al. (2019)$^{36}$</td>
</tr>
<tr>
<td>3.</td>
<td>CQDs</td>
<td>Purple perilla</td>
<td>Ag$^{+}$</td>
<td>1.4 nM</td>
<td>Zhao et al. (2019)$^{20}$</td>
</tr>
<tr>
<td>4.</td>
<td>CQDs</td>
<td>Tulsi leaves</td>
<td>Cr$^{6+}$</td>
<td>4.5 ppb</td>
<td>Bhatt et al. (2018)$^{21}$</td>
</tr>
<tr>
<td>5.</td>
<td>CQDs</td>
<td><em>Ocimum sanctum</em></td>
<td>Pb$^{2+}$</td>
<td>0.59 nM</td>
<td>Kumar et al. (2016)$^{22}$</td>
</tr>
<tr>
<td>6.</td>
<td>CQDs</td>
<td>Bamboo leaves</td>
<td>Cu$^{2+}$</td>
<td>115 nM</td>
<td>Liu et al. (2014)$^{23}$</td>
</tr>
<tr>
<td>7.</td>
<td>NCQDs</td>
<td>Carboxymethylcellulose (CMC) of oil palm empty fruit</td>
<td>Fe$^{3+}$</td>
<td>0.14 μM</td>
<td>Issa et al. (2020)$^{29}$</td>
</tr>
</tbody>
</table>
### CONCLUSION

Use of plant biomass for synthesis of nanomaterials has gained a significant attention over the last few years. These nanomaterials have wide range of applications like sensing, bio-imaging, catalysis, energy storage, etc. Depending on the method of synthesis, these nanomaterials have often been found to have better catalytic or adsorptive property than those synthesized from chemical route. In this review, we have described different types of nanomaterials derived from plant-based biomass and their application in optical sensing of heavy metal ions. The use of plant biomass as precursor for synthesis of nanomaterials has many advantages over the use of expensive and toxic chemicals. Biomass is renewable, inexpensive, has high yield, and are also biocompatible and therefore, plant biomass derived nanomaterials are becoming very popular. There is a need for commercial production of inexpensive, portable, and sensitive optical materials these days for detection and remediation of heavy metals ions from the environment. Therefore, the use abundantly available plant biomass can be a sustainable source for production of such highly sensitive and selective optical nanomaterials.

### REFERENCES

38. S. Jing, Y. Zhao, R.-C. Sun, L. Zhong and X. Peng, ACS Sustainable Chemistry & Engineering 7 (8), 7833-7843 (2019).