Utilization of waste materials for the synthesis of nano materials and their application for the removal of dyes and phenolic compounds from the water

A Summary submitted to the
Babasaheb Bhimrao Ambedkar University, Lucknow
in fulfilment of Requirement for the Award of Degree of

Doctor of Philosophy

in Environmental Science

BY

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Enrolment No. 1123/15

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LUCKNOW, UTTAR PRADESH-226025

2022

Summary

Nanotechnology has become an important part of the modern era. This technology applied in almost every field such as food industry, agriculture, medical field, electrical, energy storage, etc. Nanoparticles have a significant application in environmental remediation also specially in the area of water treatment; ground water and surface water both. Their unique physical chemical properties make them so important. However, the chemical and physical synthesis methods of nanoparticles are problematic they are high energy consuming, costly, damage environment by the release of toxic by-products. Hence, the concept of green synthesis of metallic nanoparticles using plant extract is getting attention now. Green synthesis using plant extract require less energy and cost, environmentally non-polluting, faster and comparatively easier to operate in low maintenance environment. Plant extract have different phytochemicals like phenols and flavonoids that are capable of reducing metallic ions in addition to reduction of metals phytochemicals also act as natural capping agent therefore do not require any other capping or stabilizing agent further.

Green synthesis of nanoparticles can also achieved by preparation of extract of waste biomass like vegetable waste and garden waste or problematic biomass or biomass of no social benefit like agricultural weed, it reduces the use of green and beneficial plants and also reduce the cost of synthesis. Another reason to opt for waste biomass over live green plant is its abundance and the nuisance it create due to mismanagement. Many studies have till now reported the use of different wastes for the synthesis of nanoparticles. Very less work has been done to explore secondary metal sources for the synthesis of metallic nanoparticles like metal containing waste, which are hazardous in nature but can provide metals for the development of new high value added materials like nanoparticles. It will help in resource reutilization, and primary resource conservation. In this work, metallic nanoparticles are synthesised by green synthesis method using waste biomass extract and also metallic nanoparticles are synthesised by the extraction of metals from metal containing solid wastes via green synthesis and precipitation method. The synthesised nanoparticles were applied for the removal of organic pollutants from water using adsorption,

heterogeneous Fenton like degradation process and photocatalytic degradation process.

The whole study was divided into three major phases and the key findings of these phases are summarised below:

PHASE 1: Green synthesis of iron nanoparticles using $FeCl_3$

- This is the first phase in which iron nanoparticles were synthesised using leaf extract of three plants namely, *Jatropha*, *Plumeria* (common name "Champa") and *Parthenium*. The commercially available $FeCl_3$ was used as source of iron in this phase.
- *Jatropha* is an energy crop, *Plumeria* is an ornamental plant and *Parthenium* is an exotic agricultural weed, in case of *Jatropha* and *Plumeria* their dried and fallen leaves (leaf litter) was used and in case of *Parthenium* whole plant except root was used for the preparation of extract.
- The purpose of choosing these biomass wastes was their presence in large amount and need to manage them.
- Prior to synthesise nanoparticles the collected waste biomass was subjected for proximate analysis, SEM, EDS and FTIR analysis.
- 85.22% moisture content was found in *Parthenium* while in *Jatropha* and *Plumeria* leaves only 17.49 and 22.58 % was found. Volatile organic compounds made the largest fraction in the proximate analysis of *Jatropha* (65.72%) and *Plumeria* (66.39%), whereas *Parthenium* contained lesser volatile organic matter (12.55%).
- The prepared plant extracts were examined qualitatively for the presence of different phytochemicals that were flavonoids, tannins, cardiac glycosides, steroids, saponins, alkaloids, anthroquinones, reducing sugars. All the phytochemicals were found to be present in all plant extract except for anthroquinones (in *Jatropha* and *Plumeria*) and steroids (in *Parthenium*). Total polyphenolic content was found 4.58 GAE (mg/g) in *Jatropha* extract, 10.62 GAE (mg/g) in *Plumeria* extract and 21.57 GAE (mg/g) in *Parthenium* extract.

- The iron nanoparticles were synthesised by addition of the prepared plant extract into 0.1 M $FeCl_3$ solution drop by drop in the ratio of 3:2 and the pH was adjusted 6. The reaction was carried out on magnetic stirrer at room temperature. Then the nanoparticles synthesised were washed, dried and grounded into fine powder.
- Three types of iron nanoparticles were prepared in this phase i) synthesised using *Jatropha* (Ja-FeNPs), synthesised using *Plumeria* (Pl-FeNPs) and synthesised using *Parthenium* (Pa-INPs).
- The synthesised nanoparticles were characterized using SEM, FE-SEM, EDS, FTIR, XRD, BET, XPS, PSA and pH_{ZPC}.
- The particle size of Ja-FeNPs and Pl-FeNPs was observed to be ~ 32 nm (by FE-SEM analysis) and particle size of Pa-INPs was found to be in the range of 60-120 nm (by PSA). All the synthesised iron nanoparticles were amorphous in nature with several functional groups present on their surface. The BET surface area of Ja-FeNPs and Pl-FeNPs was 23.43 m^2/g and 18.90 m^2/g, respectively. The XPS analysis of the both these nanoparticles showed the presence of iron in Fe(II), Fe (III) and Fe(0) form. The pH_{ZPC} of Ja-FeNPs, Pl-FeNPs and Pa-INPs was found to be 4.85, 5.85 and 6.75, respectively.
- All the nanoparticles were applied for the removal of crystal violet dye (CV), phenol and p-nitrophenol (PNP) in the aqueous solution, the removal carried out firstly by adsorption and then by heterogeneous Fenton like degradation.
- The removal of CV was carried out by adsorption, maximum adsorption of CV was found to be around 91 %, 96 % and 94 % using Ja-FeNPs, Pl-FeNPs and Pa-INPs, respectively. All the nanoparticles were recycled for 5 cycles and recycling Pl-FeNPs was found best, it showed good adsorption efficiency for all the 5 cycles, moreover, it also showed the maximum adsorption capacity for CV with Q_0= 125 mg/g.
- The adsorption process was optimized by varying different operating parameters (nanoparticles concentration, CV concentration, pH, temperature and reaction time), and adsorption process was analysed using adsorption isotherm, kinetics and thermodynamics.
- CV adsorption was followed best by Langmuir isotherm (by Ja-FeNPs), Temkin isotherm (Pl-FeNPs) and Freundlich isotherm (by-Pa-INPs). The

adsorption kinetics was fitted with pseudo-second-order kinetic model. Adsorption was found endothermic using Ja-FeNPs and Pl-FeNPs and exothermic using Pa-INPs.

- The removal of phenol and PNP was firstly tested by adsorption but due to less adsorption percentage the removal was carried out by Fenton like degradation process using Ja-FeNPs and Pl-FeNPs only because Pa-INPs showed very less degradation percentage of both the pollutants.
- The degradation process was optimized by varying different operating parameters; nanoparticle concentration, pollutant concentration, H_2O_2 concentration, pH, temperature and reaction time,
- The maximum degradation of phenol was found to be ~97 % and ~96 % using Ja-FeNPs and Pl-FeNPs, respectively. And the maximum degradation of PNP was found to be ~94 % and 90 % using Ja-FeNPs and Pl-FeNPs, respectively.
- The degradation efficiency of Ja-FeNPs was also tested by the assistance of ultrasonic waves and it was found that degradation process become faster took very less time, 60 min in comparison with no ultrasonic waves which took 300 min.
- The degradation process was fitted best with pseudo-first-order reaction kinetics. Both the nanoparticles were effective in upto three recycling processes.
- On comparing CV adsorption capacity of all the three iron nanoparticles synthesised in phase I Pl-FeNPs was found best which showed highest adsorption capacity, required lesser nanoparticle concentration and was recyclable for five cycles.
- Whereas, for the degradation of phenol and PNP Ja-FeNPs was found best it required lesser nanoparticle concentration, lesser H_2O_2 concentration and lesser time. Recyclability of Ja-FeNPs was also better than Pl-FeNPs.

PHASE 2: Green synthesis of iron nanoparticles using iron rust

- In this phase, two iron nanoparticles were synthesised using leaf extract of *Jatropha* and *Plumeria* as they gave better results in phase 1. The waste iron rust was used in this phase as the source of iron instead of $FeCl_3$.
- Leaching of iron rust was done using 3M HCl and the leachate was used as precursor of iron. Synthesis of iron nanoparticles was done by adding plant extract into iron rust leachate drop by drop in the ratio of 3:2 and the pH was adjusted 6. The reaction was carried out on magnetic stirrer at room temperature. Then the nanoparticles synthesised were washed, dried and grounded into fine powder
- The synthesised iron nanoparticles were named as IRNPs@Ja and IRNPs@Pl synthesised via *Jatropha* and *Plumeria* extracts, respectively. The particle size and BET surface area of IRNPs@Ja and IRNPs@Pl was found to be ~43 nm (190.2 m^2/g) and ~44 nm (18.93 m^2/g), respectively, and both were amorphous in nature. The pH_{ZPC} of IRNPs@Ja and IRNPs@Pl was found to be 6.7 and 6.03, respectively.
- Both of the IRNPs@Ja and IRNPs@Pl were found effective for the adsorption of CV with maximum removal efficiency around 94% and 96%, respectively. The adsorption process was optimized by varying different operating parameters (nanoparticles concentration, CV concentration, pH, temperature and reaction time).
- Adsorption was analysed by application of adsorption isotherms, kinetics and thermodynamic models. CV adsorption by IRNPs@Ja was best followed by Temkin adsorption isotherm, whereas, CV adsorption by IRNPs@Pl was best followed by Langmuir adsorption isotherm. Both adsorption processes were followed by pseudo-second-order kinetics and were endothermic in nature.
- The recycling efficiency of IRNPs@Ja for CV adsorption was better than IRNPs@Pl and it was effective for all 5 cycles.
- Removal of phenol and PNP was carried out by Fenton like degradation process. Maximum degradation of phenol was found to be >98 % using both the nanoparticles and maximum removal of PNP was found to be around 95 % and 92 % using IRNPs@Ja and IRNPs@Pl, respectively.
- The degradation process was optimized by varying nanoparticle concentration, pollutant concentration, H_2O_2 concentration, pH, temperature and reaction

time, and fitted best with pseudo-first-order kinetics. The recycling efficiency for degradation was good for three cycles of both the nanoparticles.

- The degradation process was also analysed by removal of chemical oxygen demand (COD) in the degradation process the COD removal of phenol was found to be 83.63 % and 88.6 % by IRNPs@Ja and IRNPs@Pl , respectively. And the COD removal for PNP was found to be 83.3 % and 84.0 % by IRNPs@Ja and IRNPs@Pl, respectively.
- In the degradation process, the amount of iron leached in the solution and there species were also determined.
- On comparing the efficiency of both the iron nanoparticles synthesised in phase 2 for the removal of CV, phenol and PNP both were found effective. There was no significant difference for CV removal but for phenol and PNP, IRNPs@Ja was found better.

PHASE 3: Synthesis of nano zinc oxide using waste batteries

- In this phase waste Zinc carbon (Zn-C) batteries were used for the recovery of Zn and synthesis of nano ZnO particles. The synthesis of ZnO was done using facile precipitation method.
- Zinc anode used Zn-C batteries was separated manually, washed, dried and shredded into small pieces manually which were leached in 5 M HNO_3. The leachate was used as the Zn precursor. ZnO particles were synthesised by precipitation of $Zn(OH)_2$ by adding NaOH. The obtained white precipitate was washed, dried and calcined at 300˚C for the preparation of ZnO and grounded into fine powder.
- The synthesised ZnO particles were highly crystalline in nature with crystallite size 23.94 nm, and BET surface area 17.52 m^2/g. The band gap was 3.1 eV and pH_{ZPC} was found to be 8.5. The XPS analysis showed the presence of Zn in (+2) form.
- ZnO particles were applied for the photocatalytic degradation of CV, phenol and PNP under the irradiation of visible light.
- nZnO showed a good catalytic efficiency for the degradation of all the three pollutants, however, the crystal violet (CV) removal was best in comparison

with the other pollutants, it was minimally effected by the increase in CV concentration.

- Maximum degradation of CV, phenol and PNP using ZnO particles was found to be >97 %, 95 % and 88 %, respectively.
- Degradation process was optimized by varying different operating conditions (ZnO concentration, pollutant concentration, H_2O_2 concentration, pH, temperature and reaction time.
- The degradation data was fitted best with pseudo-first-order kinetic model. The photocatalyst was recyclable and its regeneration ability was higher for initial three cycles.
- The degradation efficiency was tested in the presence of different concentration of carbonate and nitrate ions and it was found that increasing carbonate concentration decreased the photocatalytic degradation process, while, increasing concentration of nitrate increase the photocatalytic degradation of CV, phenol and PNP.
- The photocatalytic degradation reaction was found to be driven by the generation of $OH^{\cdot}$ radicals. The intermediate compounds formed in the process of degradation were determined by liquid chromatography and mass spectroscopy (LC-MS) analysis several intermediate compounds were identified in the degradation process of CV, phenol and PNP.
- The COD removal for phenol, PNP and CV was found to be 85.9 %, 70.8 % and 92.8 % respectively. Amount of zinc leached from ZnO catalyst in the aqueous solution of phenol, PNP and CV during the degradation process was found to be 1.659, 2.120 0.787 mg/L.
- Overall six nanoparticles were prepared in this work three iron nanoparticles in phase 1 (Ja-FeNPs, Pl-FeNPs Pa-INPs), two iron nanoparticles in phase 2 (IRNPs@Ja and IRNPs@Pl) and one ZnO nanoparticle in phase 3. All of these were efficient for the removal of CV, phenol and PNP except for Pa-INPs which was unable to remove phenol and PNP. Iron nanoparticles synthesised had good adsorbing as well as good catalytic activity, however, ZnO showed very less adsorption of the pollutants.
- Removal of pollutants was different using different nanoparticles. CV removal was best observed by the application ZnO via photocatalytic degradation.

Removal of PNP and phenol was best observed by the IRNPs@Ja using Fenton like degradation process.