

Removal of Nickel (II) Ions from Aqueous Solution using activated carbon developed from *Azadirachta indica* a low cost adsorbent

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ABSTRACT

Present paper deals with the removal of Ni(II) metal ions using activated carbon developed from carbonaceous source material neem leaves (*Azadirachta indica*) powder as an adsorbent. Heavy metals plays a vital role for proper functioning of biological systems but a large number of disorders arises from their lack or excess. Industrial effluents contain higher concentrations of heavy metals such as Cr, Ar, Cd, Pb, Ti, Hg and Ni that contaminate the water bodies. Adsorption technique was used in this research to extract Ni (II) ions from aqueous solution. Batch experiments were carried out to analyze the influence of different parameters such as solution pH, initial metal ions concentration, adsorbent dosage, contact time and temperature. Fourier-transform infrared spectroscopy (FTIR) and x-ray diffraction (XRD) used to analyze the physiochemical and morphological properties of sample. The scanning electron microscopy (SEM) revealed micro-structural properties of adsorbent sample. Specific surface area of activated carbon developed from neem leaves (*Azadirachta indica*) was 32.2 m²/g evaluated by BET. It was concluded that the maximum percentage (%) removal of Ni (II) ions was about 80%. The adsorption experimental data was best fitted to Temkin adsorption isotherm model and kinetic data was in a good agreement with pseudo first order kinetic model.

Key words : *Neem leaves, Azadirachta Indica, Nickel (II), Activated carbon, Adsorption isotherms.*

Introduction

Water is an essential compound for living organisms. Wastewater containing heavy metals such as Pb, Zn, Cu, Hg, Ar, Cr, Mn and Ni is considered as the serious environmental problem in human society (Hussain *et al.*, 2019). The stability and mobility of heavy metals is the reason which promotes them as most hazardous material for the environment (Ayangbenro and Babalola, 2017). Nickel is an essential element at trace level only but it becomes toxic at higher concentration for both plants and animals (Counotte *et al.*, 2019). According to World

Health Organization (WHO) and Environmental Protection Agency (EPA) non toxic amount of Ni ions in drinking water should not exceed more than 0.01 mg/L (Alemu *et al.*, 2017). Ni(II) ions is introduced as a pollutant from wastewater of silver refineries, electroplating, zinc-based casting industries, storage battery industries (Barakat, 2011). Human and animal studies confirmed that high level exposure of Ni (II) ions increases the risk of lungs and bone cancer, along with dermatitis (nickel itch), nausea, vomiting, shortness of breath, cyanosis, extreme weakness and DNA damage (Ibrahim and Sani, 2015). Various conventional methods have

been proposed for removing heavy metal ions such as Ni(II) ions includes chemical precipitation, electro winning, phytoremediation, ion-exchange, biological treatment and adsorption on activated carbon (Fu and Wang, 2011). But, these processes appear to be ineffective or extremely expensive, and the generation of toxic sludge or other waste from these techniques is also a problem (Eccles, 1999). The physicochemical properties of the laboratory synthesized activated carbon materials are mainly based on the source or raw materials (Yaha *et al.*, 2018). Activated carbon prepared from low cost waste materials through physicochemical activation show maximum removal capacity of heavy metals from aqueous media or wastewater (Kumar *et al.*, 2018). Numerous reports are available in the field of wastewater treatment concerning the low cost activated carbon adsorbents produced from carbonaceous source materials such as almond husk (Hasaretal, 2003), rice husk (Le and Thi, 2014), cotton seeds (Sivarajasekar *et al.*, 2017), peanut hulls (Periasamy and Namasivayam, 1996), cotton stalk (Deng *et al.*, 2010), used for efficient management of heavy metals adulterated waste water (Demiral *et al.*, 2008).

Materials and Methodology

Reagents

For this work, analytical grade reagents including Nickel sulphate hexahydrate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), conc. H_2SO_4 , HCL and NaOH was procured from Sigma Aldrich, India.

Preparation of adsorbent

Neem leaves (*Azadirachta indica*) were collected locally and washed with deionized water to eliminate dirt and sun-dried for 4-5 days. These sun-dried materials were further placed in an oven (hot air) for 5-6 hours. Domestic mixer was used to get powder from the dried leaves. The particle size of 0.147 mm (100 mesh number) was selected using sieve analysis. Further this powder was treated with conc. H_2SO_4 1:1 (w/v) at room temperature for one hour (Singh *et al.*, 2020). Afterward it was transferred to a muffle furnace at 170 °C for half an hour to remove volatile impurities. The process of slow pyrolysis leads to 18 % yield of driven biomass which converted it into activated carbon form and then washed with deionized water until the pH of

activated carbon became neutral and got free from acid residue.

Batch experiments

4.47g of $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ was dissolved in one L of double distilled water to prepare a 1000 mg/L Nickel stock solution. The specific volumes of known concentration (10-100 mg/L) were prepared using serial dilution of stock solution of nickel. The pH adjustment of solution was performed using HCL (0.1 M) and NaOH (0.1 M). 50 ml of nickel solution (in 250 ml glass reagent bottle) was used for all the batch experiments. Desired pH value, contact time, adsorbent-adsorbate dosage and reaction temperature were optimized during batch experiments. Aagitation rate of 350 rpm was given using magnetic stirrer to attain equilibrium. The stirred solution was allowed to stand for 30 minutes and then filtered through filter paper (Whatman No. 42), the concentration of Ni (II) metal ions thus determined by AAS (Agilent Technologies). The percent removal of metal ions by activated carbon can be calculated by using the Equation 1 (Bhanjana *et al.*, 2017a):

$$\% \text{ Removal} = \frac{(\text{Initial Concentration of Ni} - \text{Concentration of Ni after removal})}{\text{Initial Concentration of Ni}} \times 100$$

Result and Disussion

XRD Results

Physiochemical properties of a dried and well-powdered samples were evaluated through XRD. The dried powder of *Azadirachta indica* and activated carbon was taken before and after activation. The XRD pattern discrepancy (Fig. 1). It is clear from XRD plots that before activation there was a presence of crystalline behavior which shifted to amorphous nature after activation (Singh *et al.*, 2020).

FTIR Results

“The FTIR spectrum of the activated *Azadirachta indica* in Fig. 2. The bands at 2910 cm^{-1} indicates the existence of an aliphatic -CH group stretching (Saka, 2012). The broad band at 3100 cm^{-1} associated with -OH stretching vibration and peak at 1574 cm^{-1} matches to C=C stretching of the aromatic rings. Two peaks at 1030 and 1710 cm^{-1} were attributed to the vibration absorption of C-O (Xie *et al.*, 2014).”

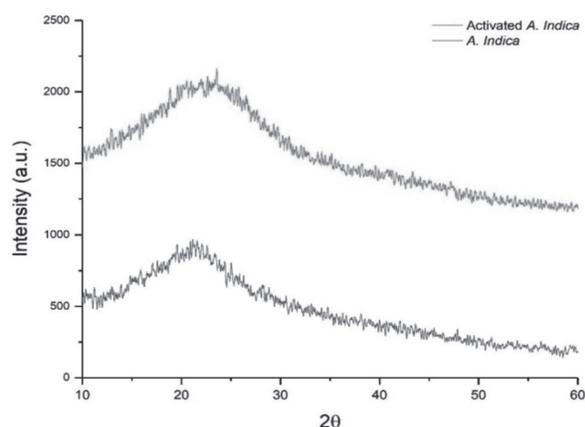


Fig. 1. Comparative XRD analysis of raw powder and activated carbon of *Azadirachta Indica*

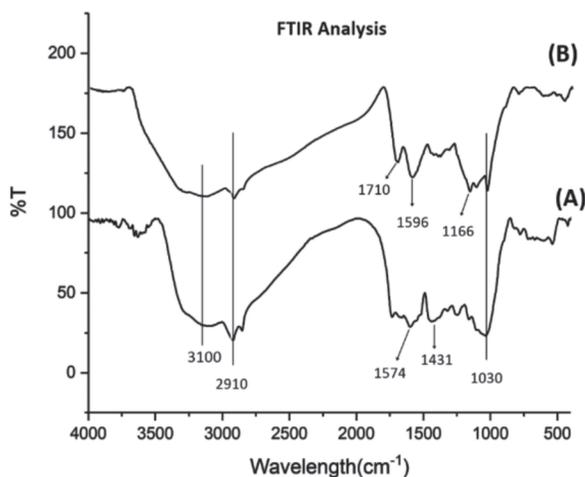


Fig. 2. Comparative FTIR spectra analysis of (A) raw *Azadirachta indica* (B) activated carbon

SEM Results

SEM image (Fig. 3 and 4) showed the surface physical morphology of *Azadirachta Indica* sample before and after activation. In the SEM configuration, the powdered *Azadirachta Indica* sample covered to be conductive are scanned in a high vacuum-chamber with a magnified range focal e⁻ beam of 30-10000 resolution 200 Å, 19kV of accelerated voltage. The micrograph of the activated carbon sample has shown partial cracking, particle aggregation and some pores/voids of various sizes. The activated carbon sample surface topology is quite different from raw material (Fig. 3 and 4). Due to the evaporation of chemical reagents, porous structure has been found in activated carbon sample leaving empty space (Deng *et al.*, 2010). The porous struc-

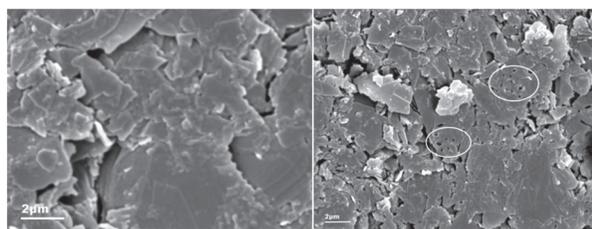


Fig. 3. Before Activation Fig. 4. After Activation

tures of *Azadirachta indica* generated activated carbon are useful for attachment of organic and inorganic contaminants. The high surface area obtained due to pores availability in the synthesized activated carbon sample will become beneficial point for the removal of Ni(II) ions.

BET Results

The most common Brunauer, Emmett and Teller (BET) method was used to measure the specific surface area of synthesized activated carbon sample (Gupta and Kumar 2019). On the basis of BET measurements, we found 32.2 m²/g specific surface area, 0.014 cc/g pore volume and 6.194 nm pore diameter (Fig. 5).

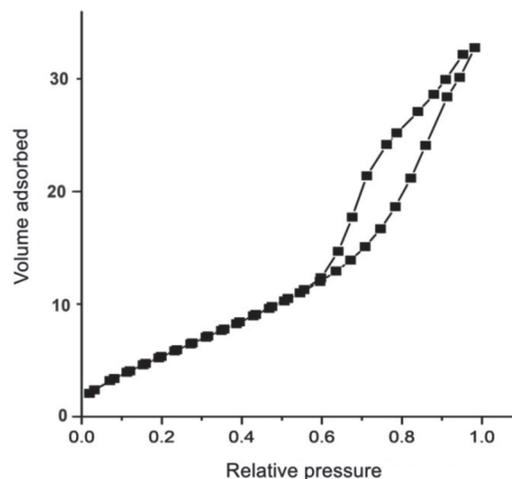


Fig. 5. BET analysis of activated carbon of *Azadirachta indica*

Effect of pH

The consequence of pH value on adsorption of Ni(II) ions on activated carbon was estimated by varying pH range from 2-12 at room temperature. 0.5 g of adsorbent was added in 50 mL of 50 mg/L Ni(II) ions concentration solution. The acidic and basic solutions was maintained by 1N HCl and 1N NaOH respectively. The rate of adsorption is also

influenced by the presence of H^+ and OH^- ions present in solution (Anah and Astrini, 2017). The ionization status of the adsorbent and adsorbate is also affected by the pH (Kumar *et al.*, 2019). It is evident (Fig. 6) that the rate of adsorption was slower at lower pH values, because in the acidic environment additional competition offered by H^+ ions which are of smaller size as compared with Ni(II) ions due to which less sites are available for binding of Ni(II) ions (Akpomie and Dawodu, 2014). On the other hand, at alkaline pH, the solution turned turbid. This turbidity is due to formation of nickel hydroxide which leads to more availability of active sites for binding of Ni(II) ions (Kabdash *et al.*, 2012). The maximum uptake of Ni (II) ions was noted at pH 6. Thus pH 6 was standardized for further experiments.

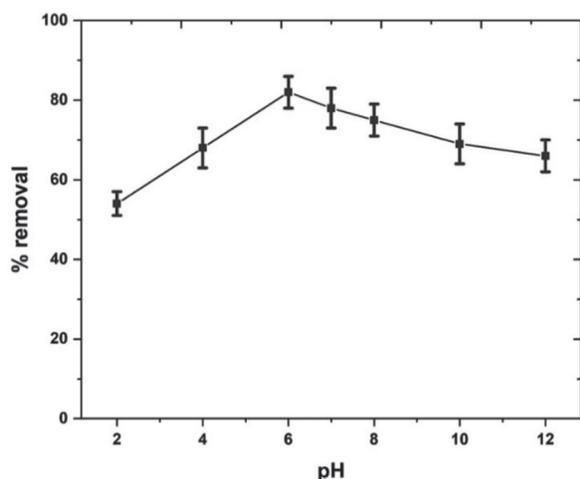


Fig. 6. Percentage removal of Ni (II) ions at different pH values.

Effect of adsorbent dosage

The adsorbent dose is also a crucial factor in achieving high adsorption rate. It has been revealed by several researchers that the rate of adsorption depends upon dose of adsorbent (Banerjee and Chattopadhyaya, 2017). The impact of adsorbent dosage on Ni(II) ions removal was studied at pH 6, concentration of Ni (II) ions in solution is 50 mg/L, volume 50 mL and a contact time of 300 minutes. Fig.7 shows that as the adsorbent dosage is increased from 0.1 to 1 g, the % removal of the Ni(II) ions also increasing instantly. The maximum removal was found around 80% at 1 g dosage. Finally, a steady value was obtained might be due to less contact of adsorbent with adsorbate present in bulk.

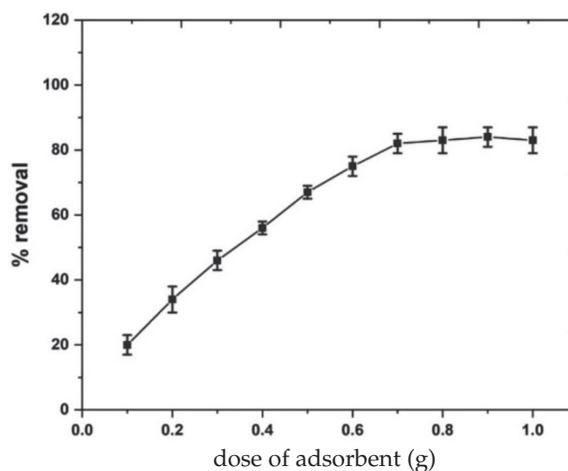


Fig. 7. Percentage removal of Ni (II) ions at different adsorbent dosage

The increase in uptake of Ni (II) ions as adsorbent dosage increased can be attributed to the availability of more surface area and active sites on the surface of adsorbent.

Effect of initial Ni (II) ions concentration

The effect of Ni (II) ions concentration of % removal was also considered for experiments. Effect of adsorbate concentration (10-100 mg/L) on adsorption efficiency of activated carbon was studied at room temperature and pH 6. A linear increase in adsorption efficiency was seen (Fig. 8) with increase in Ni (II) ions concentration to 60mg/L afterwards there was saturation in % removal with high concentrations of Ni (II) ions with no prominent change. This

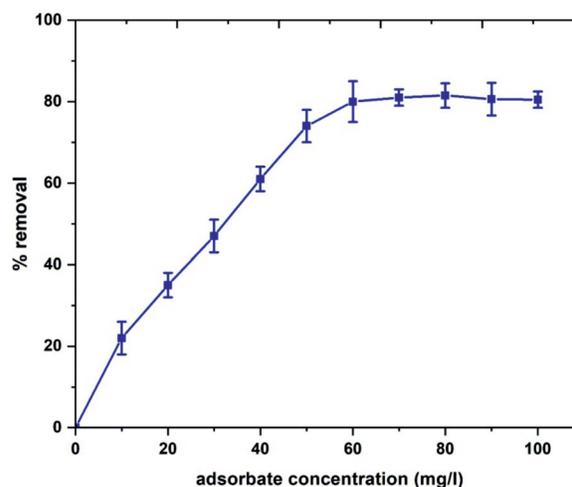


Fig. 8. Effect of adsorbate concentration (mg/L) percentage removal of Ni(II) ions.

is due to accessibility of more adsorption sites during the start of adsorption process which gets saturated at higher concentrations of Ni (II) ions. Due to this, a saturation in % removal is seen with higher concentrations of Ni ions (Akpomie *et al.*, 2015).

Effect of contact time

Fig. 9 showed that the variation of contact time has a significant role in percentage removal of Ni (II) ions. There is an increase in percentage removal of Ni(II) ions with contact time (upto 300 minutes). After, this a decrease in adsorption was observed owing to the unavailability of more vacant/active sites and movement of Ni(II) ions away from surface of adsorbent (Sevilla and Mokaya, 2014). The % removal of Ni(II) ions is also increasing gradually as the contact time is increasing. The maximum removal of Ni (II) ions was about 80 % seen at 300 minutes under conditions of pH 6, solution concentration of 50 mg/L at room temperature.

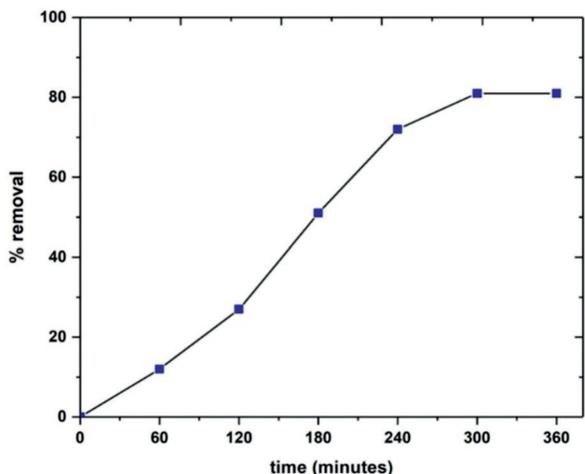


Fig. 9. Effect of Contact time on percentage removal of Ni(II) ions.

The mechanism of adsorption process depends upon isotherm and kinetic data (Pearlin *et al.*, 2015). Several isotherm and kinetic models were used and are given in Fig. 11 to 14.

Effect of temperature

The effect of reaction temperature was also studied (Aljeboree *et al.*, 2017). The effect of temperature on rate of adsorption or percentage removal of Ni (II) is offered (Fig. 10). It is interpreted from result that as the temperature was increased; there is also increase in percentage removal of nickel. Further, this in-

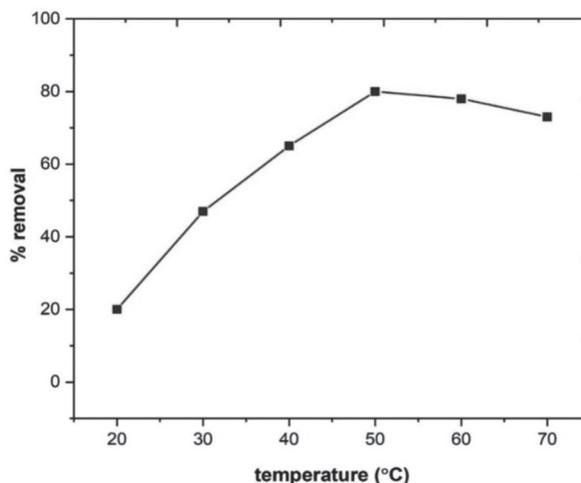


Fig. 10. Effect of temperature on removal of Ni(II) ions.

crease was till 50°C, thereafter a decrease in % removal of nickel ions was observed.

Adsorption isotherms

The given equation (Equation 2) was applied for estimation of Langmuir isotherm (Bhanjana *et al.*, 2017b, c):

$$\frac{C_e}{q_e} = \frac{C_e}{q_{max}} + \left(\frac{1}{q_{max}}\right)b \dots \dots \dots Eqn: 2$$

Where, final concentration of nickel ions is given by C_e , whereas equilibrium concentrations of Ni(II) ions (mg/L) is denoted by q_e while b and q_{max} are giving the values of isotherm constants.

Temkin isotherm model (Fig. 12) gave linear fit for data. The equation used (Equation 3) under Temkin model is given as (Kumar *et al.*, 2014; Bhanjana *et al.*, 2017a):

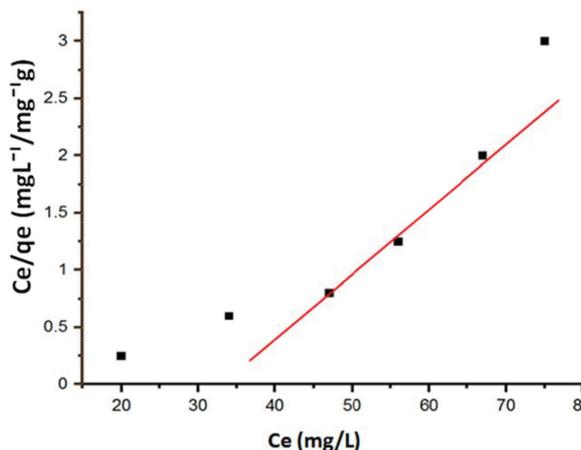


Fig. 11. Langmuir isotherm model for Ni(II) ions removal.

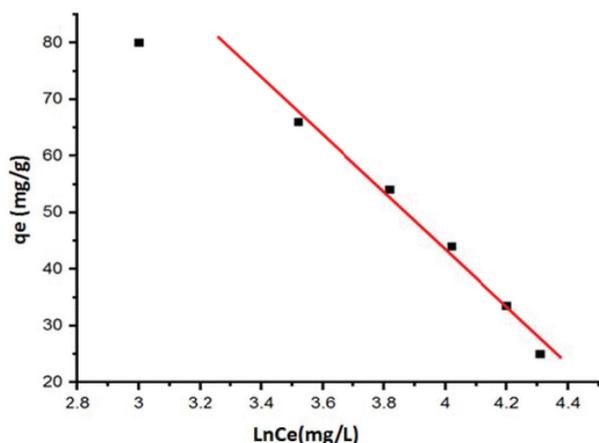


Fig. 12. Temkin isotherm model for Ni (II) ions removal.

$$q_e = \frac{RT}{b} \ln aC_e \quad \dots \text{Equation (3)}$$

Where a, b denotes Temkin constants, R represents gas constant, T is the absolute temperature and C_e belongs to final concentration with q_e as equilibrium concentration. The value of $a = 0.0065$ and $b = -0.062$

Pseudo first and second order kinetics was applied for kinetic parameters (Gupta and Kumar 2019) and the results are given in Fig. 13 and 14. It is clear from the data that the current adsorption process is best fitted to pseudo first order kinetics model.

Comparative study for adsorption capacity of various adsorbent materials towards adsorption of Ni (II) ions

The adsorptive capacity of the activated carbon developed from *Azadirachta indica* (investigated in this

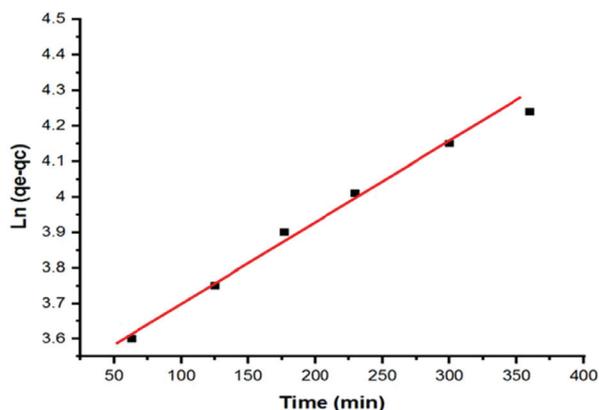


Fig. 13. Data fitting in pseudo first order kinetic model.

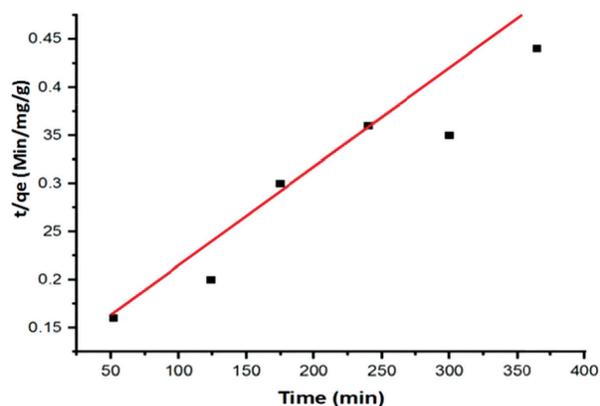


Fig. 14. Data fitting in pseudo second order kinetic model.

research) has been compared with other adsorbents that were reported in the literature whose values are showing in Table 1. The research outcome of the current work was compared with some other researcher work. Results of this research work revealed that the activated carbon developed from neem leaves (*Azadirachta indica*) has higher adsorption capacity than barley straw, Modified *Aloe barbadensis* Miller leaf powder, Kenaf fiber, Punica granatum peel waste, Citrus limettioides peel carbon (Table 1).

Conclusion

Neem leaves (*Azadirachta indica*) powder was successfully processed in activated carbon form and employed as a possible adsorbent for the removal of Ni(II) ions from aqueous. Kinetic study has shown that removal of Ni (II) ions from aqueous followed pseudo first order kinetics and in good agreement with Temkin isotherm. The % removal of Ni (II) ions was found about 80 % under conditions of pH 6, solution concentration of 50 mg/L, adsorbent dose of 0.5 g, contact time of 300 minute and 50. The adsorption rate increased with an increase in adsorbent dosage. No interference of other metal cations was observed on adsorption potential of Ni(II) ions. Physiochemical properties and porous structure of activated carbon developed from neem leaves (*Azadirachta indica*) indicates that it is an excellent adsorbent for the removal of Ni (II) ions from aqueous.

This study shall be helpful in designing of new absorbers for use in different industries for efficient management and removal of Ni (II) ions from their effluents.

Table 1. Measured Adsorbent Capacity values for different bio-waste adsorbents for the management of Ni (II) ions

Adsorbents	Adsorbent capacity(mg g ⁻¹)	References
Nano- crystalline calcium hydroxyapatite	40.00	Mobeasherpour et al. 2010
Modified <i>Aloe barbadensis</i> Miller leaf powder	28.986	Gupta et al. 2019
Kenaf fiber/ chitosan biosorbent	70.55	Florence et al. 2015
Barley straw	35.8	Kumar et al. 2019
Punica granatum peel waste	52	Kumar et al. 2019
Citrus limettioides peel carbon	38.46	Kumar et al. 2019
Activated carbon produced from neem leaves (<i>Azadirachta indica</i>)	80	Present work

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