

Equilibrium studies for the removal of nitrates from aqueous solutions using acid treated sunflower seed husk (*Helianthus annuus*)

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Abstract

Major adsorbent materials used for nitrate removal from polluted aqueous streams are expensive and difficult to regenerate. In this study, the possibility of using sunflower seed husk (*helianthus annuus*), as an alternative low cost biosorbent material to remediate nitrate pollution in waste water was investigated. The adsorbent was characterized before and after biosorption of nitrate ions by Fourier Transform-Infrared Spectroscopy (FT-IR). Functional groups such as hydroxyl, amino and carbonyl groups which are capable of binding nitrates were identified. Batch experiments were performed as a function of pH, sorbent dose, initial nitrate concentration, and contact time. The sorption capacity decreased with increasing sorbent dose while the percentage nitrate removal increased with increasing sorbent dose and also increased with increasing nitrate concentration. The optimum contact time was found to be 120 minutes, optimum biomass dose was 3.0 g and the optimum pH for nitrate removal was 2.0. The Freundlich and Langmuir adsorption isotherms were used to describe the equilibrium sorption data. The maximum adsorption capacity was 0.4924 mg/g according to the Langmuir model. The Langmuir model showed better representation of data, with correlation of determination value of 0.9941 compared to that of Freundlich of 0.8194. The findings of this investigation demonstrated the potential of using sunflower seeds husks in the removal of nitrates from aqueous solutions using a simple and cost effective treatment procedure.

Keywords: Sunflower seed husk, acid treatment, biosorption, nitrates, modeling.

Introduction

Nitrates are an important plant nutrient however when in excess they become a toxic pollutant which contaminates ground water (Afkhami, 2003). Nitrates enter the environment through industrial waste and farm run off. Nitrogen fertilisers are the main sources of nitrates in water bodies around rural areas and farm lands. Their solubility in water means they are easily washed by

rain water to natural water bodies (Thomson, 2001). Nitrates in water are an environmental hazard as they accelerate plant growth. Increased growth rate results in the plant species covering the water surface, consequently depriving water species such as fish of sunlight and oxygen. This decrease water species diversity (Lenntech, 2009).

Excess nitrates in drinking water is associated with gastric problems in adults due to the formation of nitrosamines in water (Nelson *et al.*, 2005) while in infants it is reported to be the cause of blue baby syndrome, a situation where haemoglobin is converted to methaemoglobin which does not carry oxygen (Majumdar and Gupta, 2000). It is also reported to be toxic to warm blooded animals at concentrations above 10 mg/L (Moorcroft *et al.*, 2001).

A number of techniques have been reported for the removal of nitrates from water bodies; however these techniques have some limitations (Soares, 2000). Biological denitrification is cost effective and environmentally friendly, however the process is slow especially for large volumes and highly concentrated waste water and for low temperatures (Schipper and Vijovic-Vikovic, 2001). Similarly reverse osmosis is slow and cannot efficiently be used for the treatment of large volumes of water (Schoeman and Steyn, 2003). Chemical reduction requires addition of chemicals, as a result it is not cost effective and it releases toxic compounds which are a threat to the environment (Hu *et al.*, 2001). In electro-dialysis the metal hydroxides formed clog the membrane (Hell *et al.*, 1998). Ion exchange though the most suitable and most used technique of the above due to its simplicity, effectiveness and temperature independence is costly (Bae *et al.*, 2002). Due to these drawbacks, techniques such

as biosorption which utilizes low cost adsorbents most of which are agricultural and industrial waste such as peanut hull, tea waste and wheat straw (Mishra and Patel, 2009) are a better alternative. Agro based anionic adsorbents such as rice hulls, pine barks and sugarcane bagasse have been reported to have maximum nitrate adsorption capacity (Orlando *et al.*, 2002). Research using activated carbon prepared from sugar beet bagasse has also been conducted (Demirbas, 2008). The capacity of wheat straw as an anionic sorbent for the removal of nitrates from water has also been studied (Wang *et al.*, 2007).

No notable studies have been undertaken on the removal of nitrates using sunflower seed husk. Sunflower seed husk remain in abundance as waste during cooking oil production. These can be used as a cheaper alternative for nitrate removal from waste water. This study was aimed at utilizing the sunflower seed husk for nitrate removal.

Materials and Methods

Chemicals and instruments

KNO₃, HCl, NaOH and NH₄OH were supplied by Skylabs and phenoldisulphonic acid was supplied by Merck. All chemicals used were of analytical grade. The nitrate stock solution (1000 mg/L) was prepared by dissolving 1,6451 g potassium nitrate in 1 L deionised water. Calibration standards for the UV-Vis spectrophotometer and test solutions for

batch biosorption studies were prepared by serial dilutions from this stock solution.

Instruments used were an analytical balance (GA-110 OHAUS), pH meter (Az-8601), Fourier transform infra-red spectrophotometer (Digilab Merlin Samitar), UV-Vis spectrophotometer (UV-1601 Shimadzu Japan), heating oven (Cycilo DHG-9070A) and a mechanical shaker (Vasal-401 208 Rajendra Electrical).

Preparation of biosorbent

Sunflower seed husks were collected as waste from a local oil processing company (Matembo Oil Pressers) (18° 55' 0" South, 29° 49' 0" East) in Kwekwe, Zimbabwe and washed thoroughly with distilled water to remove dirt and any soluble impurities. The washed seed husks were oven dried at 80°C for 12 hours, ground to a fine powder and sieved through a 200 µm sieve. The ground sunflower seeds husks were treated with 0.1M HCl for 4 hours at room temperature over a mechanical shaker set at 150 rpm. This was to remove the adsorbed nutrient ions, to aid in stabilization of the biomass and to retain the active sites intact. The powdered sunflower seeds husks were filtered, washed with deionised water until neutral and oven dried at 100°C to a constant mass and stored in an airtight container in a desiccator for further use.

Equilibrium adsorption experiments

Adsorption of nitrate ions onto the sunflower seeds husks was carried out by batch experiments. Replicate measurements, a mechanical shaker set at 150 rpm and a temperature of 25±2°C were used in each investigation. Determination of residual nitrates was done using UV-Vis spectroscopy. In each case the filtrate was reacted with 2 ml of phenoldisulphonic acid to produce a nitro derivative of the residual nitrate. 10 ml of concentrated ammonium hydroxide was added to the sample mixture to give a yellow colour. The development of yellow colour is due to rearrangement in the structure of the nitro derivative. The colour produced follows Beer's law and is proportional to the concentration of nitrates present in the sample (Jagessar and Alleyne, 2011). The concentration of nitrates was then determined using the UV-Vis spectrophotometer by monitoring the absorbance changes at wavelengths of maximum absorbance (420 nm).

The equilibrium adsorption uptake of nitrate ions from the aqueous solution Q_e in mg/g was calculated using the following relationship:

$$\text{Amount adsorbed, } Q_e = \frac{(C_0 - C_e)V}{M}$$

where C_0 is the initial nitrate concentration in (mg/L), C_e is the equilibrium nitrate concentration in mg/L, V is the volume of solution in L and M is the mass of the adsorbent in g.

Table 1: Langmuir and Freundlich parameters for biosorption of nitrate ions by sunflower seeds husks

Adsorption Isotherm	Parameter	Value
Langmuir	Q_{max} (mg/g)	0.4924
	b (L/g)	0.1708
	R^2	0.9941
Freundlich	K_f (mg/g)(L/mg) ⁿ	0.0687
	n (g/L)	1.6784
	R^2	0.8194

Effect of pH

The effect of pH on the amount of nitrate removal was analysed over the pH range of 1-8. pH adjustment was done using 0.1M HCl and 0.1M NaOH. In this study 50 ml of 50 mg/L nitrate solution was pipetted into 8 different 250 ml volumetric flasks. The solutions were adjusted to their respective pH. 1.0 g of powdered sunflower seeds husks were added into the 8 flasks and then run on a mechanical shaker for 24 hours to ensure that equilibrium was reached. The mixture was vacuum filtered the filtrate was analysed for the residual nitrate using the UV-Vis spectrophotometer.

Effect of contact time

This investigation was done to determine the optimum contact time for the sorption of nitrates onto sunflower seed husks. 1.0 g of powdered sunflower seed husk was placed into 8 different 250 ml Erlenmeyer flasks and 50 ml of 50 mg/L nitrate solution was added. The flasks were shaken on a mechanical

shaker. Contact time was varied from 20 minutes to 160 minutes (20, 40, 60, 80, 100, 120, 140 and 160 minutes) at pH 2 and all other parameters were kept constant. Each flask was withdrawn after the appropriate time had lapsed, filtered using vacuum and the filtrate analysed for the residual nitrate using the UV-Vis spectrophotometer.

Effect of biosorbent dose

The effect of biosorbent dose on the amount of nitrates adsorbed was determined over a mass range of 0.5-3.0g. Biosorbent mass of 0.5 g, 1.0g, 1.5g, 2.0g, 2.5g and 3.0g were placed into 6 different 250 ml Erlenmeyer flasks. 50 ml of 50 mg/L nitrate solution was pipetted into each flask. The flasks were placed on a mechanical shaker for 120 minutes at pH 2. After vacuum filtration the residual nitrate was analysed using a UV-Vis spectrophotometer to obtain the optimum sorbent dose.

Effect of initial nitrate concentration

3.0 g of sunflower seeds husks were weighed and placed in 5 different Erlenmeyer flasks. 50 ml of varying nitrate concentration from 10 mg/L to 50 mg/L were placed into the 250 Erlenmeyer flasks. The flasks were placed on a mechanical shaker at 150 rpm for 120 minutes at pH 2. Afterwards the samples were vacuum filtered and the residual nitrate was analysed using UV-Vis spectrophotometer.

Results and Discussion

FT-IR analysis of sunflower seed husk

Fig.1 and Fig. 2 below show the FT-IR spectrum of sunflower seeds husks

before and after biosorption of nitrates respectively. There were notable changes on the spectrum after biosorption as a new band was observed at 1610 cm^{-1} and was attributed to symmetric NH_2 deformation. There was stretching and broadening in absorption frequencies of amino and hydroxyl groups (3440 to 3450 cm^{-1} for the OH group and 3480 to 3490 cm^{-1} for the NH_2 group). This was due to the deformation of OH and -NH bonds as described by Nadavala and Kim (2011). This shows that there is interaction between the functional groups of sunflower seed husk with nitrates during biosorption. This was further confirmed by the broadening of the out-of plane carbonyl, C-O bond at 620 cm^{-1} which was originally at 610 cm^{-1} . Similar functional groups were described in the work of Osma *et al.*, (2007). The results of the FT-IR spectrum show the participation of amine, carboxylic and hydroxyl groups of sunflower seed husk as active binding sites for the adsorption of nitrates.

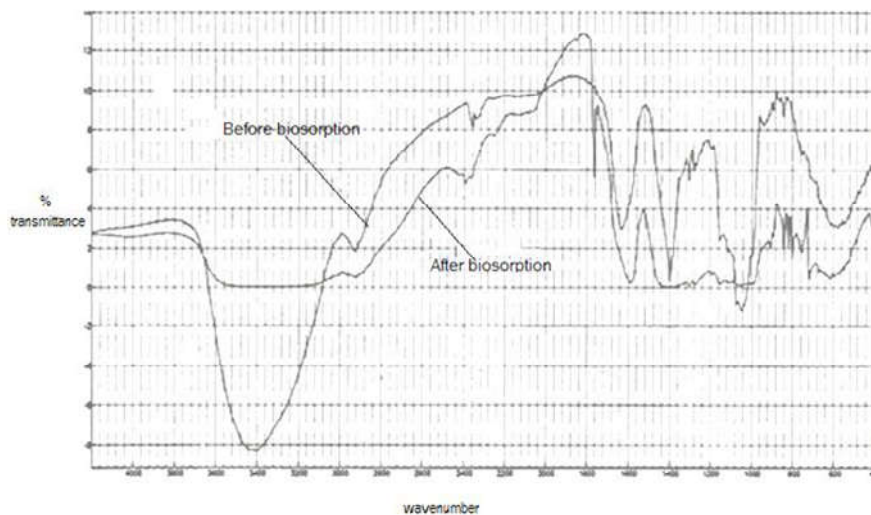


Fig. 1: FT-IR spectrum of sunflower seed husk before and after biosorption Effect of pH

The solution pH affects the chemistry of the ions, the activity of functional groups (carboxylate, phosphate and amino groups) on the cell wall as well as the competition of ions for the binding site (Dadhich *et al.*, 2004). Fig. 3 below

shows that the removal efficiency of nitrates by sunflower seed husk was maximal in acidic media at $\text{pH} = 2$, $Q_e = 1.882\text{ mg/g}$ and decreased sharply with increasing solution pH. At low pH, the sorbent surface is positively charged and

prone to electrostatic interactions with the polar portions of the sunflower seeds husk. A similar trend was observed in the work of Suteu *et al.* (2011) in their study for the removal of Orange 16 reactive dyes from aqueous solutions by sunflower seed husk.

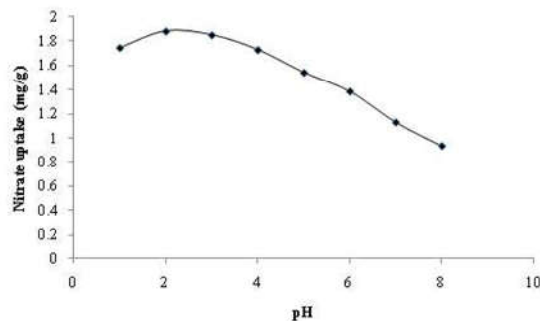


Fig. 2: Effect of pH on biosorption of nitrates

Effect of contact time

The contact time is of great importance in adsorption for the assessment of the suitability of the sunflower seeds husks to serve as biosorbents in a continuous flow system (Selatina *et al.*, 2004). Fig. 4 below indicates a gradual removal of nitrates with increase in agitation time and the concentration became almost constant after 120 minutes showing attainment of equilibrium. The initial uptake might be due to strong attractive forces between the sunflower seeds husks and the nitrate ions as a result of uncovered surface area of adsorbent. As these sites become finished the uptake rate was controlled by the rate at which the adsorbate is transported from the

exterior to the interior sites of the adsorbent particles and more time was then consumed on diffusion of ions to binding sites and this is in agreement with findings by Aydin *et al.* (2008). The equilibrium could have been attained after fast diffusion which could have occurred on the external surface and then followed by fast pore diffusion into the intra-surface matrix (Park and Jang, 2002). After 120 minutes, the nitrate uptake by the adsorbent becomes almost constant showing that there were minimum to no adsorption sites on adsorbent.

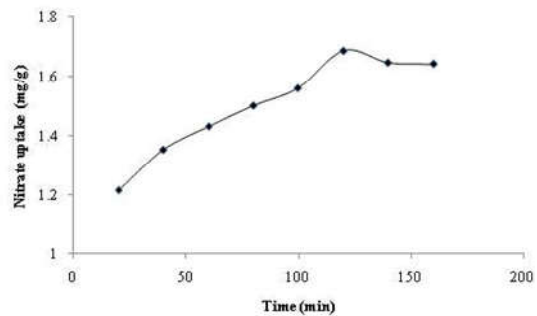


Fig. 3: Effect of contact time on biosorption of nitrates

Effect of adsorbent dosage

The effect of sorbent dose on the removal of the nitrates by sunflower seed husks was examined and from Fig. 5 it can be deduced that increasing sorbent dose from 0.5 to 1.5 g/L rapidly increased the percentage of nitrate removal from 38.80 to 68.40 %, due to the increasing number of available sorption sites. When the sorbet dose was further increased from 2.0 to 3 g/L the percentage nitrate removal remained almost constant. The findings are similar to studies reported

by Abdel-Halim *et al.*, 2003 and Alok, 2006). The biosorption capacity (mg/g) decreased with increase in sunflower seeds husks dosage because of overlapping of biosorbent sites resulting in a decrease in total biosorbent surface area available for biosorption as illustrated in Fig. 6 below. This suggests that the diffusion path length increased as a result and this causes equilibrium to be reached.

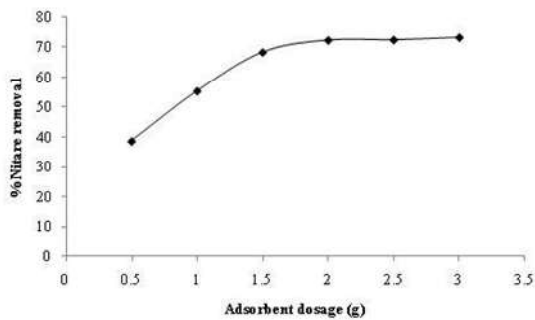


Fig. 4: Effect of adsorbent dosage on the biosorption efficiency for nitrates

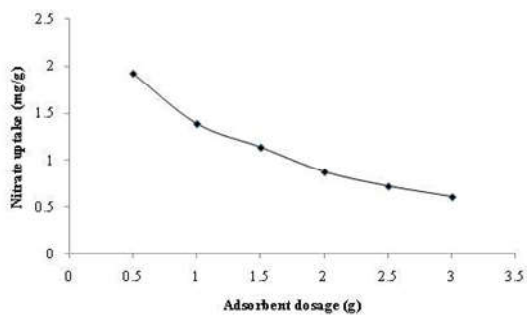


Fig. 5: Effect of adsorbent dosage on biosorption of nitrates

Effect of initial nitrate concentration

Fig. 7 below shows that the amount of nitrate retained increased with the increasing initial nitrate concentration. The amount of sorbed nitrate per unit mass of sunflower seed husk increased rapidly from 0.112 to 0.363 mg/L when the initial nitrate concentration was increased from 10 to 30 mg/L. This was possibly due to the enhancement of nitrate molecules migration into the internal macroporous and mesoporous structure of the sorbent at high nitrate initial nitrate concentrations in the aqueous solutions (Bektas *et al.*, 2004). At very high initial nitrate concentrations (40 to 50 mg/L) the uptake becomes almost constant. The reason might be due to the agglomeration of adsorbent particles at higher concentration (Zhu *et al.*, 2007). Such accumulation leads to a decrease in the total surface area of the adsorbent particles available for adsorption and an increase in the diffusional path length. The results correlate with the observations by Ong *et al.* (2010) who found out that at lower concentration the initial amount of dye molecules available to the surface area of the biomass is low subsequently the fractional sorption becomes independent of initial concentration.

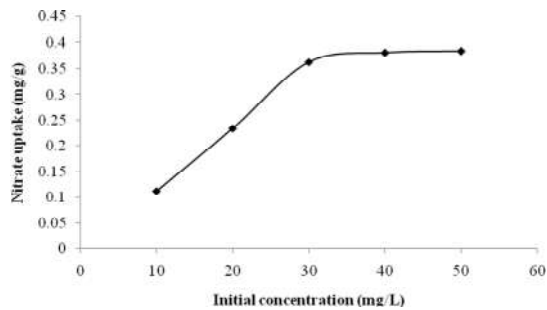


Fig. 6: Initial nitrate concentration and nitrate uptake

Equilibrium modelling: Adsorption Isotherms

Adsorption isotherms express the relationship between the amount of adsorbed nitrate ions per unit mass of biosorbent and the nitrate concentration in solution. Two important isotherms were selected in this study, which are the Langmuir and Freundlich isotherms.

The Langmuir isotherm assumes that biosorption takes place at specific homogeneous sites within the biosorbent and can be linearized as;

$$\frac{C_e}{Q_e} = \frac{1}{bQ_{max}} + \frac{C_e}{Q_{max}}$$

Where Q_e is the nitrate ions adsorbed in mg/g, b is the Langmuir constant related to energy of sorption in L/mg, Q_{max} is the maximum sorption capacity corresponding to complete monolayer coverage in mg/g and C_e is the equilibrium solute concentration in mg/L.

Fig. 8 below shows the Langmuir isotherm for biosorption of nitrates with respect to initial concentration. The value of the correlation coefficient ($R^2=0.9941$) found indicate that the adsorption of nitrate on sunflower seeds husks fits well to the Langmuir model. It also indicates the good reliability of the linear relationship between the values of C_e (mg/L) and the values of C_e/Q_e (g/L). Values of Langmuir constants Q_{max} and b were calculated from the slope and intercept in the y axis respectively. The value of b found was 0.1708 mg/L which is fairly low which implies low surface energy in the process therefore indicating a possible less bonding between nitrate ions and the sunflower

seeds husks. Orlando *et al.* (2002) reported the maximum adsorption capacities of coconut husks (0.89 mg/g), rice hulls (1.20 mg/g) and pine barks (1.06 mg/g). These adsorption capacities were far much higher compared to the adsorption capacity of sunflower seed husk (0.4924 mg/g) obtained in this study. In another study by Chatterjee and Woo, (2009) who investigated on the biosorption of nitrates on chitosan hydrobeads, a biosorption capacity of 30.21 mg/g at a temperature of 32°C was reported. The difference may be attributed to the nature of the biomass functional groups and the temperature involved in biosorption.

The empirical Freundlich isotherm model is based on a heterogenous surface. This can be linearized as;

$$\log Q_e = \log K_f + \frac{1}{n} \log C_e$$

Where Q_e is the amount of nitrate sorbet by sunflower seed husks biomass (mg/g) C_e is equilibrium adsorbate concentration in mg/L, K_f is the adsorbent capacity measure and n is the adsorption intensity.

Fig. 9 below shows that equilibrium adsorption values using Freundlich isotherm model do not show good fit to experimental equilibrium adsorption data. The values of K_f (0.0687) and n (1.6784) were calculated from the intercept and slope respectively of the plot of $\log Q_e$ against $\log C_e$. The relatively low value of the correlation coefficient (R^2) obtained from the Freundlich isotherm equation (0.8194) indicate that the adsorption process is

not much heterogeneous. The value of n obtained also confirms that the process is less heterogeneous although the value of n satisfy the heterogeneity range where the n -value must be $1 < n < 10$ (Khalid *et al.*, 2000). The Langmuir and Freundlich isotherm parameters are shown in table 1 below.

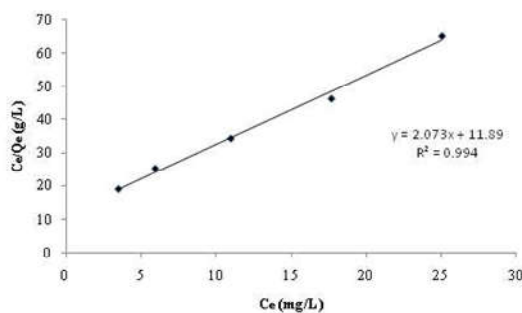


Fig. 7: Langmuir isotherm for biosorption of nitrates with respect to initial concentration.

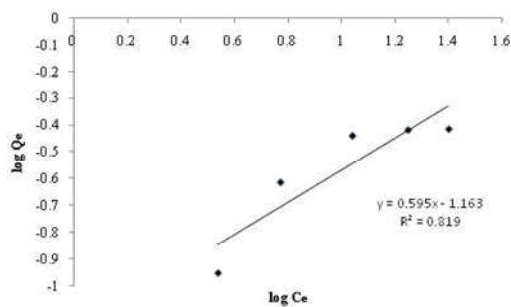


Fig. 8: Freundlich isotherm for biosorption of nitrates with respect to initial concentration.

Conclusion

The research conducted showed that waste sunflower seeds husks can be considered as a potential biosorbent for the sorption of nitrates from aqueous solutions. The results of the FI-TR spectrum revealed the presence of hydroxyl groups, carbonyl groups, amino groups and carboxyl groups which aid in interaction of nitrate ions with the biosorbent. The sorption of nitrates onto sunflower seed husk is dependent on the initial solution pH 2.0, sorbent dose of 3.0 g, the nitrate concentration and agitation time of 120 minutes. The study revealed that biosorption of nitrates increases with increasing sunflower seeds husks dosage, nitrate concentration and contact time. The experimental data was analyzed using Freundlich and Langmuir models. The sorption experimental data well fitted in Langmuir equation which had an R^2 value of 0.9941.

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References

ABDEL-HALIM, S.H, SHEHATA, A.M.A AND EL-SHAHAT, M.F. 2003. Removal of lead ions from industrial waste water by

- different types of natural material. *Water Research*, 37(7): 1678-1683.
- AFKHAMI, A. 2003. Adsorption and electrosorption of nitrate and nitrite on high-area carbon cloth: An approach to water purification and waste water samples. *Carbon*, 41(6): 1320-1322.
- ALOK, M. 2006. Removal of the dye, amaranth from waste water using hen feathers as potential adsorbent. *Electronic Journal of Environmental, Agricultural and Food Chemistry*, 5(2): 1296-1305.
- AYDIN, H, BULUT, Y, AND YERLIKAYA, C. 2008. Removal of copper (II) from aqueous solution by adsorption onto low-cost adsorbents. *Journal of Environmental Management*, 87(1): 37-45.
- BAE, B, JUNG, Y, HAN, W, AND SHIN, H. 2002. Improved brine recycling during nitrate removal using ion exchange. *Journal of Water Resources*, 36(13): 3330-3340.
- BEKTAS, N, AGIM, B.A AND CARA, S. 2004. Kinetic and equilibrium studies in removing lead ions from aqueous solution by natural sepiolite. *Journal of Hazardous Materials*, 112(1-2): 115-122.
- CHATTERJEE, S AND WOO, S. 2009. The removal of nitrate from aqueous solutions by chitosan hydrogel beads. *Journal of Hazardous Materials*, 164(2-3): 1012-1018.
- DADHICH, A.S, BEEBI, S.K, AND KAVITHA, G.V. 2004. Adsorption of Ni(II) using agro waste, rice husk. *Journal of Environmental Science and Engineering*, 46(1): 179-185.
- DEMIRBAS, A. 2008. Heavy metal adsorption onto agro-based waste materials. *Journal of Hazardous Materials*, 157(2-3): 220-229.
- HELL, F, LAHNSTEINER, J, FRISCHHERZ, H, AND BAUMGARTNER, G. 1998. Experience with full-scale electro dialysis for nitrate and hardness removal. *Desalination*, 117: 173-180
- HU, H, GOTO, N AND FUJIE, K. 2001. Effects of pH on the reduction of nitrite in water by metallic iron. *Journal of Water Resources*, 35(11): 2789-2793.
- JAGESSAR, R.C AND ALLEYNE, O. 2011. Determination of nitrate anions concentrations in waste water from selected areas of coastal Guyana via a spectrophotometric method. *International Journal of Academic Research*, 3(1): 578-590.
- KHALID, N, AHMED, S, AND TOHEED, A. 2000. Potential of rice husk for antimony removal. *Applied Radiation and Isotopes*, 52: 30-38.
- LENNTECH, B.V. 2009. Water treatment and purification, A review. *Journal of Biotechnology and Water Purification*, 35(3): 87-89.

- MAJUMDAR, D AND GUPTA, N. 2000. Nitrate pollution of ground water and associated human disorders. *Indian Journal of Environmental Health*. 42: 28-39.
- MISHRA, P.C AND PATEL, R.K. 2009. Use of agricultural waste for the removal of nitrate-nitrogen from aqueous medium. *Journal of Environmental Management*, 90: 519-512.
- MOORCROFT, M.J, DAVIS, J AND COMPTON, R.G. 2001. Detection and determination of nitrate and nitrite: A review. *Talanta*, 54(1): 785-803.
- NADAVALA, S. K AND KIM, M. 2011. Phenolic compounds biosorption onto *Schizophyllum Commune* fungus: FT-IR analysis, kinetics and adsorption isotherms modeling. *Chemical Engineering Journal*, 168: 562-571.
- NELSON, L, LEHNINGER, H AND COX, M. 2005. *Principles of Biochemistry*. 4thed. W.H.Freeman and Company, New York.
- ONG, S, PEI-SIN, K, MING-HOW, L AND YUNG-TSE, H. 2010. Equilibrium studies for the removal of basic dye by sunflower seed husk (*Helianthus annuus*). *International Journal of of the Physical Sciences*, 5(8): 1270-1276.
- ORLANDO, U.S, BAES, A.U, NISHIJIMA, W AND OKADA, M. 2002. A new procedure to produce lignocellulosic anion exchangers from agricultural waste materials. *Bioresource Technology*, 83(3): 195-198.
- OSMA, J. F, SARAIVA, V, TOCA-HERRERA, J. L. AND COUTO, S.R. 2007. Sunflower seed shells: A novel and effective low-cost adsorbent for the removal of the diazo dye reactive black 5 from aqueous solution. *Journal of hazardous Materials*, 147 (3): 900-905.
- PARK, S. J, AND JANG, Y. S. 2002. Pore structure and surface properties of chemically modified activated carbons for adsorption mechanism and rate of Cr (VI). *Journal of Colloid and Interface Science*, 249(2): 458-463.
- SCHIPPER, L.A AND VOJVODIC-VUKOVIC, M. 2001. Five years of nitrate removal, denitrification and carbon dynamics in a denitrification wall. *Water Research*, 35(14): 3473-3477.
- SCHOEMAN, J.J AND STEYN, A. 2003. Nitrate removal in a reverse osmosis in a rural area in South Africa. *Desalination*, 155: 15-26.
- SELATINA, A, BAKHTI, M.Z, MADANI, A, KERTOUS, L AND MANSOURI, Y. (2004). Biosorption of Cd²⁺ from aqueous solution by a NaOH-treated bacterial dead *Streptomyces rimosus* biomass. *Journal of Hydrometallurgy*, 75: 11-24.
- SOARES, M.I.M. 2000. Biological denitrification of ground water. *Water, Soil and Air Pollution*, 123: 183-193.

- SUTEU, D, ZAHARIA, C, AND MALUTAN. T. 2011. Removal of Orange 16 reactive dye from aqueous solutions by waste sunflower seed shells. *Journal of the Serbian Chemical Society*, 76 (4): 607-624.
- THOMSON, T.S. 2001. Nitrate concentration in private rural drinking water supplies in Saskatchewan, Canada. *Bulletin of Environmental Contamination and Toxicology*, 66: 64-70.
- WANG, Y, GAO, B, YUE, W AND YUE, Q. 2007. Adsorption kinetics of nitrate from aqueous solutions onto modified wheat residue. *Colloids Surface A: Physicochemical and Engineering Aspects*, 308(1-3): 1-5.