

# [1 addition climate change has changed temperature and](https://assignbuster.com/1-addition-climate-change-has-changed-temperature-and/)

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1     Introduction: In recent decades, population of humans hasgrown significantly which increases the demand for safe water resources everyyear. In addition climate change has changedtemperature and rainfall patterns worldwide.

Today water resource security is avery important issue for all of governments on the earth (Gao, 2014) (Evans A, 2009) (J. D. Miranda, 2011). Nitrate isone of the widespread known contaminates of surface waters and can cause anumber of health problems for human being such as cyanosis or cancer if go intothe body by drinking water. Nowadays much attention has been paid to nitrateelimination methods from water. (Yu Wang, 2007). Nitrate ionscan be eliminated through several methods such as biological de-nitrification (Chunming Su, 2007)reverse osmosis ( (Katri Häyrynen, 2009)) or physicaladsorption (Shikha Jain, 2015). Regarding to othermethods, sorption process seems to be simple, fast and cost effective.

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

Zhan, 2011). Peanut iswidely grown in different areas of earth from China to United States and is avery important product for both small and large profitmaking producers. Its 12thmost valuable cash crop grown in the United States with a farm value of overone billion U. S. dollars.

What remains after processing peanut is a hard shellthat doesn’t have a valuable price and usually will be used as a cheapfertilizer for other farms and green houses (council, n. d.). In this paper after modifications, sorption abilitiesof the peanut shell (PS)  for adsorptionof dangerous nitrate ions were studied and sorption capacity, kinetics andthermodynamic states were obtained. We found that MPS can be an effectiveanionic sorbent and this offers a fast and economic friendly way for removingof anionic pollutions.  2     Materials and methods 2. 1    MaterialsThe peanut shell residue was obtained from regional farms and was modifiedfor elimination of nitrate ions from aqueous solution. It was dried at 90C for60 min in an oven.

Nitrate ions were formed by solving 1 gr sodium-nitrate saltinto 1 liter tri-distilled water as a stock solution and all of the requiredconcentrations in sorption studies were obtained by dilution. 2. 2   PreparationThe raw solid residue was washed two times with distilled water to remove dustsand impurities.  Next, the sample wasdried in an oven for 6h at 100C to remove any humidity and then milled intopowder meshing from 200 to 300 micrometers. Five grams of raw sample was addedto 60 ml N, N-dimethylformamide (DMF) in a 600 ml flask and was treated withpyridine as a catalyst and finally 50 ml of dimethyl amine added and stirredunder 100C temperature for 5 hr. (Yu Wang, 2007)2. 3   Equipment The batch reactor was a flask inside an electricheating jacket stirring by a magnetic stirrer at 400 rpm. to determine theconcentration of nitrate after finishing every batch experiment UVspectrophotometry (camspec m501) was used at a wavelength of 200 nm.

Thesorbent was characterized by using FTIR and ElectronMicroscopy (SEM) method. FTIR spectra wereobtained to reveal the functional groups present on sorbent by a FTIRspectrometer (Bruker Tensor 27) inrange of 400-4000 cm -1 with averaging 16 scans. Surface morphologies of modified peanut shell were analyzed by SEM (LEO-1430VP)2. 4   procedure2. 4. 1     AdsorptionTo find the optimumamount of sorbent various amounts of modified sorbent were added to 100 ml ofsodium-nitrate aqueous solution with initial concentration of 100 mg/lit atconstant temperatures.  The optimumamount of sorbent was 0. 08.

The sorption capacity at equilibrium state wasobtained as follows: Where C0 is initial concentration (mg/L) , Ce is the equilibrium concentration of aqueous nitrate ion, V is theliquid phase volume and m is the mass of unloaded modified sorbent. 2. 4. 2     DesorptionIt was found that the MPScan be recycled after adsorption process by renewing active molecular sorptionsites under alkaline solutions. Desorption study was done by soaking loadedsorbent into 100 ml of KOH solution in different concentrations and temperatures. The KOH was selected in order to avoid common ion effect with NaNO3. 3     Results and discussion3.

1   The sorbent characteristics3. 1. 1     Fourier transforminfrared (FTIR) spectroscopy 3. 1. 2    Scanning electronmicroscope analysisThe 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 representingthat this material grants good characteristics to be employed as a low costadsorbent for ionic uptake, as beforehand reported  (Seyda Tasar \*, 2014). It is apparent thatthese pores provide easy contact and large surface area for the sorption of nitrateon the sorption sites. Fig. x   Before the sorption After the sorption3. 2   Equilibrium  studies3. 2.

1     Effect of temperatureFig. 2 shows that the final adsorptionpercentage of nitrate ion decreases with increasing temperature and in first 5minutes the rate of sorption process is higher in warmer temperatures. According to fig. 2 removal percentage decreased from 95. 91% to 71. 78% byvarying temperature value from 10oC to 50oC. these data shows that nitratebio-sorption via MPS is exothermic and yields higher in lower temperatures.          Figure caption  3.

2. 2    Adsorption isothermsAdsorption isotherms are used to explain absorbed materialand sorbent interaction regarding to sorption mechanism. The isotherm models arewidely used to calculate maximum adsorption capacity, which helps to understandhow 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 andFreundlich isotherms are the most commonly models among them. The Langmuir model represents the monolayeradsorption onto surface containing finite number of tantamount active siteswhich is expressed as follows:                numberThe linear form of Langmuirequation can be rearranged as:     Where, qe is adsorptioncapacity at equilibrium (mg/g), Ce is concentration of nitrate in the solution at equilibrium (mg/L), qm is the maximum adsorptioncapacity (mg/g), and KL is the LangmuirConstant related to the energy ofadsorption represents the degree of adsorption affinity the adsorbate(L/mg). The parameters KLandqm were obtainedfrom the slope and intercept of the plot of Ce/qe against Ce . A plot of Ce/ qe versus Ce should be a straight line with a slope of 1/qm .

Figure 2While Langmuir isotherm speculates that enthalpy ofadsorption is independent of the loading of the sorbate, the practicalFreundlich equation, based on sorption on heterogeneous surface, can be derivedpresuming a logarithmic decrease in the enthalpy of adsorption with theincrease in the fraction of occupied sites (al., 2012). The Freundlichequation is entirely practical based on sorption on heterogeneous surface andis given by: qe = KFC1/nwhere KF and 1/n are the Freundlich constantsdemonstrating the biosorption capacity and biosorption intensity, respectively. Eq. (x) can be linearized for the determinationof theFreundlich constants as follows: The slope and the intercept correspond to (1/n) and KF, respectively. It was revealed that the plot of log qe and log Ce yields astraight line (Fig. 12).

The results are indicated in Table 4. The parameter k relatedto the adsorption density increased with a decrease of adsorbent amount.  3. 2. 3    Thermodynamic parameters.

According to following equation Gibbsfree energy changes can be calculated at various temperatures. The equilibrium constant (Kc) is obtained from makingLangmuir Constant (Kl) dimensionless by multiplying it to 106. the standard enthalpy and entropy variations were determinedby plotting ln Kc vs 1/T according to Van’t Hoff equation. Thecalculated thermodynamic parameters are shown in TableX.  ? Sads(j/mol.

K) ? Hads(Kj/mol) ? Gads(kj/mol) Kc x 106- To (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 negativevalues of ? G are obtained in all temperatures, revealing that the adsorptionnature of nitrate onto MPS is feasible and spontaneous. The negative value of ? Hchanges indicate that the process is exothermic and the products areenergetically stable with a high binding of nitrate ions to the adsorbent sites. The positive value of ? S suggestsincreased degree of freedom while freedom of nitrate ions decreases . duringadsorption, water molecules that are formed hydration shell around nitrate ionswill be freed at the sorbate and solution interface with some structuralchanges in the adsorbate and the adsorbent and an affinity of the adsorbentstoward nitrate ions during adsorption process. 3. 3   Kinetics3. 3.

1     Dosage of sorbent studiesThe amount of sorbent required for the adsorption procedurefor each juncture is essential both in the design of the adsorptionequipmentand its usability on alarge scale. In order to obtain the favorable amount, different amounts of MPSwere tested in presence of nitrate soloution. in these series of experiments thecontact time was constant 10 minutes and the concentration had been fixed at 100mg/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 processthus the favorable amount was selected at 0. 08 g. Figure 33.

3. 2     Kinetic modelIt is well-knownthat the adsorption process is time dependent, thus it is essential to know therate 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 kineticmodelThe pseudo first-orderexpression of Lagergren which is widely used for the sorption of a solute fromliquid solution is given as (W. Jianlong, 2001) (Lagergren, 1898): This equation is linearrate expression for pseudo-first order reaction, where qt (mg/g) Is thecapacity of sorbent at time t, K1 is rate constant ofpseudo-first-order adsorption (L min-1). k1 and qe as shown in Fig.

4were calculated from the slope and intercept of the straight line plots oflog(qe? qt) against t.. Figure 43. 3. 2. 2    Pseudo-second-order modelThe pseudo-second-ordermodel is based on the assumption that the adsorption process has a chemicalbase and it is generally given as follows (A.

L. Ahmad, 2009): Where qe is the amount of nitrateadsorbed at equilibrium state; and k is the sorption rate constant ofpseudo-second order adsorption. The straight-line plots of t/qtversus t at different temperatures (Fig. 4) indicatethe applicability of the above equation to nitrate adsorption on MPS.

The values of kinetic parameters ofadsorption are summarized in Table 3 Figure 5  Model temp(°c) 10 30 50 Pseudo first order qe(exp)(mg/g) 96. 5652 80. 2029 71.

7826 qe(cal)(mg/g) 39. 35803 31. 56346 32. 20752 k1(min-1) 0. 1499 0. 1499 0.

1409 R2 0. 9148 0. 9742 0. 8993 Pseudo second order qe(exp)(mg/g) 96. 5652 80.

2029 71. 7826 qe(cal)(mg/g) 102. 0408 84. 03361 76. 92308 k2(g/mg min) 0. 0113 0.

0144 0. 0148 R2 0. 9982 0.

9987 0. 9989 Table 1 3. 4   Desorption studies3. 5   reusability studiesfor indicating the reusability of the sorbent, theadsorption–desorption progression was repeated six times for MPS. Adsorptionand desorption experiments were executed in the room temperature to simulate aneffective condition in industry.

The adsorption and desorption capacities was nearlythe same even after six runs (Figs. X)