



ADSORPTION OF Ni²⁺ FROM WASTE WATER VIA SILVER- DELONIX REGIA NANO COMPOSITE

VEENA DOSS*, PRACHI KATRE, ASMITA KULKARNI^a,
SHUBHOJIT MALLICK and AJITH NAIR

Sinhgad College of Engineering, 44/1, Off Sinhgad Road, Vadgaon (Bk), PUNE – 41 (M.S.) INDIA

^aSmt. Kashibai Navale College of Engineering, 44/1, Off Sinhgad Road, Vadgaon (Bk), PUNE – 41 (M.S.) INDIA

(Received : 01.03.2012; Revised : 19.03.2012; Accepted : 25.03.2012)

ABSTRACT

A variety of methodologies and routes have been reported for the adsorption of heavy metal ions like Cd, Hg, Cu, Zn, Ni, etc. aiming at increased potentials in waste water treatment. In this paper an elegant approach towards removal of heavy metal ions is reported using Silver-Delonix regia nanocomposite. FTIR results indicated the presence of a number of active sites in the composite comparable to Activated Charcoal. uv-vis spectra showed the formation of nano silver for the nanocomposite. Nanosilver-Delonix regia composite could well be used as a viable alternative in future for improving the adsorption potency. The nickel ions adsorbed on the nanocomposite was subjected to both Freundlich and Langmuir isotherms.

Key words: Delonix regia-silver nanocomposite, Activated charcoal.

INTRODUCTION

Heavy metals like Cu, Pb, Zn, Ni, Hg, Cr, etc present in the effluents of chemical industries like metal, finishing and electro-plating, mining and tanneries are among the chief pollutants of surface and groundwater which harm both the fauna and flora in aquatic systems and are detrimental to human health also¹. The treatment technologies include a wide range like chemical precipitation, membrane filtration, solvent extraction, ion exchange and adsorption². Of all these adsorption using activated carbon is most commonly employed for the removal of heavy metals present in aqueous systems. Nowadays emphasis is more on use of low cost natural adsorbents like biomass, rice husk, chitosan, tea leaves, coconut shells, etc.³⁻⁷ For the present study modifying the surface of a natural adsorbent, Delonix Regia using silver nanoparticles to form a nano composite as a suitable adsorbent was investigated. Composites have a wide range of applications as it allows the best properties from two or more different materials to be amalgamated into one. This gives them an edge over other pure compounds when it comes to adsorbing ions for removal from industrial waste water. Silver composites in spite of being expensive provides better adsorption and on biological composites act as an antimicrobial agent. Delonix regia (gul mohar) which is abundantly available has proven to have high anti-oxidant activity which in turn prevents Ag from getting oxidized Gul mohar has been used for a long time as inhibitors and hence protect the body from oxidative stress related diseases⁸. They are also used to protect foods from rancidity or deterioration from auto-oxidation⁹.

In the present paper, the focus is on using novel route of adsorption of heavy metal (Ni) ion on zerovalent silver supported on natural adsorbent *Delonix regia*.

EXPERIMENTAL

Preparation of gulmohar kernel powder (GKP)

Dry gulmohar fruits were collected and dried in sun for removal of moisture or any fungus etc if present. Gulmohar kernels from the fruit were taken and dried in an oven at 100°C for moisture removal or any micro-organisms or bacteria if present. Dried kernels were taken and grinded in a mixer. This powder was then screened by passing through a mesh size 10 to get uniform fine particles. Finally this grinded powder was kept in oven at 200°C for about 3 hours for final removal of moisture traces if any present. After this gulmohar kernel powder (GKP) was ready to use.

Composition of GKP is as follows:

Moisture	:	11.4-22.7%
Protein	:	15.0-22.0%
Fat/oil/lipids	:	3.9-8.0%
Crude fibre	:	2.5-8.2%
Carbohydrates	:	65.1-72.2%
Total ash	:	2.4-4.2%

Preparation and characterisation of silver nanoparticles (NPs)

0.1 M of Silver Nitrate Stock solution was and was reduced using Methanol in the ratio of 1 : 1 and was heated for 30 mins¹⁰. This was then subjected to uv-vis spectrophotometric analysis which showed a characteristic blue shift as shown in Fig. 4 confirming formation of Ag⁰. The nanoparticle, Ag⁰ prepared was then mixed with 170 mesh size fine gul mohar seeds for 30 mins in a shaker and the residue was kept in the oven at 110°C for 4 hours. The Silver-*Delonix regia* nanocomposites so formed were then analysed for its characteristics and presence of active sites by FTIR and UV –Visible Spectrophotometer.

Quantitative estimation for Ni ion solution

The Ni-DMG method was used to prepare a Beer's law calibration plot and estimation of Ni ions was determined using the uv-vis spectrophotometer at 450 nm¹¹.

Adsorption isotherm

100 mL Ni ion solution having a concentration of 100 ppm was shaken with 0.25-1 gm of Ag DR nanocomposite for a period of 4 hours. The isotherm obtained using the equation given below was validated for both Langmuir & Freundlich isotherms¹².

Equation for isotherm -

$$q_e = (C_0 - C_e) * (V/d)$$

where

C_0 = Initial concentration (mg/L)

C_e = Equilibrium concentration (mg/L)

q_e = Amount of Ni(0) adsorbed (mg/g)

V = Volume of sample taken (mL)

d = Amount of adsorbent added (g)

Adsorption kinetics

100 mL Ni ion solution having a concentration of 100 ppm was taken in a batch reactor fitted with a stirrer and mixed thoroughly for 4 hours (RPM 200). To this was added 1 gm of the nanocomposite, Ag^0 delonix regia. Samples were withdrawn every 15 min for the first hour and after every half an hour for the remaining 3 hours. The sample was then kept in centrifuge for about 2 min at 400-600 rpm for particles to settle down and then analysed using the uv-vis spectrophotometer at 445 nm.

RESULTS AND DISCUSSION

Characterisation of the adsorbent

The nanocomposite prepared was subjected to FTIR as shown in Fig. 2. The FTIR showed characteristic peaks at around 1650 cm^{-1} due to C=O stretch of carboxyl grp and 2900 cm^{-1} due to CH stretch and OH stretch of hydroxyl group which confirmed presence of surface functional groups like carboxyl and hydroxyl groups comparable to activated charcoal. The uv-vis spectra shows the blue shift.

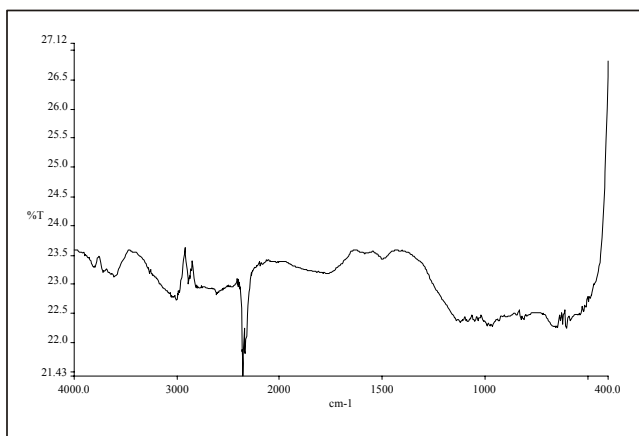


Fig. 1: FTIR of activated charcoal

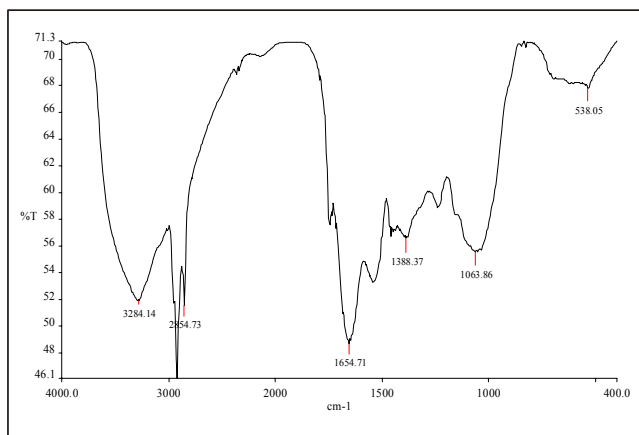


Fig. 2: FTIR of nanocomposite { Ag^0 -DR}

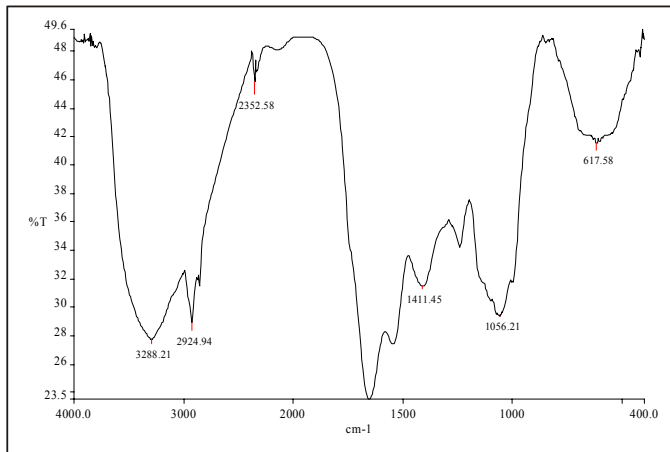


Fig. 3: FTIR of Delonix regia

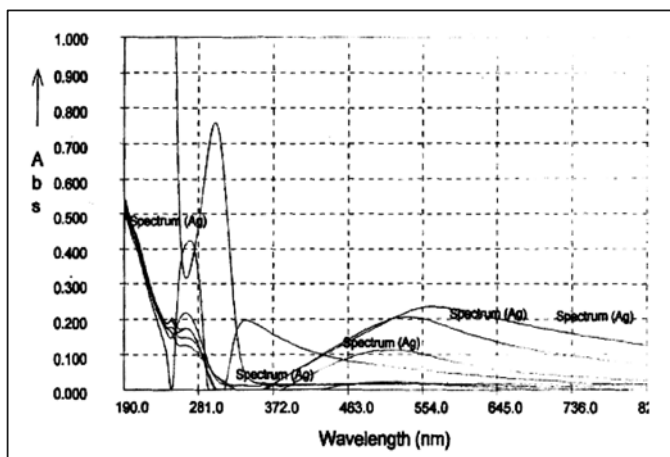


Fig. 4: UV-Vis spectra of nano valent Ag

It can be seen that the spectrum shifts to the left clearly indicating a blue shift confirming formation of nano Ag.

Calibration plot

This plot relates the absorbance for different concentration. This was in validation with Beer Lamberts law.

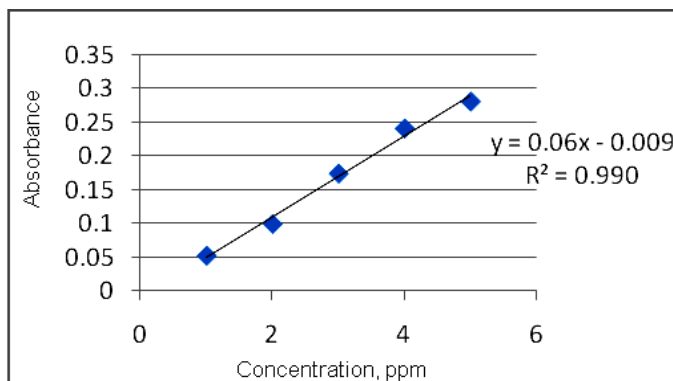


Fig. 5: Calibration plot of Ni ion

Adsorption isotherm

The adsorption isotherm was obtained by plotting q_e vs C_e . The isotherms obtained were validated to both Langmuir and Freundlich equations as shown in Figs. below:

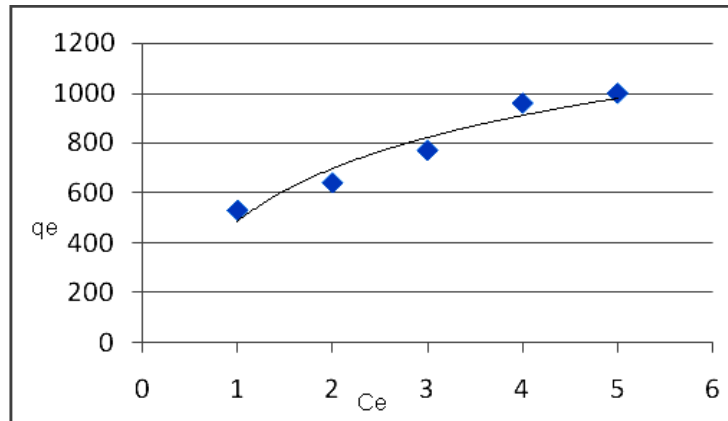


Fig. 6: Adsorption isotherm for Ni ions on nano AgDR composite

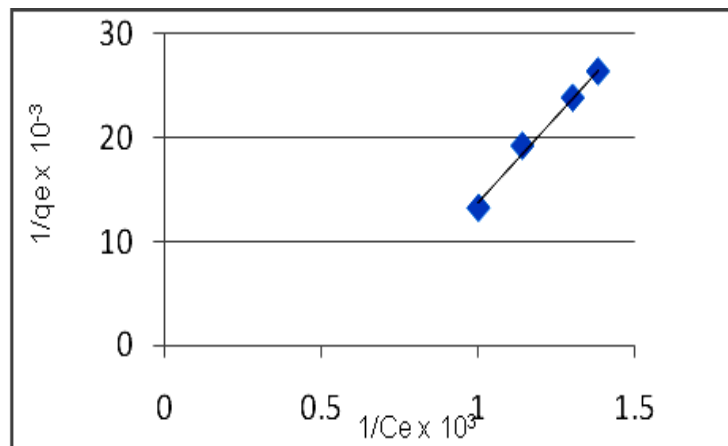


Fig. 7: Langmuir adsorption isotherm

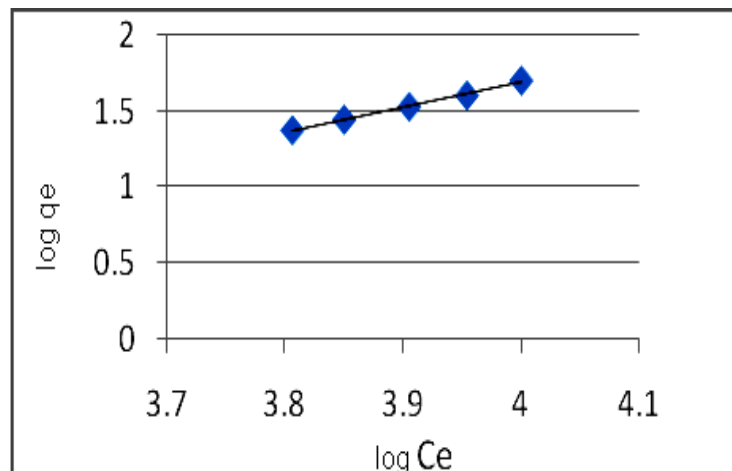


Fig. 8: Freundlich adsorption isotherm from the graphs it is observed that both Langmuir and Freundlich equations hold true

Adsorption kinetics

As seen from nature of the graph as time increases concentration decreases which indicates nickel from sample gets adsorbed by AgDR nanocomposite and with increasing time less sites are available for adsorption.

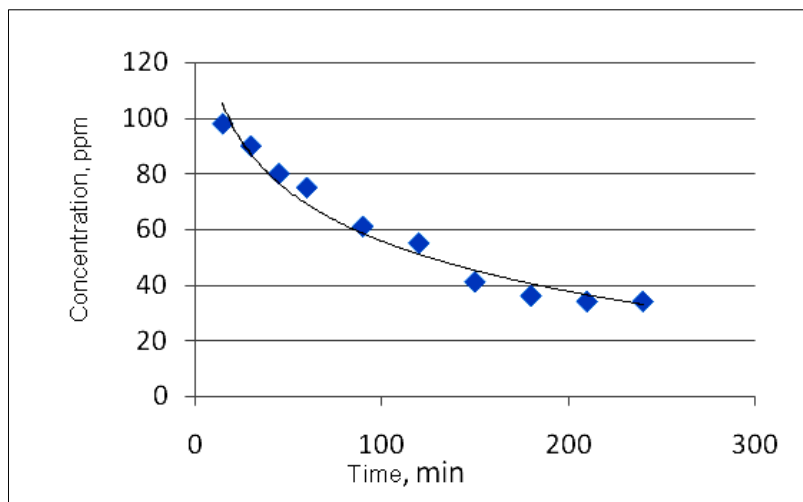


Fig. 9: Adsorption kinetics

CONCLUSION

The FTIR images show number of active sites provided by the indigenously prepared composite. The UV spectrophotometer readings provide evidence that Silver nanoparticles are formed. It has been well established that generation of nanoparticles results in a blue shift of the solution. As seen in our results, the UV-Vis spectrophotometer shows a shift on the left side as the Ag(+1) gradually converts into Ag(0). After 20 minutes of heating the Ag-methanol solution there is no more shift which confirms the Ag NP formation. Clearly, methanol worked as a reducing agent which helped reduce the Ag ion to Ag zero valent. The adsorption isotherm and its validation to both Freundlich and Langmuir isotherms prove beyond doubt that heavy metal ions get easily adsorbed onto the surface of the composite confirming our views of Silver-Delonix regia nanocomposite being a suitable natural adsorbent.

ACKNOWLEDGMENT

The study was conducted with support from BCUD, University of Pune, Pune.

REFERENCES

1. S. Cheng, Effects of Heavy Metals on Plants and Resistance Mechanisms, *Environ. Sci. Pollut. Res. Int.*, **10(4)**, 256-64 (2003).
2. S. C. Reed, E. J. Middlebrooks and R. W. Crites, *Natural Systems for Waste Management and Treatment*, New York, McGraw-Hill (1988).
3. Ayhan Demirbas, Heavy Metal Adsorption onto Agro-Based Waste Materials: A Review, *J. Hazardous Mater.*, **157**, 220-229 (2008).
4. Katsutoshi Inoue et al., Adsorptive Removal of As (V) and As (III) from Water by a Zr (IV)-Loaded Orange Waste Gel, *J. Hazardous Materials*, **154**, 1066-1074 (2008).

5. Mehmet Emin Argun et al., Heavy Metal Adsorption by Modified Oak Sawdust, Thermodynamics and Kinetics, *J. Hazardous Materials*, **141**, 77-85 (2007).
6. E.-S. Z. El-Ashtoukhy et al., Removal of Lead (II) and Copper (II) from Aqueous Solution Using Pomegranate Peel as a New Adsorbent Desalination, **223**, 162-173 (2008).
7. Gonzalo Vazquez et al., Chestnut Shell as Heavy Metal Adsorbent: Optimization Study of Lead, Copper and Zinc Cations Removal, *Journal of Hazardous Materials*, **172**, 1402-1414 (2009).
8. Silver Colloid Nanoparticles, Synthesis, Characterization and their Antibacterial Activity, *J. Phys. Chem. B*, **110**, 16248-16253 (2006).
9. Antioxidant and Antimicrobial Attributes and Phenolics of Different Solvent Extracts from Leaves, Flowers and Bark of Gold Mohar [*Delonix regia* (Bojer ex Hook.) Raf.] *Molecules*, **16**, 7302-7319 (2011).
10. P. P. Katre et al., Nanocomposite of Pd-polyaniline as a Ethanol Sensor, *Sensors and Actuators B: Chemical* (2005).
11. A. Vogel, *Quantitative Inorganic Analysis*, ELBS, Longman Group Limited, England (1979) p. 901.
12. O. Altin, H. O. Ozbelge and T. Dogu, Use of General-Purpose Adsorption Isotherms for Heavy Metal-Clay Mineral Interactions, *J. Colloid Interf. Sci.*, **198**, 130-140 (1998).