Removal of Nitrate, Ammonium, and Phosphate from Water Using Conocarpus and Paulownia Plant Biochar

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ABSTRACT: *In this research, the biochar ability of Conocarpus and Paulownia plant as adsorbents to remove Nitrate, Ammonium, and phosphate from the water were investigated. For this purpose, the effect of contact time, initial concentration, and pH of solution on the removal of Nitrate, Ammonium, and phosphate by the biochar of Conocarpus and Paulownia plants have studied. The Conocarpus and Paulownia plants have been modified by ferrous chloride for nitrate removal. Conocarpus and Paulownia have been modified by potassium hydroxide for ammonia removal. Also, Conocarpus have been modified by ferrous chloride and Paulownia has modified by Potassium hydroxide for phosphate removal. The studied adsorbent properties with FT-IR and SEM, which their physical properties are: density, organic material percent, ash percent, mass moisture and special surfaces have been determined by the methylene blue method. The Pseudo-First-order order, Pseudo-Second-order, Elovich, Intraparticle diffusion, and power have been used for describing the kinetic data. In addition, the Langmuir model, Freundlich, Temkin, Halsy, and Langmuir-Freundlich have used for describing the isotherm adsorption data. The results of this study showed that the Nitrate, Ammonium, and phosphate adsorption level has increased bypassing the time and after 60 and 120 min, they have reached their maximum level respectively. The maximum Ammonium adsorption level in modified biochar of Conocarpus was in pH=6, and in Polonia biochar was in pH=2 and the maximum nitrate adsorption was in pH=2. In addition, the maximum phosphate adsorption was in pH=8. By increasing the initial concentration of phosphate and nitrate, the removal efficiency has increased. The maximum phosphate removal efficiency in the concentration of 14mg/L in modified paulownia and Conocarpus biochar was 100%. In addition, the concentration of 50mg/L nitrate in modified Paulownia biochar was 98.37%. The maximum Ammonium removal efficiency in the concentration of 5 mg/ L by modified Conocarpus biochar was 82%.*

KEYWORDS: *Nitrate; Ammonium; Phosphate, Biochar; Kinetic, Isotherm.*

INTRODUCTION

The ground water pollution by different nitrogen compound was a growing issue all over the world [1]. Various nitrogen compounds such as Ammonia, nitrite and particularly nitrate may exist in a large amount of drinking water, household, agriculture and industrial effluent. Nitrogen (N) and phosphorus (P) and Ammonia

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are three plant nutrients of major concern for surface and groundwater quality, mainly as a result of agricultural activities [2]. The excessive application of fertilizer has caused the leaching of these nutrients from agricultural soils. Nutrient Leaching may pose a great threat to environmental health, leading to surface and groundwater pollution or eutrophication, depleted soil fertility and rapid soil acidification.

The environmental protection agency of U.S and the European Union and W.H.O have declared the Nitrate maximum allowed level 45 and 50 mg/L respectively. In addition, the phosphate level in polluted water was in the range of 0.16-2.72mg/L [3]. Nitrate could cause serious problems such as eutrophication and diseases like cyanosis and gastrointestinal tract cancer [4]. In recent years using the cheap adsorbent as a replacement for activated carbon have attract a lot of attention to itself because of the high cost of activation process in activated carbon, While many of the previous studies were based on the biochar and mainly focused on the heavy metal and organic pollutant removal. The researcher's attention to the nutritional component removal was less [5-7]. One alternative method to increase nutrient retention and reduce nutrient leaching is the application of biochar. Biochar was one of the components, which attract a lot of attention from researchers for various pollutant removals from aqueous solution. Biochar is the carbon-rich material obtained when biomass or organic materials are heated in a closed container either without oxygen or with limited oxygen at a relatively low temperature (700 °C) [8]. In adsorption process biochar structure is similar to activated carbon while its production in comparison with activated carbon is faster, cheaper and simpler [8, 9]. Studies have demonstrated the biochar, attributed to its surface area and surface charge, has the capability to serve as an environmental sorbent [10]. A single type of biochar, however, may not be appropriate to be a sorbent for all substances. The sorption and release of ammonium ($NH_4{}^+$), nitrate ($NO_3{}^-$), and phosphate ($PO_4{}^{3-}$) from independent biochar (not mixed into soils) has not been widely studied. Multi-disciplinary action of biochar has attracted the researchers to work in a new period of engineering science [10, 11]. Several previous investigations focusing on $NH_4{}^+$, $NO_3{}^-$, and $PO_4{}^{3-}$ have shown that the sorption affinity of biochar varies greatly with biochar characteristics and nutrient types [12)].

Sustainable production of biochar may limited the sources, Therefore, the bio mass for producing biochar should not have lack of other values such as food safety, soil fertility and forest safety [13]. Recently Biochar as a successful global adsorbent have used in curing the organic and non-organic polluted water [8, 14] .Biochars need engineering or modifying for increasing their adsorption efficiency. Overall, the biochar engineering could have reached by Pyrolysis process control or physical changes [15, 16]. Particularly, by the chemistry science, biochar could have modified by curing the raw material before converting to biochar or care it after producing. Different chemical materials such as sulfuric acid and oxalic acid [16], magnesium hydroxide [17], polyethylene amine [18], and methanol [19] have experimented for modifying biochar. In addition, some of the biochar have higher capability in pollutant adsorption in comparison with activated carbon [9]. The researchers have reported that biochar could have used after nitrate, ammonium and phosphate adsorption from polluted water without any specific danger for environment (as a modifier for developing the agricultural lands fertility) [20]. A lot of studies have done about the pollutant removal by the botanical adsorbent such as coconut [21], lentils and wheat peel [22]. In a research, the nutritional removal by using aqueous hyacinth from plant treatment in municipal sewage effluent has evaluated. The plant observation has done by the weigh scale, plant adsorption and developing new stem. Aqueous hyacinth have effectively almost 49% COD, 81% Ammonia, 67% phosphorous and 92% nitrate removal [23]. *Gao et al.* have showed that the obtained biochar from agricultural waste could effectively help the ammonia removal from aqueous solution [24]. *Ahmed et al.* (2016) have showed that the organic and inorganic pollutant removal by modifying biochar have increased, and the Langmuir isotherm model was the best model for heavy metal and ionic pollutant adsorption [25]. *Naghizadeh et al.* (2008) have show that the submerged membrane bioreactor could efficiently remove the pollutants. Average removal rates of chemical oxygen demand, total Kejeldal nitrogen removal, total nitrogen and phosphorous reached to as high as 99.3%, 98.1%, 85.5% and 52%, respectively [26]. *Naghizadeh et al.* [27] have showed that Study of the thermodynamics related to the process indicated that it was a spontaneous and endothermic one. The polypyrrole coated on perlite composite could be used as an effective adsorbent to remove nitrate from aqueous solutions [27].

Naghizadeh et al. [28] in research valuated Application of polypyrrole coated on perlite zeolite for removal of nitrate from wood and paper factories wastewater. Study of the thermodynamics related to the process indicated that it was a spontaneous and endothermic one. The ppy/perlite composite could be used as an effective adsorbent to remove nitrate from aqueous solutions[28].

Farzi et al [29] batch and continuous adsorption kinetic models of cadmium from aqueous solutions using sugarcane straw nano-structure absorbent evaluated. The results showed that maximum adsorption capacity of second order kinetics model was exactly equal to maximum actual adsorption capacity. Continuous test results showed that with increasing concentrations of 5 to 20 mg/L cadmium, the maximum adsorption capacity increased from 0.91 to 2.08 mg/g and the adsorption efficiency decreased from 48.8 to 30.32. The model of *Thomas* and *Yon-Nelson* with the correlation coefficient up to 0.95 were more consistent with laboratory data of fixed bed columns compared to Bohart-Adams, and Dose Response models [29]. *Farasati et al.* [30] evaluated Cd removal from aqueous solution using agricultural wastes. The result showed that P. australis and sugarcane straw can be used to remove cadmium ions during water treatment process. Compared with P. australis adsorbent, sugarcane straw showed higher level of capability of cadmium adsorption[30].

Purmohamad et al. [31] cadmium removal and recovery from aqueous solution using conocarpus nanostructure evaluated. The study showed that conocarpus nanostructure is an effective adsorbent for cadmium removal from aqueous solution[31].

Shams et al. [32] in research post-denitrification with canola oil and starch beads was investigated in the final clarifier of a coupled upflow bioreactor and aerobic system treating synthetic dairy farm wastewater, and showed a denitrification efficiency of >90%. Beads faded in 12 days due to alginate degradation. Therefore, enhancement in bead strength or use of more stable nontoxic gel would be required to further prolong the treatment. Moreover, this study was conducted at laboratory scale and further research is needed for application in real systems[32].

Kalderis et al. [33] Adsorption of 2,4-dichlorophenol on paper sludge/wheat husk biochar: Process optimization and comparison with biochars prepared from wood chips, sewage sludge and hog fuel/demolition waste investigated. it was concluded that pH-dependent electrostatic interactions and non-covalent π-electron donor-acceptor mechanisms play the most important role. Finally, there was indication that high concentrations of Ca and K may promote the adsorbate-adsorbent interactions and enhance adsorption[33]. *Mannai et al.* [34] Green process for fibrous networks extraction from Opuntia (Cactaceae): Morphological design, thermal and mechanical studies . The study of the fibrous-networks crystallinity and the thermostability indicate that water-immersion processing ameliorated the thermal stability in some temperature regions. The fibrous networks mechanical studies were examined, and the results showed a good response strength, especially for uniaxial tensile layers, which has led to the highest strength and elastic modulus[34].

Naghizadeh and *Ghafouri* [35] showed that the maximum adsorption capacity in optimum condition was estimated to 87.74 mg/g. Lab data displayed that the results were in compliance with Langmuir isotherm. the standard Gibbs free energy (ΔG°) was negative and kinetics of adsorption process follows the pseudo-second-order model [35].

According to the growing problem of water pollution resources in the country and spending a lot of money for eliminating these problems the present study have done with the aim of nitrate, ammonium and phosphate pollutant removal from water by cheap Conocarpus and Paulownia plant, instead of activated carbon which its preparation have a high cost.

EXPERIMENTAL SECTION

Initial preparation

For doing this research the Conoarpus plant have provided from Ahwaz and Paulownia plant have provided from Gonbad Kavoos university. After washing, the obtained material was dried on oven at 60°C for 12 hours. After drying, these materials have crushed by electrical grinding machine. Then it has passed through a 2mm sieve in order to achieve smooth uniform particles.

Adsorption studies

For selecting appropriate adsorbent for nitrate, ammonium and phosphate removal by various methods, the Conocarpus and Paulownia plants have modified, which these modifications are:

First method: the Conocarpus and Paulownia plant have washed with distilled water and have dried in an oven with 60°C in 12 hours. Then Pyrolysis has happened in electrical oven with 300°C and 600°C for 4 hours.

Second method: the biochar, which have obtained in 300°C and 600°C have mixed with KOH by the proportion of 1 to 3 and have kept in that form for 24 hours. After passing the determined time, the compound have smoothed and washed with the distilled water. Then it have put in an oven in order to dry and after that again the pyrolysis have happened in an electrical oven with 600°C for 2hours.

Third method: the raw Conocarpus and Paulownia plant with 1 molar $FeCl_2$ (pH=10) have mixed and rested for 2 hours. After passing the determined time, it have smoothed and washed with distilled water and have dried in an oven with 60°C in 12 hours. Then the pyrolysis has happened in an electrical oven with 400°C in 4 hours.

Finally, for each studied plants, 5 various biochar have prepared which include: Conocarpus 300, Conocarpus 600, Conocarpus KOH 300, Conocarpus KOH 600 and Conocarpus $FeCl_2$. Also, it has included Paulownia 300, Paulownia 600, Paulownia KOH 300, Paulownia KOH 600 and Paulownia $FeCl_2$. Each prepared biochar have used in nitrate, ammonium and phosphate experiment. Scanning Electron Microscopy (SEM) was used for scrutiny and seeing samples with high-resolution and magnification. Also Fourier Transforms InfraRed (FT-IR) spectroscopy spectroscopic assignments of modified biochars performed.

Adsorption experiments

To test the biochars for nitrate, phosphate and ammonium removal from aqueous solution, batch sorption kinetics experiments were conducted. For ammonium (or nitrate) sorption, nutrients were added as NH_4Cl (or KNO_3) with initial concentrations 0, 5, 10, 20, 50 and 100 mg/L. For phosphate sorption, nutrients were added as KH_2PO_4 with initial concentrations of 3.5, 7, 14, 35 and 50 mg/L. Three replicates were conducted for each concentration and each nutrient type. The samples were then shaken on a horizontal shaker at ambient temperature at a constant speed of 250 rpm for 120min to reach equilibrium. After equilibration, the suspensions were filtered (Whatman No. 42) to separate the supernatant. After filtration, the NO_3^{-1}, NH_4^{-1}, PO_4^{-2} concentrations of the supernatant solutions was analyzed by spectrophotometer. These kinetic batch experiments were conducted at initial pH_s of 2, 4, 6 and 8. The removal efficiency (1) and the adsorption rate (2) have obtained from the bellows formula:

$$\%R = \frac{C_i - C_f}{C_i} \times 100 \tag{1}$$

$$q = \frac{C_i - C_f}{m} \times V \tag{2}$$

Where:

q; the amount of dissolved adsorption substance per adsorbent mass unit (mg/g), C_i; the initial concentration of dissolved substance (mg/g). c_f; the residual dissolved substance concentration (mg/g) after passing the equilibrium time. *M;* the amount of adsorbent. *V;* the volume of solution (L).

For evaluating the specific adsorbent surface the methylene blue adsorption method have used. The specific adsorbent surface have calculated by the Eq. (3), [36]:

$$S_g = b\frac{N_A}{M_{MB}}\sigma_{MB} \tag{3}$$

Where:

b; the number of methylene blue adsorbed molecule to the adsorbent based on (mg/g)

Na; the Avogadro number which was $6.02*10^{23}$ M_{MB}; the Molecular weight of methylene blue which was 319.85 gr/mol. σ_{MB}; The occupied surface by a methylene blue molecule was 1.08nm. s_g; a specific adsorbent surface based on m^2/g

The density of the studied adsorbent have determined by the bellow equation [37]:

$$\rho = \frac{m_s}{V_t} \tag{4}$$

Which in it, m_s; the dried weight of sample (g). v_t; total volume of taken sample (m L), ρ; density(mg/L)

The moisture adsorbent mass have determined by the mentioned method in standard of (D2867-99) ASTM.

$$\text{Moisture weight\%} = \frac{(C - D)}{(C - B)} \times 100 \tag{5}$$

Which in it: *B;* the sampling container weight. *C;* the container weigh and initial sample. *D;* the container weigh and dried sample.

The ash and organic percent have obtained by the bellows equation:

$$\text{Ash\%}=((M_2-M_1)\times 100)/M_0 \qquad (6)$$

$$\text{Organic matter\%}=100 - \text{Ash\%} \qquad (7)$$

M_0 ; the sample weigh. M_1 ; the container and its lid weight. M_2 ; the container and its lid weight plus ashes. For evaluating the nitrate, ammonium and phosphate concentration, the botanical samples have dried in 65c°for 48 hours. For performing the wet degradation, 0.3gr of dried plant tissue have transferred to a 50mL balloon. Then 2.5 lit of a sulfuric acid and Salicylic acid and H_2O_2 mix have added to it. This compound has rest for 24 hours, then put it in 180 c° for 1 hour and then again put it on a heater with 280c° for 45 minute. After this step each 5 minute, 5 drop of H_2O_2 have added to the balloon until the sampler color changed to white, this action should have repeated. After cooling the balloon should have volume and after stirring, finally this extract have used for evaluating nitrate, phosphate and ammonium.

pH_{ZPC} (Zero Point of Charges)

The point of the pH where the surface charges are equal to zero is also called the isoelectric point. It is important to specify this point in order to determine the surfaceadsorbent properties, so that at the pH above the above point the adsorbent surface has a negative charge, thus opposite ions (positive ions) are readily absorbed. Also, at lower pH, surface charges are positive and negatively charged ions are absorbed more quickly. At first different series of flasks containing 40 mL of 0.1Normal NaCl were prepared with initial pH values in the range of 2-8(by using Hcl and NaOH). About 0.5g of adsorbent was placed in each flask of the series and samples were placed on a vibrating machine at 120 rpm for 24 hours. The final pH was then measured and plotted against the initial pH for each series. The pH_{ZPC} can be readily obtained from the point at which the initial pH versus final pH curve crossed the y=x line on the graph [38, 39].

The adsorption isotherm model

For the studies of adsorption isotherms, experiment data by using five adsorption isotherm models including Freundlich-langmuir, Temkin, Halsey and Langmuir and Freundlich isotherms was analyzed. The Frundlich isotherm is an experimental model for explaining the multilayer adsorption with heterogeneous energy distribution of active site along with the interaction between the adsorbed molecules. The following equations represent the mathematical model of these isotherms:

Langmuir equation:

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{a_L}{K_L} C_e \qquad (8)$$

Where:

q_c; the equilibrium nitrate concentration on the adsorbent based on the mg/g. *C_c;* the equilibrium nitrate concentration based on mg/L. *K_l;* L/g and a_l ; l/mg are the Langmuir constant, the a_l and K_l amount are the slope and width of curve C_e/q_e in versus C_c and q_{max} (K_l/ a_l) the maximum adsorption capacity based on mg/g.

Frundlich equation:

$$\ln q_e = \ln K_F + \frac{1}{n} C_e \qquad (9)$$

Where:

K_f; the isotherm constant in relation with the adsorption amount based on L/g. *1/n;* the adsorption intensity, which have changed by non-uniformity of the substances.

Temkin equation:

$$qe = b_T \mathrm{Ln} K_T + b_T \mathrm{Ln} C_e \qquad (10)$$

Where*:*

b_T is Temkin's constant and is expressed in units of J/mol, and is related to the temperature of adsorption; *a_t* is the constant of Temkin isotherm (L/g); *R* is the universal constant of gases and *T* is absolute temperature (K). Halsey equation:

$$qe = \left\{ \left(\frac{1}{n_H}\right) \mathrm{Ln} K_H - \left(\frac{1}{n_H}\right) \mathrm{Ln} \left(\frac{1}{C_e}\right) \right\} \qquad (11)$$

Where: *q_e*; the equilibrium nitrate concentration on the adsorbent based on the mg/g, *C_c* ; the equilibrium nitrate concentration based on mg/L, *n_H*: power coefficient and *K_H* is Halsey constant.

Langmuir-Frundlich equation:

$$q_e = -\frac{b q_m C_e^{1/n}}{\left(1 + b C_e^{1/n}\right)} \qquad (12)$$

Where:

q_e; the equilibrium adsorption capacity (mg/gr). C_e ; the adsorbed substance concentration in equilibrium form of liquid phase (mg/ L). n; the heterogeneous index, which is variable between 0-1. b; the isotherm equilibrium constant (L /mg).

The adsorption Kinetic model

Kinetic equations examine the transfer of particles of adsorbate versus time and determine the rate of adsorption [38]. In our study, we examined the kinetic models of Pseudo-first-order kinetic model, Pseudo-second-order kinetic, Intraparticle diffusion, Elovich model and Power model kinetics. The linear relation of these five models has been shown in Equations (13) to (17).

Pseudo first order kinetic model:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{13}$$

Where:

q_e; the equilibrium adsorption capacity based on the mg/g, q_t; the adsorbed nitrate amount at time t, k_1; the adsorption constant based on L/min.

Pseudo second order kinetic model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2 + \frac{t}{q_e}} \tag{14}$$

Where:

K_2 $\mathrm{gm/g.min}$: constant and q_c; the equilibrium adsorption based on mg/g. q_t; the adsorbed nitrate amount at time t mg/g.

Intraparticle diffusion:

$$q_t = k_p t^{1/2} \tag{15}$$

Where:

K_p $\mathrm{gm/g.min^{0.5}}$:constant.

Elovich model:

$$qt = \left(\frac{1}{\beta}\right)\ln(\alpha\beta) + \left(\frac{1}{\beta}\right)\ln t \tag{16}$$

Where:

α; the initial adsorption velocity ($\mathrm{mg/g.min}$). β; desorption constant (g/mg), q_t; the adsorbed nitrate in the time (mg/g).

In Elovich model α have showed the initial adsorption velocity. By increasing α amount, the initial adsorption velocity has increased too.

Power model:

$$q_t = at^b \tag{17}$$

Where: a and b are the equations constant. q; the adsorbed nitrate amount in t time (mg/g).

RESULTS AND DISCUSSION

The adsorption primitive test

The aim of presenting Fig. 1 diagram is selecting the most appropriate adsorbent for doing nitrate, ammonium and phosphate experiment. According to Fig. 1 the maximum nitrate removal rate from water have done by two Conocarpus and Paulownia modified adsorbent FeCl2 in pH=2 which their removal rate were 58.68 and 56.84% respectively. In ammonium removal from water by Conocarpus KOH600 and Paulownia 600 modified adsorption in pH=6 and pH=2, the removal rate were 98.84 and 97.71% respectively and these rate was the maximum removal rate. The phosphate removal from water by Conocarpus $FeCl_2$ and Paulownia KOH300 modified adsorbent, the maximum removal rate were 84.62 and 84.62% in pH=8 respectively. The subsequent experiments have continued by the selected adsorbent.

Initial contaminants concentration of different biochars

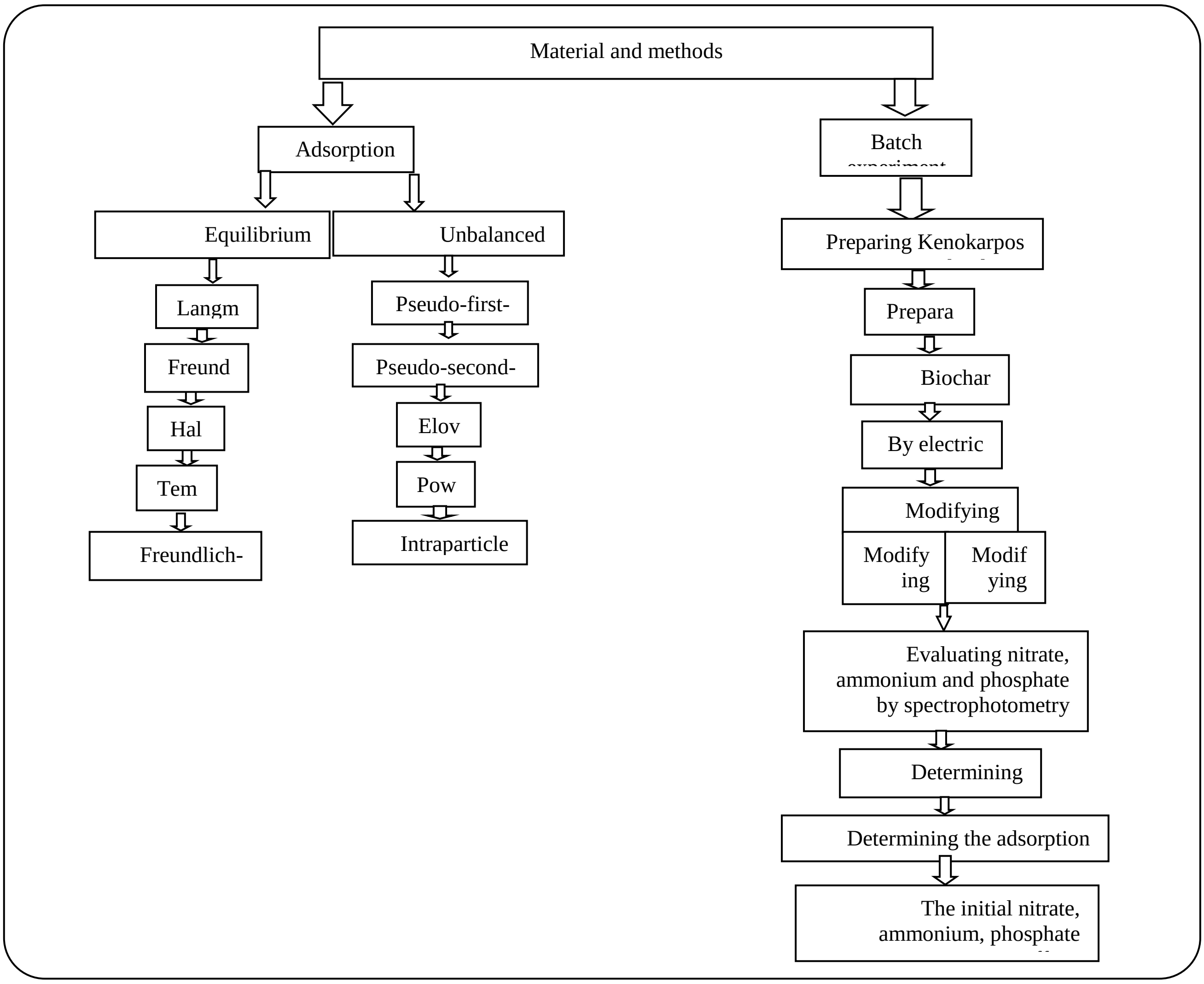
The concentration of nitrate, ammonium and phosphate in conocarpus and paulownia modified adsorbent, before adsorption showed in Table 1. Table 1 showed that studied adsorbents have less amount of nitrate, ammonium and phosphate.

The adsorbent physical properties

In Table 2, the studied adsorbents' physical properties have presented. Based on Table 2 the modified Conocarpus KOH600 and modified Paulownia with $FeCl_2$ have the maximum specific surface rate. High specific surface have provided this possibility for adsorbent, which have many pollutant adsorption site.

The SEM analysis

In Fig. 2, the SEM analysis has done for presenting the modified biochar morphology. For determination of the accurate diameter of biochars, the SEM method was used.



This technique gives information regarding surface morphology of the samples. According to Fig. 2, minimum particle size of biochars was around 20micrometer. It is clear that Fig. 2 has a considerable numbers of pores and there is a good possibility for nitrate, phosphate and ammonium to be adsorbed in to these pores. Also according to Fig. 3, the high level and porous structure is necessary factors of an adsorbent. The SEM images clearly indicated the rough and porous surfaces of biochars. As a result, the modified biochar have a great potential for pollutant removal.

The pH effect

One of the important parameters in adsorption process is pH solution, which have an important role in determining the anion and cation type concentration. The pH solution effect on adsorption capacity of nitrate, ammonium and phosphate ion by biochars in STP situation with 25°C have evaluated. The nitrate and ammonium concentration was 5mg/L and phosphate concentration was 3.5 mg/L. also, the solution volume was 50 ml and the contact time was 2 hours. Fig. 3 have showed the changes removal efficiency with pH increasing. About the effect of pH on the pollutant q_e by the studied adsorbent, the pH have considered in the range of 2-8. Fig. 4 have showed that, the q_e in different pH was various. For removing nitrate from water, based on Fig. 3 (a) by increasing the pH, the nitrate removal efficiency by studied adsorbent have decreased and the maximum adsorbent efficiency have observed in pH=2. In optimum adsorbent pH, the q_e for conocarpus $Fecl_2$ was 0.3mg/g and for paulownia $FeCl_2$ was 0.2mg/g.

the highest NO_3 removal at the lower pH is mainly due to the increase of positively charged sites in on the surface of sorbents and adsorbed nitrate ions by positive sites. Generally, a positively charged surface site on the adsorbent favors the adsorption of anions due to electrostatic attraction [40].

The researchers have showed that the conocarpus biochar and modified conocarpus in pH=2 have showed more nitrate adsorption efficiency [41].In another research the maximum nitrate efficiency have reported by the modified Spruce residual in pH=6 [42]. According to Fig. 3(b) the ammonium removal percentage for Paulownia 600 adsorbent has decreased by the neutral pH. However, in Alkali and acidic pH have showed higher removal efficiency. The maximum removal efficiency have observed in Paulownia 600 with pH=2, q_e was 0.5mg/g. However, in conocarpus adsorbent KOH600, the maximum qe of ammonium adsorption in pH=6 was 0.4mg/g. Based on Fig. 3(c), by increasing the pH the phosphate removal efficiency have increased. The maximum phosphate adsorption efficiency was in pH=8. In optimum adsorption pH, the q_e for Conocarpus $FeCl_2$ was 0.3 mg/g and for Paulownia KOH300 was 0.25mg/g too. In a research which have done on a phosphate adsorption by modified Spruce biochar, the best adsorption efficiency have reported in pH=2 [43].

The studied biochar structures contain ligands which are giving nitrogen (N-H) and mainly oxygen (H-O). A reduction in pH and consequent increase in acidity of ambient can cause an increase in proton within the adsorbent pores. Also, there is potential to adsorb negative charges of ambient by adsorbents due to positive charge of adsorbent surface. Therefore, the highest nitrate sorption occurred at pH of 2. With an increase in alkalinity of ambient, produced negative oxygen ion can combine with phosphate ion and create phosphate esters which can be adsorbed by studied biochars. Moreover, phosphate ion can be adsorbed by cationic wall of biochars in the acidic ambient. Hence, the phosphate absorption in alkaline ambient was increased. For ammonium, since electron donor groups such as oxygen and nitrogen are lack of H^+ in the biochar wall, and their electron pairs are free and also in the form of electrostatic attraction, they can be chelated and complexed with ammonium ions. Therefore, there would be a potential for absorption of ammonium ions in the alkaline ambient.

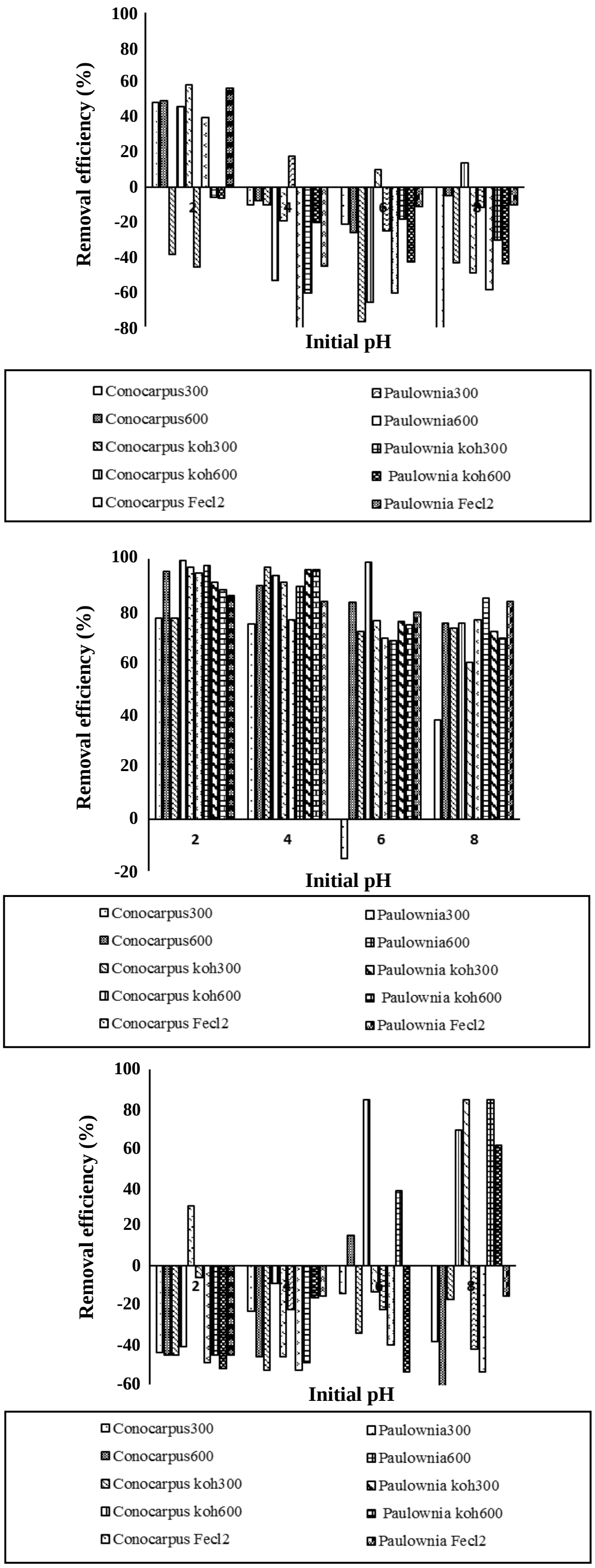


Fig. 1: Removal efficiency of different biochars with increasing initial pH (a) No_3, (b) NH_4 &(c) PO_4

Table 1: Initial contaminants concentration of different biochars.

Paulownia KOH300	Paulownia $FeCl_2$	Paulownia600	Conocarpus KOH600	Conocarpus $FeCl_2$	Absorbent pollutant (mg/L)
2.1	4.35	1.95	3.6	4.1	Nitrate
2.32	2.84	0.96	1.8	2	Ammonium
0.98	0.75	0.5	0.18	0.1	Phosphate

Table 2: Phisical Charactricitecs of different biochars.

Biochar	Moisture weight (%)	Density(kg/m^3)	Organic Matter (%)	Ash (%)	Surface area (m^2/g)
Cononcarpus $Fecl_2$	1.14	0.01	11.4	88.6	85.1
Conocarpus KoH600	2.32	0.02	23.2	76.8	102
Paulownia 600	2.76	0.06	43.32	56.67	93.4
Paulownia $Fecl_2$	2.4	0.002	2.4	97.6	99.8
Paulownia KoH300	2.04	0.02	28.4	71.6	77.3

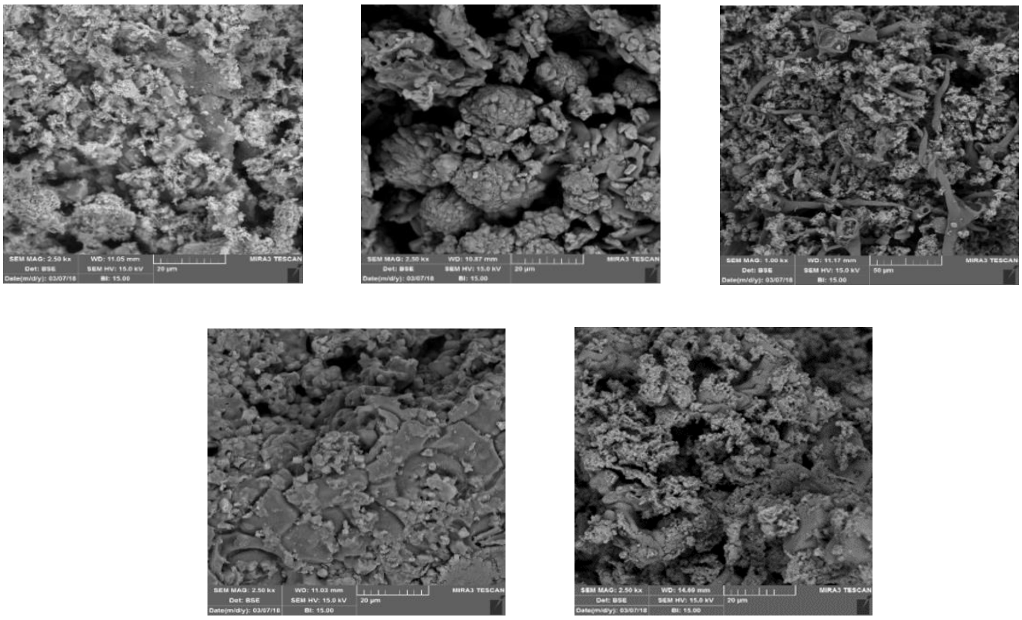


Fig 2: SEM images of different biochars, (a)Paulownia $FeCl_2$,(b)Paulownia KOH300,(c)Paulownia 600, (d)Conocarpus KOH600,(e)Conocarpus $FeCl_2$.

Fig. 4 shows that for the improved adsorbent of Conocarpus $FeCl_2$, $pH_{pzc}$is equal to 7. While for the improved adsorbent of Paulownia $FeCl_2$, pH_{pzc} is equal to 6. Since the optimum pH of the modified adsorbents of Conocarpus $FeCl_2$ and Paulownia $FeCl_2$ is less than pH_{pzc}, this indicates that the surface of adsorbents has a positive charge and can absorb anions. Hence, adsorbents can well absorb nitrate and remove this onion from the water.

The contact time

After determining the optimum pH, the contact time effect on nitrate, ammonium and phosphate pollutant have evaluated by the studied adsorbent. In a stage the adsorbent mass was 0.5gr and the nitrate, ammonium concentration were 100mg/L and in phosphate was 50 mg/L and the optimum pH have considered in previous stage. The contact time have changed from 5 minute to 2 hours.

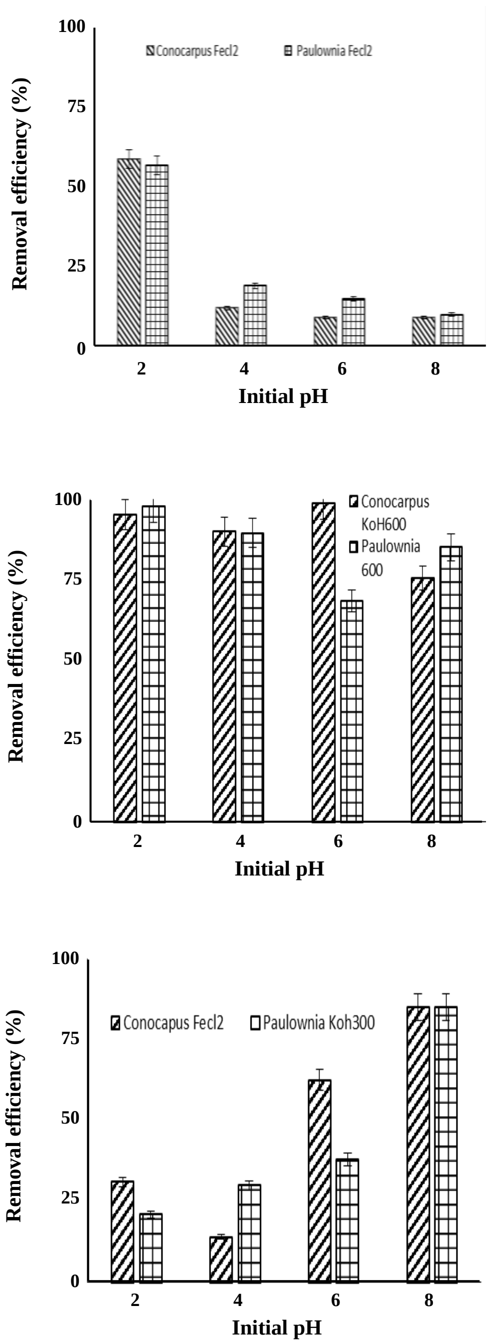


Fig. 3: Adsorption Capacity of different biochars with increasing initial pH (a) No$_3$, (b) NH$_4$ (c) PO$_4$.

Fig. 5 (a) have showed the variation of output concentration in proportion to nitrate input concentration during the time. If the C/C$_0$ have closed to zero, the adsorption efficiency rate of the adsorbent is higher. According to the presented figures, during the time the adsorption efficiency amount have increased.

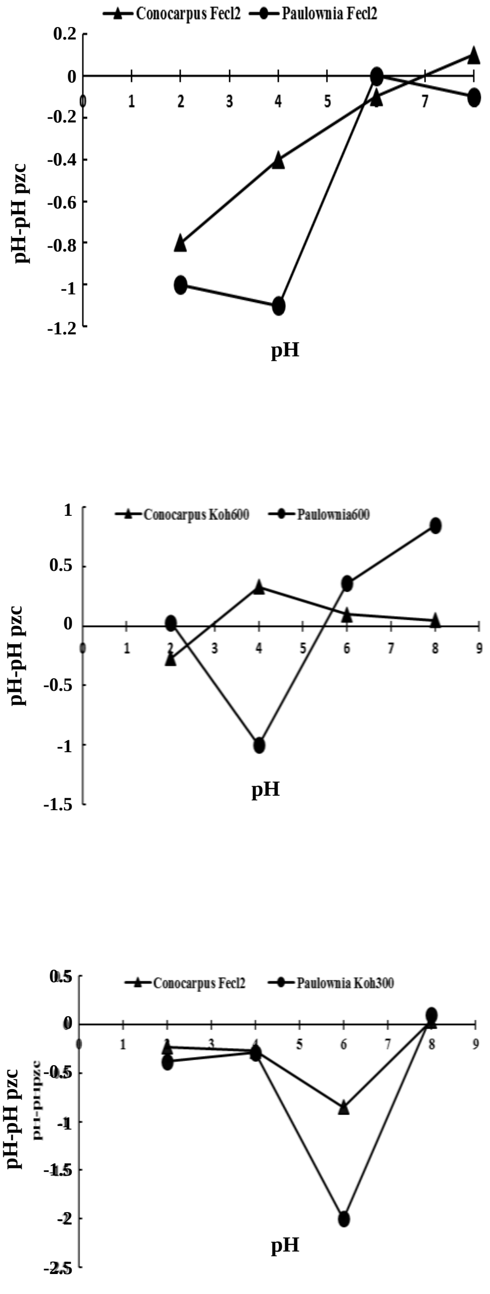


Fig. 4: pHpzc for conocarpus Fecl$_2$ and Paulownia Koh300(a)Nitrate(b)Amonium(c)phosphate.

The Conocarpus Fecl$_2$ and Paulownia Fecl$_2$ adsorbent have the maximum removal efficiency in 60 minute and after that showed a stable trend. In a study which have done on nitrate adsorption by modified Soya biochar, the results have showed that during the time the nitrate adsorption have increased and have balanced in 15 minute [42].

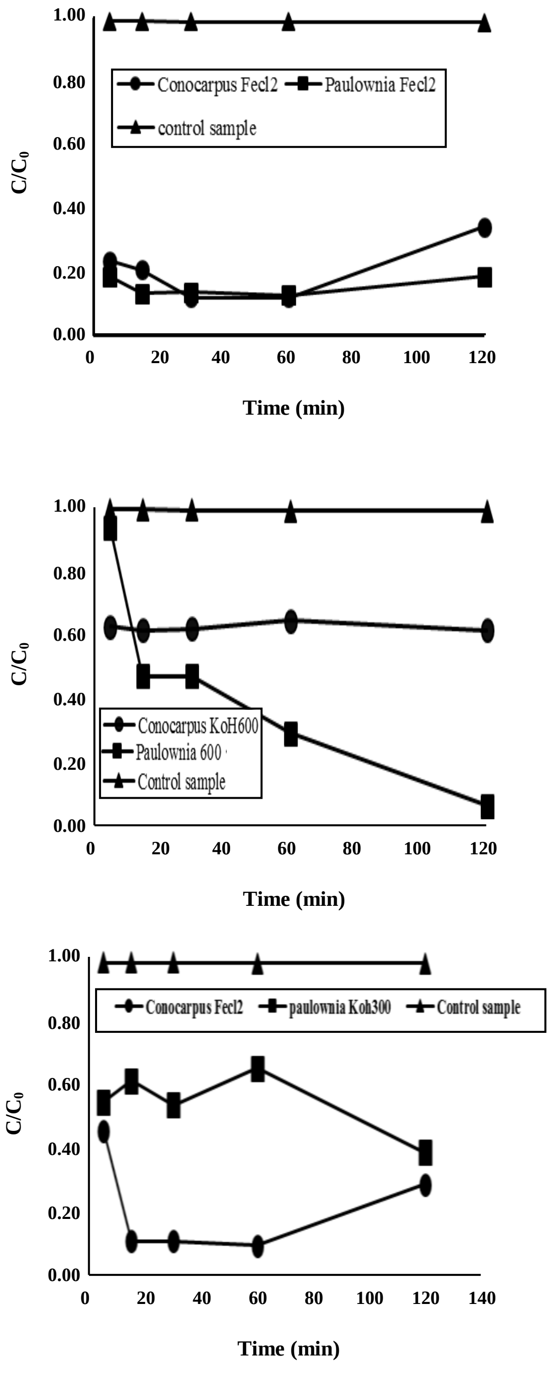


Fig. 5: Concentration of output to input relative to time (a) No_3, (b) NH_4 &(c) PO_4.

In addition, in a research about the modified rice residual, after 80 minute the nitrate adsorption have reached to maximum level [44]. In the evaluation of nitrate adsorption on organosilicate, the results have showed that the nitrate adsorption during the time in the primitive stage have increased slowly during the time and velocity [45]. Fig. 5 (b) have showed the ammonium output concentration in proportion to input concentration during the time. In 120 minute, the Paulownia 600 and Conocarpus KOH 600 adsorbent have the maximum removal efficiency. In the evaluation of ammonium adsorption on modified soya biochar, it have observed that the ammonium adsorption have increased during the time and have balanced in 20 minute [42]. Fig. 5(c) have showed the phosphate output concentration variation in proportion with input concentration. In 120 minute, the Paulownia KOH300 and the Conocarpus $FeCl_2$ adsorbent have the maximum removal efficiency. The reason of the removal efficiency increased during the time is the fact that the adsorbent have a high specific surface and porous, which during the time the adsorbent have more contact with the solution and keep more pollutant in its holes. Some of the researchers have declared the phosphate adsorption equilibrium on modified soya residual after 5 minute (which this adsorption process has increased slowly in the primitive stage during the time [41].

The adsorbent removal efficiency

The aim of presenting concentration-efficiency diagram is removing the selection of best adsorbent in nitrate, ammonium and phosphate pollutant removal from water and equilibrium concentration. The solution concentration is an effective factor in equilibrium time and adsorption capacity. The removal efficiency have discussed by initial concentration increasing and considering the optimum situation of previous stage. According to Fig. (6(a)) in the concentration of 5 mg/L because of the fact that the Conocarpus and Paulownia adsorbent have the nitrate initial concentration, the adsorption capacity in both Conocarpus and Paulownia adsorbent was zero. In addition, because the initial concentration of the solution was low and the nitrate initial level of evaluated adsorbent was almost equals to solutions initial concentration, the nitrate removal capability from water by Conocarpus and Paulownia adsorbent have decreased and in addition to the input concentration of solution, the adsorbent concentration have added. The solution concentration and the removal efficiency have decreased in the concentration of 50mg/L nitrate. The $FeCl_2$ adsorbent with 9mg/g has the maximum adsorption capacity and by the increased of the nitrate concentration, the adsorption capacity has increased.

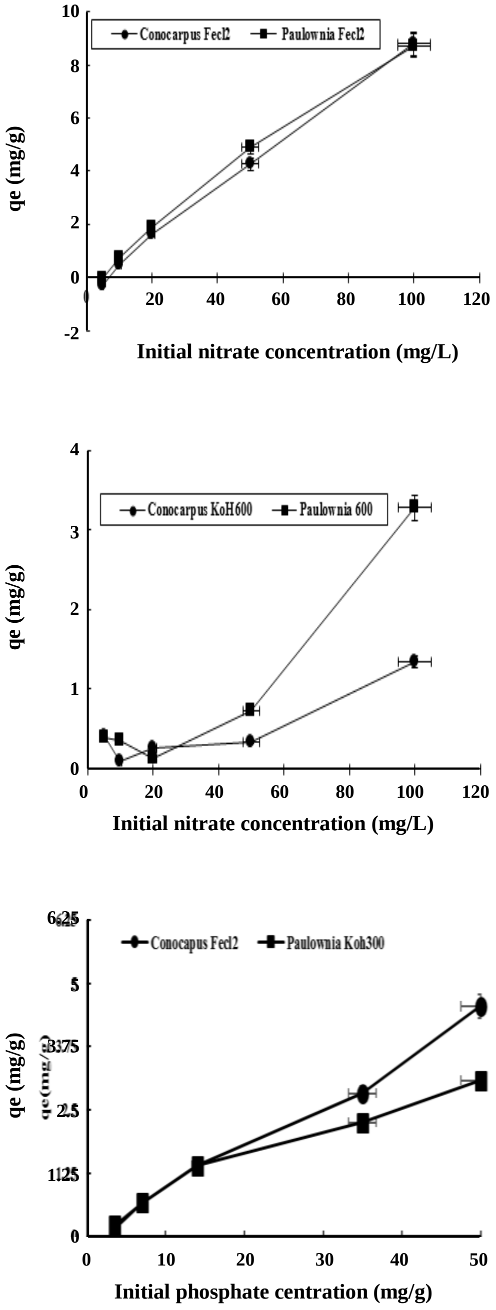


Fig. 6: Adsorption capacity of different biochars with increasing initial concentration (a) NO_3, (b) NH_4 & (c) PO_4 concentration.

This fact has showed that in low concentration more ions have fill with adsorbents pores and removes. By increasing the nitrate, concentration the ions number have increased and their contact with adsorbent have reduced, and the saturated adsorption locations and removal efficiency have decreased. Similar results have presented by Asrari et al. (2012) [45]. However, about the Conocarpus $FeCl_2$ adsorbent, the maximum adsorption capacity (q_e) was 9 mg/g in concentration of 100 mg/L. The Fig. 6(b) have showed the ammonium adsorption capacity from water by the evaluated adsorbent with ammonium initial concentration increased in water. Decreasing trend of ammonium removal from water by the evaluated adsorbent has observed with the ammonium initial concentration increased in water. In concentration of 5 mg/L ammonium in water, the Conocarpus KOH600 and Paulownia 600 adsorbent have the maximum ammonium adsorption (q_e) from water which was 3.5mg/g and 1.5mg/g respectively. From 5-20 mg/L ammonium concentration a sudden decreasing trend of q_e from water by the Conocarpus KOH600 and Paulownia 600 adsorbent have observed, which were from 0.5mg/g to 1.5mg/g and from 0.5mg/g to 3.5mg/g. This increasing trend has continued until the 100 mg/L ammonium concentration in ammonium adsorption. Fig. (6 (c)) have showed the phosphate adsorption by the evaluated adsorbent with the phosphate initial concentration increasing in water. According to the Fig. (6(C)) in conocarpus $FeCl_2$ and Paulownia KOH300 adsorbent, by the increased of the phosphate concentration in water from 3.5mg/L to 14 mg/L a sudden increased in phosphate adsorption capacity(q_e) from water by the mentioned adsorbent have observed. In addition, in Conocarpus $FeCl_2$, the adsorption capacity (q_e) was from 0.25 to 4.8mg/g and in Paulownia KOH300 is from 0.25 to 3mg/g and after that it have subtle decreasing trend. A higher adsorption removal and lower adsorption capacity at lower initial concentration may be due to the high adsorption affinity between the NO_3 ions and the biochar. At higher initial concentrations, the availability of binding sites for adsorbing NO_3 ions might tend to decrease, preventing further adsorption of NO3 ions on the adsorbent surfaces [17].

Adsorption isotherm

For considering the nitrate, ammonium and phosphate adsorption on the studied adsorbent, 5 Langmuir-Freundlich, Halsey, Temkin , Langmuir and Freundlich isotherm model for the experimental data have evaluated. According to the data of Table 3, in nitrate, ammonium and phosphate adsorption by using the modified

Table3: Parameters of NO_3^-, NH_4^+ and PO_4^{3-} adsorption isotherms.

sample	Adsorbate	Langmuir				
		K_l (L mmol-1)	q_m (mg/g)		R^2	STDEV
Conocarpus $FeCl_2$	NO_3^-	5.86	0.78		0.324	0.0
Paulownia $FeCl_2$	NO_3^-	0.02	0.51		0.388	0.04
Paulownia600	NH_4^+	0.19	2.72		0.238	0.86
Conocarpus KOH600	NH_4^+	0.008	2.14		0.620	0.35
Conocarpus $FeCl_2$	PO_4^{3-}	26.22	3.40		0.042	1.47
Paulownia KOH300	PO_4^{3-}	0.11	4.21		0.734	1.33
		Freundlich				
		K_f (L mmol-1)	N		R^2	STDEV
Conocarpus $FeCl_2$	NO_3^-	0.07	0.58		0.619	1.07
Paulownia $FeCl_2$	NO_3^-	1.31	2.74		0.234	0.82
Paulownia600	NH_4^+	0.22	2.98		0.488	0.28
Conocarpus KOH600	NH_4^+	0.2	5.09		0.354	0.11
Conocarpus $FeCl_2$	PO_4^{3-}	0.79	1.89		0.385	0.90
Paulownia KOH300	PO_4^{3-}	0.92	40.32		0.657	1.39
		Langmuir-Freundlich				
		K (L mg^{-1})	n	q_m (mg/g)	R^2	STDEV
Conocarpus $FeCl_2$	NO_3^-	0.04	5.86	0.82	0.134	2.25
Paulownia $FeCl_2$	NO_3^-	1.06	2.74	0.009	0.099	0.0
Paulownia600	NH_4^+	9.88	2.998	0.34	0.220	0.0
Conocarpus KOH600	NH_4^+	1.83	5.09	0.33	0.194	0.02
Conocarpus $FeCl_2$	PO_4^{3-}	185.4	1.89	0.43	0.028	0.07
Paulownia KOH300	PO_4^{3-}	18.22	40.32	0.55	0.006	0.24
		Halsey				
		K_H	N_H		R^2	STDEV
Conocarpus $FeCl_2$	NO_3^-	0.21	0.58		0.619	1.71
Paulownia $FeCl_2$	NO_3^-	2.11	2.74		0.015	0.94
Paulownia600	NH_4^+	0.01	2.98		0.488	0.28
Conocarpus KOH600	NH_4^+	3	5.9		0.354	0.11
Conocarpus $FeCl_2$	PO_4^{3-}	11.80	106.38		0.105	0.04
Paulownia KOH300	PO_4^{3-}	25.99	40.32		0.144	0.12
		Temkin				
		K_t (L g^{-1})	b_t (kJ mol^{-1})		R^2	STDEV
Conocarpus $FeCl_2$	NO_3^-	0.24	5.65		0.433	2.43
Paulownia $FeCl_2$	NO_3^-	5.65	1.16		0.122	1.25
Paulownia600	NH_4^+	0.70	0.44		0.334	0.75
Conocarpus KOH600	NH_4^+	2.57	0.13		0.241	0.24
Conocarpus $FeCl_2$	PO_4^{3-}	16.77	0.12		0.100	0.56
Paulownia KOH300	PO_4^{3-}	19.47	0.08		0.120	0.40

Table4: Parameters of NO_3^-, NH_4^+ and PO_4^{3-} adsorption kinetic.

sample	Adsorbate	Pseudo-first-order			
		K_l (L mmol-1)	q_m (mg/g)	R^2	STDEV
Conocarpus $FeCl_2$	NO_3^-	0.006	0.867	0.187	0.18
Paulownia $FeCl_2$	NO_3^-	0.012	0.158	0.013	0.04
Paulownia600	NH_4^+	0.007	1.96	0.815	0.44
Conocarpus KOH600	NH_4^+	0.018	0.063	0.010	0.02
Conocarpus $FeCl_2$	PO_4^{3-}	0.01	0.23	0.035	0.06
Paulownia KOH300	PO_4^{3-}	0.0	0.94	0.954	0.08
		Pseudo-second-order			
		K_f (L mmol-1)	N	R^2	STDEV
Conocarpus $FeCl_2$	NO_3^-	0.02	6.57	0.001	1.24
Paulownia $FeCl_2$	NO_3^-	-0.74	8.13	0.218	0.10
Paulownia600	NH_4^+	0.002	5.36	0.872	1.20
Conocarpus KOH600	NH_4^+	0.913	1.33	0.997	0.07
Conocarpus $FeCl_2$	PO_4^{3-}	0.07	3.60	0.455	0.57
Paulownia KOH300	PO_4^{3-}	0.02	3.19	0.754	0.76
		Intraparticle diffusion			
		K (L mg^{-1})	n q_m (mg/g)	R^2	STDEV
Conocarpus $FeCl_2$	NO_3^-	0.09	8.54	0.129	0.33
Paulownia $FeCl_2$	NO_3^-	0.009	8.51	0.012	0.03
Paulownia600	NH_4^+	0.30	0.07	0.867	1.04
Conocarpus KOH600	NH_4^+	0.0002	1.31	0.0002	0.0
Conocarpus $FeCl_2$	PO_4^{3-}	0.05	3.65	0.048	0.17
Paulownia KOH300	PO_4^{3-}	0.14	1.40	0.947	0.49
		Elovich			
		α (mg g^{-1} min^{-1})	β(g mg^{-1})	R^2	STDEV
Conocarpus $FeCl_2$	NO_3^-	2.12	8.14	0.026	0.15
Paulownia $FeCl_2$	NO_3^-	2.12	35.21	0.682	0.05
Paulownia600	NH_4^+	0.009	1.12	0.942	1.09
Conocarpus KOH600	NH_4^+	0.27	500	0.003	0.0
Conocarpus $FeCl_2$	PO_4^{3-}	1.10	3.54	0.193	0.34
Paulownia KOH300	PO_4^{3-}	0.01	2.62	0.860	0.46
		Power			
		a (mg kg^{-1})	B (mg kg^{-1} min^{-1})	R^2	STDEV
Conocarpus $FeCl_2$	NO_3^-	8.45	-0.02	0.024	0.19
Paulownia $FeCl_2$	NO_3^-	8.35	0.003	0.013	0.03
Paulownia600	NH_4^+	0.10	0.87	0.806	1.63
Conocarpus KOH600	NH_4^+	1.32	-0.002	0.003	0.0
Conocarpus $FeCl_2$	PO_4^{3-}	2.92	0.086	0.161	0.41
Paulownia KOH300	PO_4^{3-}	1.29	0.164	0.899	0.45

Conocarpus biochar, the Freundlich model with R^2 =0.619, Langmuir model with R^2=0.620, Freundlich with R^2= 0.385 have consistent with observed data. Also, in modified Paulownia biochar the Langmuir with R^2= 0.388, Freundlich and Halsey with R^2=0.488 and Langmuir model with R^2=0.734 respectively have consistent with the observed data. In a research which have done for nitrate removal from water by the modified Conocarpus biocha and the Conocarpus biochar, Langmuir model with R^2=0.993-0.998 could have described the adsorption isotherm properly [40]. In another research which have done for ammonium removal from aqueous solution with modified peanut shell, corn stick and cotton stem biochar, the Langmuir with R^2 higher than 0.8 have fitted the adsorption data properly. In phosphate adsorption study with modified spruce biochar, the Langmuir-Freundlich model has described the adsorption isotherm properly [42].

The adsorption kinetic

In order to determine the reaction kinetics of nitrate, ammonium and phosphate removal from aqueous solution by Conocarpus $FeCl_2$, Paulownia $FeCl_2$, Paulownia600, Conocarpus KOH600, Conocarpus $FeCl_2$ and Paulownia KOH300 we used the linear regression of pseudo first order, pseudo second order, Elovich, Power and intraparticle diffusion kinetic models. The result of kinetic experiments is presented in Table 4. According to the obtained results from Table 4, in nitrate, ammonium and phosphate adsorption by modified Conocarpus biochar the first order pseudo models with R^2=0.187, pseudo second order with R^2=0.997 and again pseudo second order with R^2=0.455 respectively could have described the kinetic adsorption model properly. Also, in modified Paulownia biochar the Elovich model with R2=0.682 and 0.942 and pseudo first order with R2=0.954 respectively could have described the kinetic adsorption model properly. In a research the results of nitrate and phosphate removal from water by modified spruce biochar have showed that the second order kinetic model with the maximum correlation coefficient could have fixed the adsorption data properly [41]. Also, in ammonium removal from water by soya biochar the interstitial emission kinetic model could have described the kinetic data properly [42].

CONCLUSIONS

The results of this research have showed that the nitrate, ammonium and phosphate adsorption level have increased during the time and after 60 and 120 minute have reached their maximum respectively. The ammonium maximum adsorption in modified Conocarpus biochar was in pH=6 and for Paulownia biochar was pH=2. The nitrate maximum adsorption was in pH=2 and the phosphate maximum adsorption was in pH=8. By the increased of phosphate and nitrate initial concentration the adsorption capacity have increased and the phosphate maximum adsorption capacity in 14 mg/ L concentration by the modified Conocarpus and Paulownia biochar was 0.25mg/g and in 50mg/ L concentration, the nitrate in modified Paulownia biochar was 0.45mg/g. By the increased of the ammonium, initial concentration the adsorption capacity increased and the ammonium maximum adsorption capacity in 5mg/ L, concentration by the modified Conocarpus biochar was 0.5mg/g. Nowadays, according to the increased of the water resources pollution and spending a high cost for purification of water resource, using the cheap agricultural waste attract a lot of attention to itself. In this study, by the use of Conocarpus and Paulownia biochar, it has tried to reach the nitrate, ammonium and phosphate level in water. According to the obtained results the botanical Paulownia adsorbent with higher adsorption capacity in comparison with Conocarpus adsorbent have selected as an optimum adsorbent for nitrate and phosphate removal from water and the Conocarpus adsorbent for ammonium removal have showed an higher adsorption capacity. According to the fact that there is no study about the aqueous pollutant removal with paulownia plant, using this plant have considered as an innovation.

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