

# 1 addition climate change has changed temperature and

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1 Introduction: In recent decades, population of humans has grown significantly which increases the demand for safe water resources every year. In addition climate change has changed temperature and rainfall patterns worldwide.

Today water resource security is a very important issue for all of governments on the earth (Gao, 2014) (Evans A, 2009) (J. D. Miranda, 2011). Nitrate is one of the widespread known contaminants of surface waters and can cause a number of health problems for human being such as cyanosis or cancer if go into the body by drinking water. Nowadays much attention has been paid to nitrate elimination methods from water. (Yu Wang, 2007). Nitrate ions can be eliminated through several methods such as biological denitrification (Chunming Su, 2007) reverse osmosis (Katri Häyrynen, 2009) or physical adsorption (Shikha Jain, 2015). Regarding to other methods, sorption process seems to be simple, fast and cost effective.

Generally adsorption is the procedure of accumulating solvable components from a solution on a suitable solid surface. The key practice in adsorption process is to find a low-cost and effective sorbent. Various cheap materials have been tested for removal of nitrate from aqueous solution such as modified clay minerals (Yunfei Xi, 2010) modified rice husk (Reza Katala, 2012) natural zeolites (Y.

Zhan, 2011). Peanut is widely grown in different areas of earth from China to United States and is a very important product for both small and large profit-making producers. Its 12th most valuable cash crop grown in the United States with a farm value of over one billion U. S. dollars.

What remains after processing peanut is a hard shell that doesn't have a valuable price and usually will be used as a cheap fertilizer for other farms and green houses (council, n. d.). In this paper after modifications, sorption abilities of the peanut shell (PS) for adsorption of dangerous nitrate ions were studied and sorption capacity, kinetics and thermodynamic states were obtained. We found that MPS can be an effective anionic sorbent and this offers a fast and economic friendly way for removing of anionic pollutions.

2 Materials and methods

2.1 Materials The peanut shell residue was obtained from regional farms and was modified for elimination of nitrate ions from aqueous solution. It was dried at 90°C for 60 min in an oven.

Nitrate ions were formed by solving 1 gr sodium-nitrate salt into 1 liter tri-distilled water as a stock solution and all of the required concentrations in sorption studies were obtained by dilution.

2.2 Preparation The raw solid residue was washed two times with distilled water to remove dusts and impurities. Next, the sample was dried in an oven for 6h at 100°C to remove any humidity and then milled into powder meshing from 200 to 300 micrometers. Five grams of raw sample was added to 60 ml N, N-dimethylformamide (DMF) in a 600 ml flask and was treated with pyridine as a catalyst and finally 50 ml of dimethyl amine added and stirred under 100°C temperature for 5 hr. (Yu Wang, 2007)

2.3 Equipment The batch reactor was a flask inside an electric heating jacket stirring by a magnetic stirrer at 400 rpm. to determine the concentration of nitrate after finishing every batch experiment UV spectrophotometry (camspec m501) was used at a wavelength of 200 nm.

The sorbent was characterized by using FTIR and Electron Microscopy (SEM) method. FTIR spectra were obtained to reveal the functional groups present on sorbent by a FTIR spectrometer (Bruker Tensor 27) in range of 400-4000  $\text{cm}^{-1}$  with averaging 16 scans. Surface morphologies of modified peanut shell were analyzed by SEM (LEO-1430VP).

**2.4.1 Adsorption** To find the optimum amount of sorbent various amounts of modified sorbent were added to 100 ml of sodium-nitrate aqueous solution with initial concentration of 100 mg/lit at constant temperatures. The optimum amount of sorbent was 0.08.

The sorption capacity at equilibrium state was obtained as follows: Where  $C_0$  is initial concentration (mg/L),  $C_e$  is the equilibrium concentration of aqueous nitrate ion,  $V$  is the liquid phase volume and  $m$  is the mass of unloaded modified sorbent.

**2.4.2 Desorption** It was found that the MP can be recycled after adsorption process by renewing active molecular sorption sites under alkaline solutions. Desorption study was done by soaking loaded sorbent into 100 ml of KOH solution in different concentrations and temperatures. The KOH was selected in order to avoid common ion effect with  $\text{NaNO}_3$ .

**3. Results and discussion**

**3.1. The sorbent characteristics**

**3.1.1 Fourier transform infrared (FTIR) spectroscopy**

**3.1.2 Scanning electron microscope analysis** The surface morphology of MPS determined by SEM is shown in Fig. x. The MPS is made up of a porous uneven surface.

This surface can be seen to have high quantities of small pores representing that this material grants good characteristics to be employed as a low cost adsorbent for ionic uptake, as beforehand reported (Seyda Tasar \*, 2014). It is apparent that these pores provide easy contact and large surface area for the sorption of nitrate on the sorption sites. Fig. x Before the sorption After the sorption

### 3. 2 Equilibrium studies

#### 1 Effect of temperature

Fig. 2 shows that the final adsorption percentage of nitrate ion decreases with increasing temperature and in first 5 minutes the rate of sorption process is higher in warmer temperatures. According to fig. 2 removal percentage decreased from 95. 91% to 71. 78% by varying temperature value from 10°C to 50°C. these data shows that nitrate bio-sorption via MPS is exothermic and yields higher in lower temperatures.

Figure caption 3.

#### 2. 2 Adsorption isotherms

Adsorption isotherms are used to explain absorbed material and sorbent interaction regarding to sorption mechanism. The isotherm models are widely used to calculate maximum adsorption capacity, which helps to understand how effective is a specific sorbent (Seyda Tasar \*, 2014) (X. Liu and L.

Zhang, 2015). Several models are often applied to process equilibrium data while Langmuir and Freundlich isotherms are the most commonly models among them. The Langmuir model represents the monolayer adsorption onto surface containing finite number of tantamount active sites which is expressed as follows:

number

The linear form of Langmuir equation

can be rearranged as: Where,  $q_e$  is adsorption capacity at equilibrium (mg/g),  $C_e$  is concentration of nitrate in the solution at equilibrium (mg/L),  $q_m$  is the maximum adsorption capacity (mg/g), and  $K_L$  is the Langmuir Constant related to the energy of adsorption represents the degree of adsorption affinity the adsorbate (L/mg). The parameters  $K_L$  and  $q_m$  were obtained from the slope and intercept of the plot of  $C_e/q_e$  against  $C_e$ . A plot of  $C_e/q_e$  versus  $C_e$  should be a straight line with a slope of  $1/q_m$ .

Figure 2 While Langmuir isotherm speculates that enthalpy of adsorption is independent of the loading of the sorbate, the practical Freundlich equation, based on sorption on heterogeneous surface, can be derived presuming a logarithmic decrease in the enthalpy of adsorption with the increase in the fraction of occupied sites (al., 2012). The Freundlich equation is entirely practical based on sorption on heterogeneous surface and is given by:  $q_e = K_F C_e^{1/n}$  where  $K_F$  and  $1/n$  are the Freundlich constants demonstrating the biosorption capacity and biosorption intensity, respectively. Eq. (x) can be linearized for the determination of the Freundlich constants as follows: The slope and the intercept correspond to  $(1/n)$  and  $K_F$ , respectively. It was revealed that the plot of  $\log q_e$  and  $\log C_e$  yields a straight line (Fig. 12).

The results are indicated in Table 4. The parameter  $k$  related to the adsorption density increased with a decrease of adsorbent amount. 3. 2.

### 3 Thermodynamic parameters.

According to following equation Gibbs free energy changes can be calculated at various temperatures. The equilibrium constant ( $K_c$ ) is obtained from

making Langmuir Constant (K<sub>L</sub>) dimensionless by multiplying it to 10<sup>6</sup>. the standard enthalpy and entropy variations were determined by plotting  $\ln K_c$  vs  $1/T$  according to Van't Hoff equation. The calculated thermodynamic parameters are shown in Table X.  $\Delta S_{ads}$  (J/mol.

K)  $\Delta H_{ads}$  (KJ/mol)  $\Delta G_{ads}$  (kJ/mol)  $K_c \times 10^6$  - T<sub>o</sub> (K) 20. 60 25. 853 -31. 734 0.

72049 283 -31. 781 0. 58139 293 -31. 785 0. 46428 298 -32.

151 0. 34905 303 According to table x negative values of  $\Delta G$  are obtained in all temperatures, revealing that the adsorption nature of nitrate onto MPS is feasible and spontaneous. The negative value of  $\Delta H$  changes indicate that the process is exothermic and the products are energetically stable with a high binding of nitrate ions to the adsorbent sites. The positive value of  $\Delta S$  suggests increased degree of freedom while freedom of nitrate ions decreases. during adsorption, water molecules that are formed hydration shell around nitrate ions will be freed at the sorbate and solution interface with some structural changes in the adsorbate and the adsorbent and an affinity of the adsorbent toward nitrate ions during adsorption process. 3.

### 3 Kinetics 3. 3.

1 Dosage of sorbent studies The amount of sorbent required for the adsorption procedure for each juncture is essential both in the design of the adsorption equipment and its usability on a large scale. In order to obtain the favorable amount, different amounts of MPS were tested in presence of nitrate solution. in these series of experiments the contact time was constant 10 minutes and the concentration had been fixed at 100 mg/L.

according to fig. 2 over 90% of sorbate was absorbed during the first 10min and the effect of dose of sorbent decreased after that point in sorption process thus the favorable amount was selected at 0.08 g. Figure 33.

3.2 Kinetic model It is well-known that the adsorption process is time dependent, thus it is essential to know the rate of adsorption when designing a unit like biosorption reactor (Seyda Tasar \*, 2014). To this end, the adsorption data were analyzed with three kinetic models, i.

e., pseudo first-order, pseudo second-order and Morris-weber kinetic models.

3.3.2.1 Pseudo first-order kinetic model The pseudo first-order expression of Lagergren which is widely used for the sorption of a solute from liquid solution is given as (W. Jianlong, 2001) (Lagergren, 1898): This equation is linear rate expression for pseudo-first order reaction, where  $q_t$  (mg/g) is the capacity of sorbent at time  $t$ ,  $K_1$  is rate constant of pseudo-first-order adsorption ( $L \cdot min^{-1}$ ).  $k_1$  and  $q_e$  as shown in Fig.

4 were calculated from the slope and intercept of the straight line plots of  $\log(q_e - q_t)$  against  $t$ . Figure 43.

3.2.2 Pseudo-second-order model The pseudo-second-order model is based on the assumption that the adsorption process has a chemical base and it is generally given as follows (A.

L. Ahmad, 2009): Where  $q_e$  is the amount of nitrate adsorbed at equilibrium state; and  $k$  is the sorption rate constant of pseudo-second order adsorption. The straight-line plots of  $t/q_t$  versus  $t$  at different temperatures (Fig. 4) indicate the applicability of the above equation to nitrate adsorption on MPS.



The values of kinetic parameters of adsorption are summarized in Table 3

Figure 5 Model temp(°C) 10 30 50 Pseudo first order  $q_e(\text{exp})(\text{mg/g})$  96. 5652 80. 2029 71.

7826  $q_e(\text{cal})(\text{mg/g})$  39. 35803 31. 56346 32. 20752  $k_1(\text{min}^{-1})$  0. 1499 0. 1499 0.

1409  $R^2$  0. 9148 0. 9742 0. 8993 Pseudo second order  $q_e(\text{exp})(\text{mg/g})$  96. 5652 80.

2029 71. 7826  $q_e(\text{cal})(\text{mg/g})$  102. 0408 84. 03361 76. 92308  $k_2(\text{g/mg min})$  0. 0113 0.

0144 0. 0148  $R^2$  0. 9982 0.

9987 0. 9989 Table 1 3. 4 Desorption studies 3. 5 reusability studies for indicating the reusability of the sorbent, the adsorption-desorption progression was repeated six times for MPS. Adsorption and desorption experiments were executed in the room temperature to simulate an effective condition in industry.

The adsorption and desorption capacities were nearly the same even after six runs (Figs. X)