



Adsorption of Ni(II) ion from aqueous solution on bio-carbon prepared from Bilva (*Aegle marmelos*) leaf powder

KEYWORDS

Adsorption isotherm, Bilva leaf powder carbon (BLPC).

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ABSTRACT Systematic batch mode studies of adsorption of Ni(II) ion on bilva leaf powder carbon (BLPC) were carried out. Parameters like initial Ni(II) ion concentration, dosage of adsorbent, pH, agitation time and temperature are noted to test the equilibrium data by using Freundlich isotherm phenomena. The results indicated that the adsorption of Ni(II) ion on BLPC is maxima in acidic solutions. The effect of BLPC adsorbent was analyzed by scanning electron microscope (SEM) and justified that the adsorption is reasonably agreed.

1. Introduction

Numerous techniques such as ion-exchange,¹ chemical precipitation,² electrochemical methods³ and membrane technology⁴ are adopted for the effluents-treatment.^{5,6} Recent years, bio-sorption has inherent advantages in effluents-treatment; the applications of bio-sorption have been extensively reviewed.^{7,9} Many adsorbents like chitosan,¹⁰ geothite,¹¹ silica-gel,¹² red mud,^{13,14} paper mill sludge¹⁵ and bituminous coal¹⁶ were investigated for metal and dye removal. Recently some agricultural and forestry wastes like seed coal,¹⁷ saw dust,¹⁸ rice husk,¹⁹ rice shells, cotton seed shell,²⁰ stalks,²¹ almond shell²² and oak wood waste, corn stover,²³ coir,²⁴ banana pith²⁵ and jute²⁶ have been recognized as new adsorbents. The utility of bio-carbons in adsorption is said to be eco-friendly - easily accessible, inexpensive and abundant in nature.

It is trusted that the bio-carbons are possessing active sites. Secondary metabolites like alkaloids, terpenoids, chromones, coumarins, anthocyanins, flavones and flavonoids are suggested as active sites in plant carbons. Isolation and structural predictions of coumarins, amides and alkaloids are successfully explained by us in our earlier phytochemical investigations on *Rutaceae* plants, *Feronia limonia* and *Limonia crenulata*.^{27,28}

Bilva, represents the wide availability of *Rutaceae* in the Asian countries called as *Aegle marmelos*. The present investigation focusses to study the isotherm of the adsorption of Ni(II) ion which explores the optimum conditions for adsorption of the metal.

2. Materials and Methods

2.1. Preparation of bio-carbon

Bilva plant leaves were collected and dried in shade for 48 hours. The dried leaves were ground to obtain the homogeneous powder. It was further used for the preparation of bio carbon. Activated bio carbon of the *Aegle marmelos* was prepared by treating the homogeneous powder with concentrated sulphuric acid (Sp. Gr. 1.84) in a weight ratio of 1:1.8 (biomaterial:acid). The resulting black product was kept in a hot air - oven at 160C for 6 hours. A successive washing by distilled water to remove the excess acid is followed then it was kept in oven for further 2 hours at 105C. The particle size of active bio-carbon is varied in range between 90µm and 125.

Preparation of metal solution

Analytical reagent grade 0.672 g/litre of nickel ammonium sulphate stored in polythene bottles are used to prepare Ni(II)

ion solutions.

Adsorption studies

A series of batch experiments were conducted to study the adsorption mechanism and isotherm. The prologue investigations were carried out in batches at different conditions such as by varying the parameters like pH, concentration, contact time, the amount of adsorbent and etc. However the dye concentration is also varied between 20-100 mg/L during the study of adsorption percentage. In each practice, 100 ml of metal solution with known concentration was poured to a known amount of adsorbent. The mixture was continuously shaken for a known time. The metal removal was determined calorimetrically by using photoelectric calorimeter. The percentage of removal and equilibrium adsorption uptake q_e mg/g was calculated using equations 1 and 2 as follows

$$\text{Removal\%} = 100(C_0 - C_e) / C_0 \quad \text{.....Eq.1}$$

$$q_e = (C_0 - C_e) V / m \quad \text{.....Eq.2}$$

Kinetics studies

50 ml Nessler flask is used to carry out the kinetic experiments; 100mL of 100mg/L and 200mg/L solution concentrations are taken as optimum concentration at ambient temperature and predetermined time intervals (30 - 180 min). The mixture was shaken well before collecting as sample. The mixture is analyzed calorimetrically using photoelectric calorimeter.

Results and discussion

Characterization of the BLPC

FT-IR spectrum for the samples before and after adsorption of Ni(II) ion (Figure 1 and Figure 2) on bio-carbon are studied. The comparative studies of Figure 1 and Figure 2 has shown that remarkable shifts in stretching vibrations are observed; whereas we concluded that the functional groups on bio-carbons are participated in Ni(II) ion removal process.

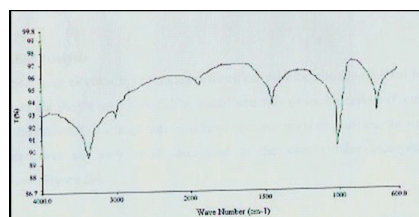


Fig. 1. FT- IR spectrum of the bio-carbon before adsorption

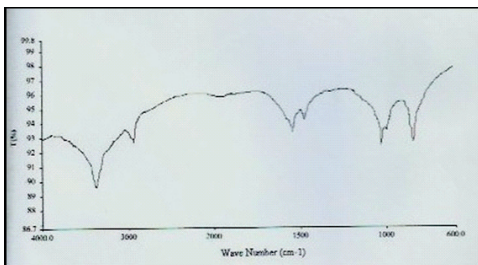


Fig. 2. FT- IR spectrum of the bio-carbon after adsorption

Scanning electron micrographs of the bio-carbon and Ni(II) ion loaded bio-carbon are illustrated in Figure 3 and Figure 4. The initial structure of the bio-carbon (Figure 3) showed the presence of a large macro pores with various size at the surface, however the number of macropores are very much decreased in the sample after adsorption of Ni(II) ion (Figure 4).

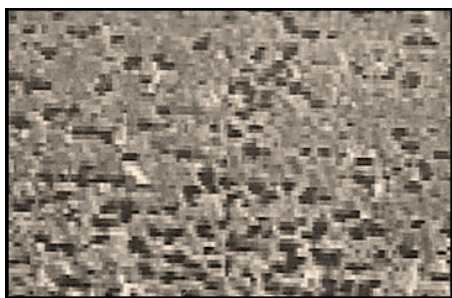


Fig. 3. SEM photograph of bio-carbon before adsorption

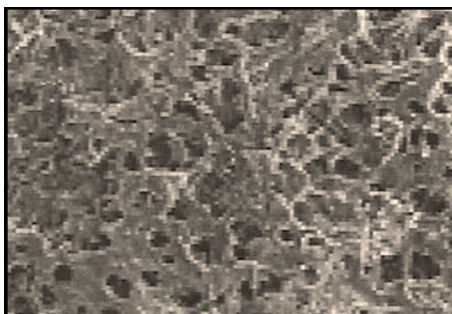


Fig. 4. SEM photograph of bio-carbon after adsorption

Effect of contact time and initial dye concentrations

The effect of contact time on the adsorption of Ni(II) ion on BPLC adsorbent was shown in Figure 5. The results indicated that the dye uptake from water was dependent to concentration and increased with initial concentration of metal ion. The equilibrium time was found to be at 120 min. The metal ion uptake increased rapidly in the initial stages of contact time, then become almost constant which denotes the attainment of equilibrium. This may be considered that, due to all active sites on the adsorbent surface were vacant at initial stage and the solution concentration was high. After that period, a few surface active sites were available for adsorption, thereby a metal ion uptake was increasing marginally is observed.²⁹

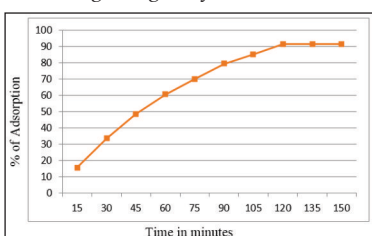


Figure 5. Effect of contact time and initial dye concentrations

Effect of pH

pH is an important parameter for adsorption of metal ions from aqueous solution because it affects the solubility of the metal ions, concentration of the counter ions on the functional groups of the adsorbent and the degree of ionization of the adsorbate during reaction.³⁰ The percentage of sorption increased from 60% at pH 3.5 to 91.6% at pH 4.2. Then it significantly decreased with increase in pH, like at pH 6 it was around 60%. From this study we can conclude that in pH range 4-5 the bio carbon showed maximum percentage of bio sorption.

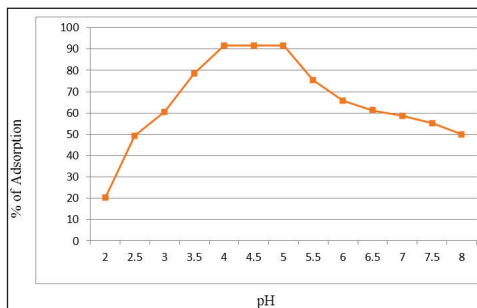


Figure 6. Effect of pH

Effect of solid/liquid ratio

Solid/liquid (abbreviated as S/L) is the ratio of the mass of adsorbent/volume of solution is an important parameter affecting the efficiency of the metal ions adsorption. Figure 7 shows the effect of S/L ratio on the Ni(II) ion adsorbed by BLPC.

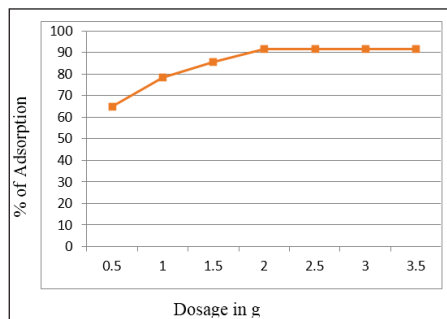


Figure 7. Effect of solid/liquid ratio

However the adsorption efficiency increased as the S/L ratio increased. When S/L ratio is minimum, the active sites for binding adsorption surface are less and the adsorption efficiency is low; whereas adsorption efficiency is maximum when S/L ratio increase until it reach saturation.³¹ Figure 7 shows S/L ratio of 200 mg/ 100ml as chosen in this study.

Adsorption isotherm

Adsorption isotherms are basic requirements for the design of adsorption systems. These data may provide information about the capacity of the adsorbent or the amount required for removing a unit mass of pollutant under the system concentrations. Freundlich isotherm has been tested has been tested in the present study to analyze the equilibrium data of solute between adsorbent and solution. Based on the assumption that all adsorption in active sites are equivalent and adsorption active sites is independent of whether the adjacent is occupied, the linear form of Freundlich adsorption can be expressed as shown in the following equation.³²

Freundlich model		
K_f	$1/n$	R^2
426.530	0.265	0.985

$$\log q_e = \log k_f + 1/n \log C_e$$

Where k_f and n are the Freundlich adsorption constants, which can be determined by the plot of $\log q_e$ versus $\log C_e$ as shown in Figure 8.

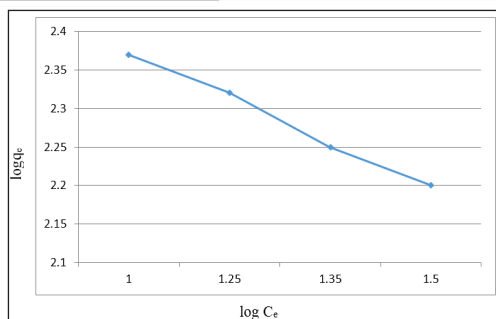


Figure 8. Freundlich adsorption isotherm

As it can be seen in the following table, which indicates the adsorption of Ni(II) ion onto BPLC that obeyed Freundlich isotherm.

Conclusion

The bio-carbon is readily accessible, environmentally friendly, it shows large holes for adsorption and inexpensive. The pH value had agreed influence on the adsorption efficiency, whereas at low pH value the adsorption efficiency was relatively high. SEM exhibited that, BPLC had a considerably numbers of pores where, there was a good possibility for Ni(II) ion to be trapped and adsorbed into pores. The present removal of Ni(II) ion in the synthetic waste-water system was 91.6% with effective bio carbon load 2.5/100ml of the sample. The experimental results were analyzed by using Freundlich equation. Any type of industrial effluents can be treated with preliminary cleaning operations. This methodology can be extended to the colour removal process in waste-water systems.

References

- L. Koene, L. J. Janssen, *Electrochem. Acta.* 47, 2001, 695 - 703.
- Y. Benito, M. L. Ruiz, *Desalination.* 142, 2002, 229 - 234.
- B. Volesky, Z. R. Holan, *Biotechnol. Prog.* 11, 1995, 235 - 250.
- A. Kapoor, T. Viraraghavan, *Bioresour Technol.* 53, 1995, 195 - 206.
- J. A. S. Tenorio, *Espinosa Waste Manage.* 21, 2001, 637 - 642.
- M. M. Matlock, B. S. Hwerton, D. A. Atwood, *Water Res.* 36, 2002, 4757 - 4764.
- F. Veglio, F. Beolchini, *Hydrometallurgy.* 44, 1997, 301 - 316.
- T. A. Davis, B. Volesky, A. Mucci, *Water Res.* 33, 2003, 4311 - 4330.
- N. Kuyucak, B. Volesky, *Biotechnol. Bioeng.* 33, 1989, 809 - 814.
- R. A. A. Muzzarelli, R. Rocchetti, *Metal adsorption by modified chitins. In: Thompson, R. (Ed.), Trace metal removal from aqueous solution. The Royal Society of Chemistry.* 44, 1986.
- B. B. Johnson, *Environ. Sci. Technol.* 24, 1990, 112 - 118.
- N. L. D. Filho, Y. Gushiken, W. L. Polito, J. C. Moreiza, *Talanta.* 42, 1995, 1630 - 1663.
- R. Apak, E. Tutean, M. Huguul, J. Hizal, *Water Res.* 32, 1998, 430 - 440.
- E. Lopez, B. Soto, M. Arias, A. Nunez, A. Rubinos, M. Barnal, *Water Res.* 32, 1998, 1314 - 1322.
- N. Calace, E. Nardi, B. M. Petronio, G. Pietroletti, Tosti, *Chemosphere.* 51, 1997, 797.
- D. Singh, N. S. Rawat, *Indian J. Chem. Technol.* 1, 1994, 266 - 270.
- S. Rengaraj, B. Arabindoo, V. Murugesan, *Indian J. Chem. Technol.* 6, 1999, 1 - 4.
- N. Sivarajasekar, *Carbon Lett.* 8, 2007, 236 - 243.
- P. K. Malik, *Dyes Pigments.* 56, 2003, 239 - 249.
- T. Y. Kim, I. H. Baek, Y. D. Jeoung, S. C. Park, *J. Ind. Eng. Chem.* 9, 2003, 254 - 260.
- A. A. Attia, A. A. El-Hendway, S. Khedrmel, Nabaraway, *Adsorption Sci. Tech.* 22, 2004, 411 - 426.
- E. Demirbas, M. Koby, Senturk, T. Ozakan, *Water SA.* 30, 2004, 533 - 539.
- T. Zhang, W. P. Walawender, L. Fan, M. Fan, D. Daugaard, R. C. Brown, *Chem. Eng. J.* 105, 2004, 53 - 59.
- C. Namasivayam, K. Kadirvelu, *Bioresour Technol.* 76, 1997, 63 - 69.
- K. Kadirvelu, M. Kavipriya, C. Karthika, M. Radhika, N. Vennilamani, S. Pattabhi, *Bioresour Technol.* 81, 2003, 78 - 83.
- S. Senthilkumaar, P. R. Varadarajan, K. Porkodi, C. V. Subbhuraam, *Colloid. Surface. B.* 28, 2005, 78 - 83.
- P. Pitchai, R. Ulagi, P. S. Mohan, R. M. Gengan, *Int. J. Res. Phytochem. Pharmacol.* 3(1), 2013, 914.
- P. Pitchai, R. Ulagi, P. S. Mohan, R. M. Gengan, *Ind. J. Chem.* 51B, 2012, 1771 - 1775.
- M. D. Tamez Uddin, S. Akhtarul Islam, M. D. Mahmoud Rukanuzzaman, *J. Hazard. Mater.* 164, 2009, 53 - 60.
- C. Namasivayam, D. Kavitha, *Dyes pigments.* 54, 2002, 47 - 58.
- S. Liang, C. N. Feng, Q. H. Tian, *Colloid. Surface. B.* 73, 2009, 10 - 14.
- I. Langmuir, *J. Am. chem. Soc.* 40, 1918, 1361 - 1403.