REMOVAL OF AMMONIUM FROM WATER BY PINE CONE POWDER AS BIOSORBENT

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Abstract

Pine cone, a popular agricultural waste, was investigated as a novel ammonium biosorbent in its raw and sodium hydroxide modified form. Surface modification of pine cone powder were carried out using sodium hydroxide solution of concentarions (0,05 and 0,1mg/L). The effects of physico-chemical parameters such as solution pH, contact time and biosorbent dosage were investigated in the biosorption of ammonium onto pine cone powder. It was found that the biosorption capacity was optimal using 6–10 solution pH range and the rate of sorption was very fast, during the first 15 min. Biosorption kinetics and equilibrium data for the romoval of NH4+ ions onto pine cone powder were examined by fitting the experimental data to various model. The biosortion was described by a pseudo-second-order model predicting a chemisorption process. In addition, the equilibrium data were well characterized by the Langmuir isotherm model that confirmed the mono-layer coverage. The surface properties of raw pine cone powder and its sodium hydroxide modified form were analyzed by Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS) and powder X-ray diffraction (XRD). The chemical composition of pine cone powder before and after biosorption of ammonium is discussed in relation to the XRD and SEM-EDS results. The results showed that the surface of pine cone powder samples is modified by sodium hydroxide solution and the chemical composition of pine cone powder samples is changed after biosorption of ammonium. This from presents an interesting option for tertiary wastewater treatment (as a possible non-conventional biosorbent for the removal of ammonium).

Keywords: Ammonium; Removal; Water; Biosorption; Pine cone; X-ray; SEM-EDS

ÇAM KOZALAK TOZUNUN BİOSORBENT OLARAK KULLANILRAK SUDAN AMONYUMUN UZAKLAŞTIRILMASI

Özet

Doğal ve sodyum hidroksit ile modifiye edilmiş çam kozalağı tozunun amonyum biosorbenti olarak kullanılmasını araştırıldı. Çam kozalağı tozunun yüzey modifikasyonu için 0.05 mg/L ve 0.1 mg/L sodyum hidroksit çözeltileri kullanıldı. Biosorpsiyon olayına fizikokimyasal etkilerini; pH, başlangıç derişimi ve temas süresi gibi parametrelerle araştırıldı. Bisorpsiyon kapasitesine pH (optimum pH aralığı =6-10) ve temas süresine (ilk 15 dakika) bağımlı olduğu saptanmıştır. Adsorpsiyon kinetikleri ve izotermleri belirlenmiştir. Adsorpsiyon verileri, Langmuir izotermini uymaktadır. SEM, XRD analizleri ile biosorpsiyon karakterizasyonu yapılmıştır. Elde edilen sonuçlara göre çam kozalağının sodyum hidrosit ile modfikasyonu sonucu yüzey alanın değiştiğini, modifiye edilmiş çam kozalağının atıksuların arıtılmasında kullanılması ilgi çekici bir durum olduğu tespit edilmiştir.

Anahtar Kelimeler: Ammonyum, Giderim, Su, Biosorpsiyon, Çam kozalağı, XRD, SEM-EDES

1 Introduction

Ammonia has been found to appear in various types of agricultural, municipal, and industrial wastewaters and one of the best understood consequences of human pollution associated with environment is water eutrophication [1, 2, 3]. Ammonium often present in different types of waters and wastewater, can end up in lakes, rivers and drinking water reservoirs with effluent discharges. Higher concentration of ammonium will cause a sharp decrease of dissolved oxygen and obvious toxicity in aquatic organisms [4, 5, 6]. For those instances, ammonia removal from the polluted waters has become necessary in order to maintain proper water quality for the environmental problems.

Different physical, chemical and biological methods such as adsorption, chemical precipitation, membrane filtration, reverse osmosis, ion exchange, air stripping, breakpoint chlorination and biological nitrification and denitrification were used for removal of ammonia from polluted waters [4, 5, 6].

Several authors have reported the adsorption of ammonia from polluted waters on activated carbon and zeolite [7, 8, 9]; however, the high cost of activated carbon and the low abundance of zeolite in many countries, as well as the high costs of regeneration processes by chemical and thermal procedures, are a problem [6]. In addition, several research works have been performed to search for efficient and low-cost materials such as clay and zeolite [10, 11, 12, 13]; limestone [14]; waste paper, refuse cement and concrete [15]; fly ash and sepiolite [9] to remove ammonia from aqueous solutions. However, the adsorption capacity of these different materials used for the removal of ammonium presented a high sensitivity towards the variation of temperature and pH. In addition, these materials require chemical and thermal procedures to regenerate the exhausted adsorbent which increases the cost and the operational steps [5].

Adsorbents such as activated carbon and zeolite are efficient and most often used for ammonium removal [7, 8]. Conventional wastewater treatment technologies, however, are expensive to build and also have associated operational and maintenance problems. Among all the approaches proposed, adsorption is one of the most popular methods and is currently considered as an effective, efficient, and economic method for water purification [5].

Agricultural waste materials, being economic and ecofriendly due to their unique chemical composition could be considered as a promising material for the removal of ammonium [5]. Agricultural wastes are lignocellulosic in nature. Lignin in plant materials serve two major purpose: (1) to strengthen the cellwalls and (2) to protect the microfibrils of the cell wall from chemical, physical, and biological attack. Therefore, these properties of lignin may help to explain the lowtotal negative charge and low carboxyl group content displayed by agricultural wastes with high lignin concentrations. Dilute sodium hydroxide solution treatment is known to solubulize a small fraction of the lignin and soluble organics in the plant waste; improving the penetration of modifying agents such as citric acid into the biosorbent matrix and thereby increasing sorption capacity [16].

Pine seeds are carried in cones. Large quantities of pine cones are produced annually throughout the world, especially in pine plantations grown for the pulp and paper industry. They are collected, dried to facilitate seed release, and generally discarded. Some nurseries grind the cones into mulch or they may be sold for crafts, but consumer demand for cones is small compared to by-products from other industries [16]. The aim of this study is investigation that ammonium biosorption on agricultural waste materials such as Pine Cone is of great significance for understanding its transference in the environment and its effect on terrestrial ecological system. For these reasons, the effects of pH, contact time, and initial ammonia concentrations on the biosorption capacity were investigated on Pine Cone Powder. Moreover, a series of analysis through Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS) and powder X-ray diffraction (XRD) were conducted to elucidate the biosorption of ammonium onto pine cone powder.

2 MATERIALS AND METHODS

2.1 Materials

Pine tree cones were obtained from a plantation in Muğla (Turkey). Pine tree cones were collected September 2010.

The stock solution of NH4CI (merck) was prepared by dissolving an accurately weighed amount of the salt in deionized water.

2.2 Equipment and Analysis

Measurements of pH were made using a pH meter (WTW). A calibrated electrode was immersed in the testing liquid to be tested, and was measured very accurately. The concentrations of ammonium were determined colorimetrically by phenat method (640 nm) according to the Standard Methods [17]. The method was applied to the Turkish Accreditation Agency (TÜRKAK) for our laboratory. The laboratory analyzes conducted on-site as well as the addition of water, wastewater and sea water sampling within the framework of ISO IEC 17025 Laboratory accreditation are available in our laboratory.

2.3 Biosorbent

The cones were washed to remove impurity such as sand and leaves, the washed cones were then dried at 90 ∘C for 48h in an oven. The scales on the cones were then removed and blended in a food processing blender. The resultant powder was sieved. It was then passed through a 48-mesh size screen before use.

2.4 Surface modification with NaOH solution

A weighed amount (50 g) of pine cone powder was contacted with 0.5 L of sodium hydroxide solutions of concentration (0.05 and 0.10 mol/L) and the slurry stirred for 18 h at room temperature. The powder was rinsed with 0.5 L of distilled water. This procedure was repeated two more times to ensure removal of sodium hydroxide from the powder. The residue was then dried overnight at 90 ∘C. The samples were marked PCP 0.05, PCP 0.10 and while the raw sample was marked PCP.

2.5 Preparation of synthetic sample

A stock solution of ammonium (1000 mg/l) was prepared using distilled water. All working solutions of varying concentrations were obtained by successive dilution. The ranges of ammonium concentrations were varied between 10 and 50 mg/L in this study.

2.6 Batch sorption experiments

The sorption experiments were carried out in a routine manner using a batch technique. Closed Pyrex glass Erlenmeyers flaks containing a volume of 100 cm³ of the known-concentration solutions of ammonium were placed in a shaking assembly. The raw pine cone powder (PCP) as dry (0.3 g) was shaken with 50 ml of ammonium solution at a concentration of 50 mg/l in a shaker at room temperature (22 ± 0.5 °C) for various periods of time (0, 10, 30, 60, 90, 120 min). Then the particles were separated by filtration through a 0.45 μm membrane filter. The amounts of the pine cone powder sorbed in each case were determined by the difference between the initial and the final concentrations.

The procedure was repeated for PCP 0.05, PCP 0.1. All the experiments were carried out in duplicates. To calculate the ammonium removal, biosorption capacity at the equilibrium time (qe) will be determined according to the following equation:

$$q_e = V \frac{(C_0 - C_e)}{M} \qquad (1)$$

where V is the sample volume (l), Co is the initial concentration of ammonium (mg/I), Ce is the equilibrium or final concentration of ammonium (mg/I), M is the dry weight of the (0.3 g for this study), and qe is the biomass biosorption capacity of the biomass at equilibrium time.

2.7 Effect of solution pH

Effect of initial pH was investigated at various pH values ranging between 2 and 12. In the experiments, a 0.3 g sample of pine cone powder was added to each 100 mL volume of synthetic ammonium solution having an initial concentration 50 mg/L for a constant sorption time, one hour. The pH of the solution adjusted using 0.1mol/l HCl or NaOH. The flasks were shaken at 125rpm and room temperature.

2.8 Effect of biosorbent dose

The effect of sorbent dose on the equilibrium uptake of ammonium was investigated with sorbent masses of 0.1, 0.2,

0.3, 0.4 and 0,5 g. The experiments were performed by adding the known weights of pine cone powder to 100 cm3 closed pyrex glass Erlenmeyer flaks containing 50 mg/L solution at pH 8.0. The flasks were shaken at 125rpm and room temperature for 1 h and the equilibrium concentration of ammonium remaining was determined.

2.9   Scanning electron microscopy

The structures of the samples were characterized by powder X-Ray Diffraction (XRD) and Scanning Electron Microscopy with Energy Dispersive Spectroscopy (SEM-EDS). Powder X-ray diffraction (XRD) patterns were collected using CuK$_\alpha$ monochromatic radiation (λ=1.54056Å) at room temperature on a Rigaku-SmartLab Diffractometer. Scanning Electron Microscopy (SEM) was performed using a JEOL SEM 7700F. Local composition was analyzed by Energy-Dispersive X-Ray Spectroscopy (EDS) with an analyzer system attached to a JEOL SEM 7700F. XRD and SEM-EDS investigations were performed in the Research Centre Laboratory at Mugla Sıtkı Koçman University.

3   RESULTS AND DISCUSSION

3.1   Influence of pH

The pH of the aqueous solution in which sorption is being conducted is an important controlling parameter in the sorption process. The magnitude of electrostatic charges imparted by the ionized metal ions and the functional groups on the adsorbent surface are primarily controlled by pH of the medium [16, 18, 19]. According to the equilibrium reaction of Bronsted–Lowry acid base reaction, given by Eq. (2) the ammonium removal should be greater at lower pH values and smaller at higher pH values, if the cation-exchange mechanism occurs only by means of the ammonium ions.

$$NH_3 + H_2O \leftrightarrow NH_4^+ + OH^- \qquad (2)$$
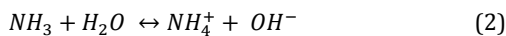
However, the lower capacities obtained at lower pH may be due to the ammonium ions having to compete with hydrogen ions among the exchange sites. On the other hand, at high pH, ammonium ions are transformed to aqueous ammonia [3].

Ammonia–ammonium equilibrium in solution is largely pH dependent [5, 6]. and it stands to reason that only the ionised form can be removed from solution by ion exchange. At pH $\sim$ 8 and below the substantial majority of ammoniacal nitrogen is present in the ionised form. Above pH $\sim$ 8 the equilibrium shifts rapidly towards the non-ionised form and these conditions become increasingly less favourable [20, 21]. Adsorption capacity of adsorbent increased remarkably with increasing pH values up to 8, and then increase rate was lower with increasing pH over 8.

It was observed for the adsorption of ammonium by zeolite synthesized from fly ash, sawdust and Posidonia oceanica fibers within the pH range 5.5–10.5 [5, 6, 22] and by composites of g-alumina/KAS gel within the pH range 5–10 [23]. However the optimum removal efficiency of ammonium by the most types of zeolite tested is achieved when operating at pH value of 6 and 7 [8, 24]. On the other hand, the agriculture residues seem to allow the removal of ammonium within a wide range of pH. This was well demonstrated by many researches, on composting of animal wastes by agricultural wastes, which showed that the lignocellulosic materials reduce the volatilization of ammonia [5, 6].

The effect of solution pH on the sorption of ammonium ions from aqueous solution using PCP, PCP0.005 and PCP0.1 is shown in Fig. 1. It shows the relationship between amounts of

ammonium adsorbed and initial solution pH. At solution pH 2, the amount of ammonium removed from solution is smaller than for any other initial solution pH tested, this is can be attributed to the competition between ammonium ions and H+ for biosorption sites. The NaOH modified samples had higher ammonium sorption capacities than the raw pine cone powder. PCP 0.1 adsorbed (3,06 mg/g) more ammonium than other two samples and adsorption capacity increased for samples treated with increasing concentration of NaOH solution. As solution pH increases, the ammonium capacities of the samples increase up to solution pH 8-10. This can be attributed to the increase in negative charge on the biosorbents surface with increasing solution pH.
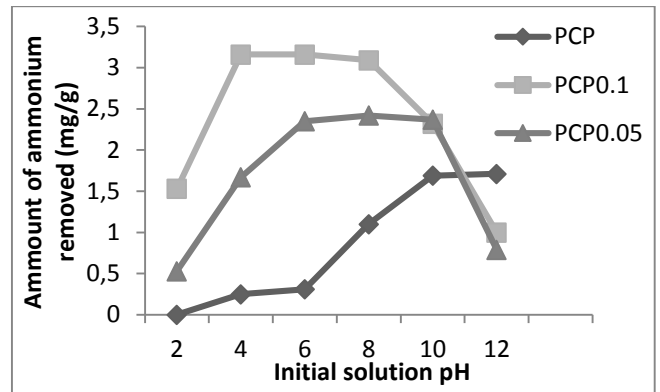

Figure 1. The effect of pH on the sorption capacity of ammonium onto dried pine and pine cone powder and NaOH treated pine cone powder (ammonium concentration: 50 mg/I, temperature: 22±0.5°C, agitation rate:125 rpm).

3.2   Effect of contact time

The relationship between contact time and ammonium sorption on PCP, PCP0.05 and PCP 0.1 is presented in Fig. 2. The rates of sorption were very fast, during the first ~15 min. This situation shows that ammonium ions may be the fast diffusion onto the external surface. Then, there was a relatively slow intraparticle diffusion process. The other hand, the results show that the adsorption capacity of PCP 0.1 is more than other samples.
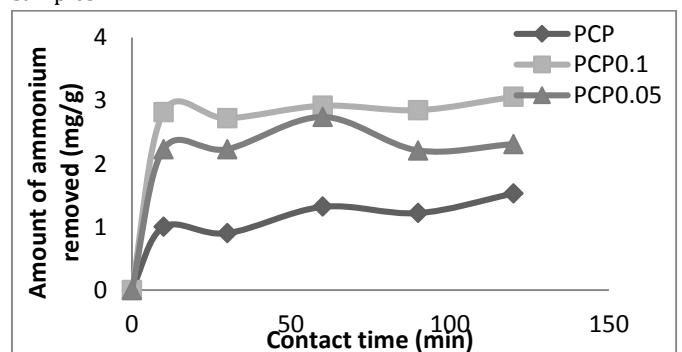

Figure 2. Sorption equilibration time of ammonium onto raw pine cone powder and NaOH modified pine cone powder (biomass concentration 10 g/I, initial solution pH 8, temperature: 22±0.5°C).

3.3   Effect of biosorbents dose

The effect of biosorbent dosage on the removal of ammonia was investigated at 50 mg/L ammonia concentration at pH 8 and room temperature. The amount of ammonium adsorbed per unit mass of pine cone powder was found to decrease with biosorbent dose. The pattern in the results shows that the

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ammonium capacity for all samples versus biosorbent dose was low for PCP and high PCP 0.1 (Fig. 3). For PCP 0.1, the change in dose from 2 to 10 g/L, produced a capacity reduced from 35,0 to 54,6 mg/g. Quite similar tendency was reported for cupper (II) adsorption onto pine cone powder [16].
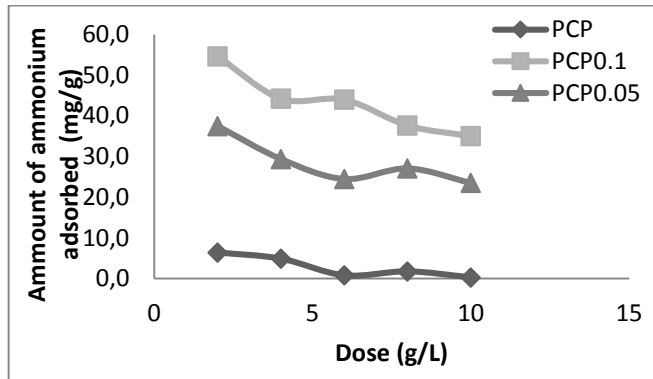
Figure 3. Effect of dose on ammonia removal by raw pine cone powder and NaOH modified pine cone powder (initial solution pH 8, temperature: 22±0.5°C).

3.4 Kinetics Studies

Adsorption of a given solute on a solid is a fairly complex mechanism. Indeed, the speed of adsorption is strongly influenced by several parameters such as the status of the solid matrix that has generally heterogeneous reactive sites, and the physicochemical conditions under which the adsorption takes place. The study of adsorption kinetics is very useful for understanding the mechanisms that are involved and also for the design of future facilities adsorption on a large scale [5, 6]. The three most popular kinetic model and their linear forms are shown in Table 1.

In this study, to investigate the mechanism of adsorption, three kinetic models were used to fit the experimental data, namely, irreversible first-order, pseudo-second-order and intraparticle diffusion models. The best-fit model was selected based on both linear regression correlation coefficient (R^2) and the calculated qe values.

Table 1. The three most popular kinetic model and their linear forms.

Model	Equation	Linear forms
Pseudo-first-order	$dQ_t/dt = k_1(Q_e-Q_t)$	$Ln(Q_e-Q_t) = LnQ_{el} - k_1t$
Pseudo-second-order	$dQ_t/dt = k_1(Q_e-Q_t)^2$	$t/Q_t = 1/k_2Q_{ell}^2 + 1/Q_{ell}t$
Intraparticle diffusion		$Q_t = K_p\sqrt{t}$

In many cases, the kinetics of adsorption by any biological material has been tested for the first-order expression given by Lagergren. However, it has also been shown that a pseudo-second-order model can sometimes provide a better description of the adsorption kinetics [25]. Pseudo-first-order model parameters for the effect of 50 mg/L concentration are illustrated in Table 2.

Table 2. Kinetic rate constants related to sorption of ammonium onto pinecone powder (initial concentration of ammonium:50 mg/L)

Kinetic models	PCP	PCP0.05	PCP0.1
Experimental Q_e	1,530	2,740	3,608
Irreversible first-order model $K_1(min^{-1})$	0,014	0,004	0,014
Calculated Q_{el} (mg/g)	0,252	0,362	0,680
R^2	0,6672	0,4242	0,4705
Pseudo-second-order model K_2(g/mg min)	0,488	0,192	0,110
Calculated Q_{ell} (mg/g)	1,430	2,280	3,007
R^2	0,9587	0,9908	0,9972
Intraparticle diffusion model Kp(mg/g√min)	0,150	0,280	0,345
R^2	0,7535	0,2972	0,3683

The first-order model did not fit the data well at all, and it was not applicable to all the results. In other hand, the theoretical Qel did not give acceptable values when compared to the experimental ones. The trend with equilibrium biosorption capacity with concentration of NaOH modified (PCP, PCP0,05, PCP0,1) was similar to the trend in experimental equilibrium capacity. But this cannot be seen by observing the values of correlations, R2 therefore, the reaction involved in present biosorption system is not of the first order. The pseudo-first order kinetics does not sufficiently describe the whole range of whole range of kinetic data.

The pseudo-second-order kinetic model was suitable for all the data. The results are shown in Table 2. The pseudo-second-order predicted Qell (mg/g) are the most agreeing values with the experimental dat. The equilibrium capacity values for the pseudo-second order model were higher than for the pseudo-first order and the modified pseudo-first order kinetic models. The equilibrium capacities were higher for PCP 0.1 than for PCP 0.05 and least for PCP Raw. The pseudo-second order rate constant, k2, were found to increase with NaOH pretreatment and with NaOH concentration. The values of k2 were much higher for the PCP 0.05 and PCP 0.1 than for the PCP raw. Thus, these results suggest that the pseudo-second-order model, based on the assumption that the rate limiting step might be chemical biosorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate, and provides the best correlation of the data [5, 6, 26].

Intraparticle diffusion model parameters for the effect of 50 mg/L concentration are shown Table 2. As shown in Table 2, the rate constant (kp; g/mg min) increased from 0.280 to 0.345, when the concentration of NaOH was raised from 0.05 to 0.1M. These results indicate that increasing NaOH concentration increases the intraparticle diffusion.

3.5 Sorption Isotherms

Sorption isotherms can be described by mathematical expressions such as the Langmuir and Freundlich equations [27]. The sorption process is then discussed in terms of constants that are characteristic of the individual systems. The Langmuir equation assumes that there is no interaction

between the adsorbate molecules and that the sorption is localized in a monolayer. The Freundlich equation is an empirical relationship that describes the sorption of solutes from a liquid to a solid surface [28].

The Langmuir model was originally developed to represent monolayer sorption on a set of distinct, localized sorption sites. It gives uniform energies of monolayer sorption onto the sorbent surface with no transmigration of sorbate in the plane of the surface. There are no interactions between the sorbed molecules, no steric hindrance between sorbed molecules and incoming ions, and all the sorption sites are alike and uniform on a microscopic scale [28]. The sorption data is applied to the following linearized form of the Langmuir isotherm:

$$\frac{1}{q_e} = \frac{1}{Q^m} + b\frac{1}{C_e} \tag{3}$$

The magnitude of Q^m indicates the amount of ammonium per unit weight of sorbent required to form a complete monolayer on the surface. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless, constant, separation factor or equilibrium parameter R_L [29]. The maximum monolayer adsorption capacity obtained for CPC 0.1, CPC 0.05, and CPC were 6,150, 2,275, 0,165 mg/g, respectively.

The essential characteristics of Langmuir isotherm have been described by the dimensionless separation factor or equilibrium constant, R_L which is defined as

$$R_L = \frac{1}{(1 + bC_0)} \tag{4}$$

where Co is the initial concentration (mg/I), and b is the Langmuir constant. This indicates the nature of adsorption as

RL > 1 unfavourable

RL = 1 linear

0<RL < 1 favourable

RL = 0 irreversible

The values of range (0.011-0.191) indicate that sorption is highly favorable for all the samples in this study.

Freundlich isotherm

The Freundlich isotherm is derived by assuming a heterogeneous surface (multilayer adsorption) with a non-uniform distribution of heat of adsorption over the surface. This isotherm assumes that the adsorption sites are distributed exponentially with respect to the heat of adsorption and is given by

$$q_e = K_f C e^{1/n} \tag{5}$$

The ammonium sorption isotherm followed the linearized Freundlich model. The relationship between the sorption capacity of biomass for ammonium and the residual ammonium concentration at equilibrium is given by:

$$\log q_e = \frac{1}{n}\log Ce + \log K_f \tag{6}$$

where K_f (mg g^{-1}) and $1/n$ relates the multilayer adsorption capacity and intensity of adsorption, $1/n$ also known as the heterogeneity factor. Freundlich coefficients are shown in Table 3. The values of $1/n$ were also found to be less than 1 for all the samples, signifying again that adsorption is favourable.

Table 3 . Soption ishoterms constants for ammonium onto pine cone powder.

|	Langmuir			Freundlich		
	Qm	B	R^2	1/n	K$_f$	R^2
PCP	0,165	2,092	0,7189	0,362	0,9323	0,5955
PCP0.05	2,275	1.778	0,9674	0,404	0,1236	0,4820
PCP0.1	6,150	0,413	0,9757	0,435	0,8789	0,6488

The Langmuir and Freundlich adsorption constants estimated from the isotherms at room temperature (22±0.5°C) and the corresponding correlation coefficients are listed in Table 3. The highest regression correlation coefficient (0.9757) was observed for PCP0.1 in Langmuir model. This indicates that the Langmuir model was the most suitable for describing the biosorption equilibrium of ammonium onto pinecone powder. This result indicates the formation of monolayer coverage of ammonium molecules at the outer surface of the sorbent. The maximum adsorption capacity (Qm) determined from the Langmuir isotherm was calculated to be 6,150 mg/g for PCP0.1 (Table 3). This relatively high adsorption capacity shows the strong electrostatic force of attraction between the ammonium molecules and the biosorbent bending- sites [30].

Furthermore, in order to situate the raw pinecone powder among the raw mineral adsorbents used to remove ammonium ions from aqueous solutions, a comparison based on Langmuir saturation capacity, Qm, has been made and indicated that the sawdust (0.165 mg/g) was not more efficient than soils (0.28, 0.9 mg/g) [31]; sawdust (1.7 mg/g) [5]; sepiolite (1.47 mg/g) [32] and some zeolites (0.9 mg/g) [21] (1.27 mg/g) [33], and could be considered as a promising material to remove ammonium even when compared with some efficient zeolites as Natural Chinese clinoptilolite (2.02 mg/g) [33], Chabazite (2.94 mg/g) [34]. It should be noted that our study used raw have a lower surface area. The treatments of pine cone powder (6.150) were more efficinet than these materials. The treatments of pine cone powder with NaOH can be improve the adsorption process by increasing the surface area and causing the liberation of new adsorption sites on the pine cone powder surface.

### 3.6 Surface characterization

3.6.1 SEM and EDS analysis

Powder XRD pattern of the samples were recorded over the at 2θ = 10–80◦ range and XRD patterns are shown in Fig. 4. All of the samples display sharp crystalline peaks indicating their crystalline nature and do not exhibit well-defined crystalline peak (2θ = 22o) due to their amorphous nature. The average crystallite sizes of the samples calculated using Scherre's formula. The samples have an average crystallite size between 50nm and 52nm, suggesting that the complexes are in nanocrystalline phase.
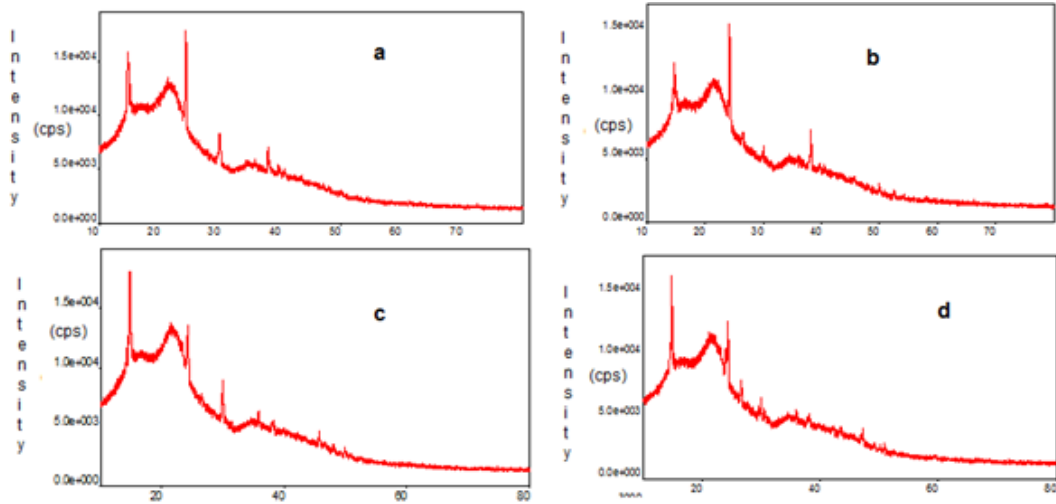
Figure 4. XRD pattern of pine cone powder samples. (a) PCP, before the biosorption of ammonium. (b) PCP0.1, before the biosorption of ammonium (c) PCP, after the biosorption of ammonium (d) PCP0.1 after the biosorption of ammonium.

The surface morphology of the samples is observed by SEM and are shown in Fig. 5. SEM micrographs were taken at 1kV accelerating voltage and magnification was fixed according to x1000. It is not determined to different from the morphology of the samples by SEM. There is not clear indicator adsorbed ammonium on pine cone powder in SEM pictures. Energy dispersive spectroscopy (EDS) allows determining the chemical composition of the samples. Therefore, the compositions the samples were defined by EDS analysis. EDS spectrums and the chemical composition of the pine cone powder samples are shown in Fig. 6 and Table 4, respectively.
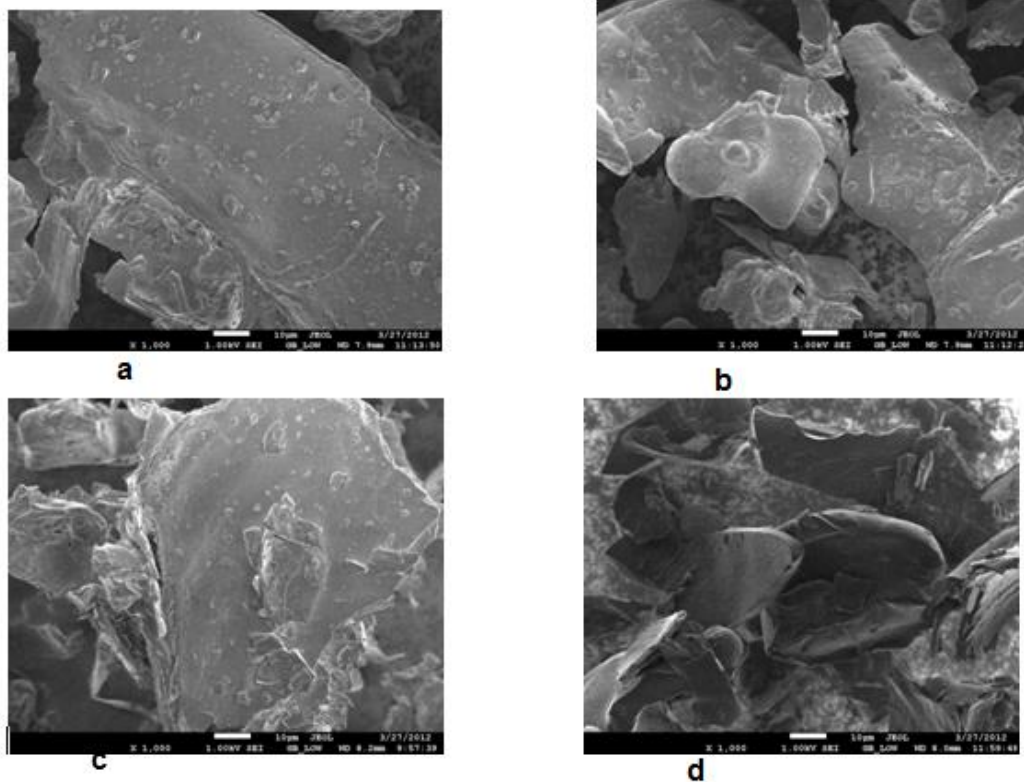
Figure 5. SEM picture of pine cone powder samples. (a) PCP, before the biosorption of ammonium. (b) PCP0.1, before the biosorption of ammonium (c) PCP, after the biosorption of ammonium (d) PCP0.1 after the biosorption of ammonium
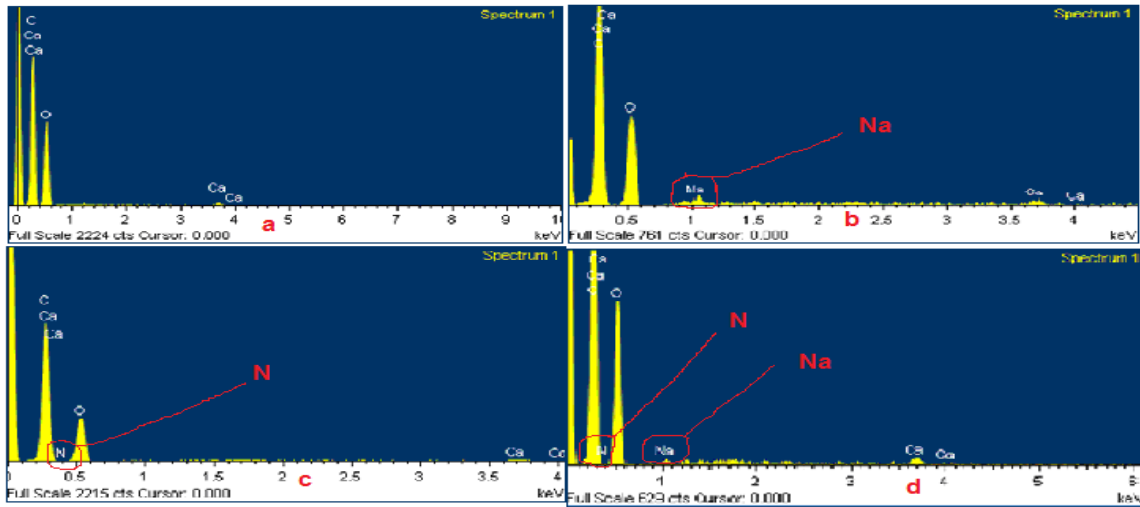
Figure 6. EDS spectrums of pine cone powder samples. (a) PCP, before the biosorption of ammonium. (b) PCP0.1, before the biosorption of ammonium (c) PCP, after the biosorption of ammonium (d) PCP0.1 after the biosorption of ammonium

Table 4. The chemical composition of the pine cone powder samples

Elements	PCP before the biosorption of ammonium (%wt)	PCP0.1 before the biosorption of ammonium (%wt)	PCP after the biosorption of ammonium (%wt)	PCP0.1 after the biosorption of ammonium (%wt)
C	50.54	57.34	53.67	52.16
O	48.83	41.10	39.36	38.66
Ca	0.63	0.74	0.50	0.78
Na	-	0.82	-	0.17
N	-	-	6.47	8.23

4 CONCLUSIONS

1.It was found that the biosorption capacity was optimal using 6–10 solution pH range and the rate of sorption was very fast, during the first 15 minute. 2. Biosortion can be described by a pseudo-second-order model predicting a chemisorption process. 3. The equilibrium data were well characterized by the Langmuir isotherm model, which confirmed the mono-layer coverage. 4. The results showed that pine cone surface was modified by sodium hydroxide treatment. 5. Engineering studies to develop this biosortion ammonium currently going on in our laboratory. 6. The results of this study show that pine cone powder is an efficient material for the removal of ammonium and may be used a permeable. The use of pinecone powder presents an interesting option for both tertiary wastewater treatments (as a possible non-conventional biosorbent for the removal of ammonium.

5 References

[1] S.H. Lin, C.L. Wu. Ammonia Removal from Aqueous Solution by Ion Exchange. Ind. Eng. Chem. Res. 35 (1996) 553-558.

[2] L.R. Cooperband, L.W. Good, Biogenic phosphate minerals in manure: implications for phosphorus loss to surface waters. Environmental Science and Technology. 36 (23) (2002) 5075-5082.

[3] A.M. Yusof, L.K. Keat, Z. Ibrahim, Z.A. Majid, N.A. Nizam, Kinetic and equilibrium studies of the removal of ammonium ions from aqueous solution by rice husk ash-synthesized zeolite Y and powdered and granulated forms of mordenite. Journal of Hazardous Materials. 174 (2002) 380–385.

[4] H. Zheng, L. Hanb, H. Maa, Y. Zheng, H. Zhang, D. Liu, S. Liang, Adsorption characteristics of ammonium ion by zeolite 13X. J. Hazard. Mater. 158, (2008) 577–584.

[5] M.A. Wahab, S. Jellali, N. Jedidi, Ammonium biosorption onto sawdust: FTIR analysis, kinetics and adsorption isotherms modeling. Bioresource Technology. 101 (2010a) 5070–5075

[6] M.A. Wahab, S. Jellali, N. Jedidi,. Effect of temperature and pH on the biosorption of ammonium onto Posidonia oceanica fibers: Equilibrium, and kinetic modeling studies. Bioresource Technology. 101 (2010b) 8606–8615.

[7] P. Vassileva, P. Tzvetkova, R. Nickolov, Removal of ammonium ions from aqueous solutions with coal-based activated carbons modified by oxidation. Fuel 88 (2008) 387–390.

[8] H. Huang, X. Xiao, B. Yan, L. Yang, Ammonium removal from aqueous solutions by using natural Chinese (Chende) zeolite as adsorbent. J. Hazard. Mater. 175 (2010) 247–252.

[9] M. Uğurlu, H. Karaoğlu, Adsorption of ammonium from an aqueous solution by fly ash and sepiolite: Isotherm, kinetic and thermodynamic analysis. Microporous and Mesoporous Materials 139 (2011) 173–178

[10] D. Karadag, Y. Koc, M. Turan, B. Armagan, Removal of ammonium ion from aqueous solution using natural Turkish clinoptilolite. J. Hazard. Mater. B 136 (2006) 604–609.

[11] Z.Y. Ji, J.S. Yuan, X.G. Li, Removal of ammonium from wastewater using calcium form clinoptilolite. J. Hazard. Mater. 141 (2007) 483–488.

[12] N. Karapınar, Application of natural zeolite for phosphorus and ammonium removal from aqueous solutions. J. Hazard. Mater. 170 (2009) 1186–1191.

[13] S. Wang, Y. Peng, Natural zeolites as effective adsorbents in water and wastewater treatment. Chem. Eng. J. 156 (2010) 11–24.

[14] H.A. Aziz, M.N Adlan, M.S.M. Zahari, S. Alias, Removal of ammoniacal nitrogen (N–NH3) from municipal solid waste leachate by using activated carbon and limestone. Waste Manage. Res. 22 (5) (2004) 371–375.

[15] S. Ahsan, S. Kaneco, K. Ohta, T. Mizuno, K. Kani, Use of some natural and waste materials for wastewater treatment. Water Res. 35 (15) (2001) 3738–3742.

[16] A.E. Ofomaja, E.B. Naidoo, S.J. Modise, Removal of copper(II) from aqueous solution by pine and base modified pine cone powder as biosorbent. J. Hazard. Mater. 168 (2009) 909–917.

[17] STANDARD METHODS, for the examination of water and wastewater, 2005

[18] M. Dogan, M. Alkan, Adsorption kinetics of methyl violet onto perlite. Chemosphere. 50 (2003) 517–528.

[19] Y. Nuhoglu, E. Oguz, Removal of copper(II) from aqueous solutions by biosorption on the cone biomass of Thuja orientalis. Process Biochemistry. 38 (2003) 1627-1631

[20] T.Y. Chan, Ammonia removal in wastewater with anaerobic ammonium oxidation process.(Thesis in The Department of Bulding, Civil and Environmental Enginnering) Concordia University, Montreal, Quebec, Canada (2003).

[21] A. Thornton, P. Pearce, S.A. Parsons, Ammonium removal from solution using ion exchange on to MesoLite, an equilibrium study. J. Hazard. Mater. 147 (2007) 883–889.

[22] D. Wu, B. Zhang, C. Li, Z. Zhang, H. Kong, Simultaneous removal of ammonium and phosphate by zeolite synthesized from fly ash as influenced by salt treatment. J. Colloid Interface Sci. 304 (2006) 300–306.

[23] K. Okada, Y. Ono, Y. Kameshima, A. Nakajima, K.J.D. MacKenzie, Simultaneous uptake of ammonium and phosphate ions by compounds prepared from paper sludge ash. J. Hazard. Mater. 141 (2007) 622–629.

[24] Z.Y. Ji, J.S. Yuan, X.G. Li, Removal of ammonium from wastewater using calcium form clinoptilolite. J. Hazard. Mater. 141 (2007) 483–488.

[25] K. Mohanty, M. Jha, B.C Meikap, M.N. Biswas, Biosorption of Cr(VI) from aqueous solutions by Eichhornia crassipes, Chem. Eng. J. 117 (2006) 71-77.

[26] V. Vadivelan, K. Kumar, Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk, J. Colloid Interf. Sci. 286 (2005) 90–100.

[27] P.W. Atkins, Physical Chemistry, Oxford University Press, Oxford, 1978.

[28] A. Demirak, Ö. Dalman, E. Tilkan, D. Yıldız, E. Yavuz, C. Gökçe, Biosorption of 2,4 dichlorophenol (2,4-DCP) onto Posidonia oceanica (L.) seagrass in a batch system: Equilibrium and kinetic modeling.MİCROCHEMİCAL Journal 99 (2010) 97-102.

[29] Z. Aksu, J. Yener, A comparative adsorption/biosorption study of monochlorinated phenols onto various sorbents, Waste Manag. 21 (2001) 695–702.

[30] P. Kaewsarn, Q. Yu, Cadmium removal from aqueous solutions by pretreated biomass of marine algae Padina sp.. Environ. Pollut. 112 (2001) 209–213.

[31] W.A.R.N. Fernando, K. Xia, C.W. Rice, Sorption and desorption of ammonium from liquid swine waste in soils. Soil Sci. Soc. Am. J. 69 (2005) 1057–1065.

[32] M.P. Bernal, J.M. Lopez-Real, Natural zeolites and sepiolite as ammonium and ammonia adsorbent materials. Bioresour. Technol. 43 (1993) 27–33.

[33] Y. Wang, S. Liu, Z. Xu, T. Han, S. Chaun, T. Zhu, Ammonia removal from leachate solution using natural Chinese clinoptilolite. J. Hazard. Mater. B 136 (2006) 735–740.

[34] O. Lahav, M. Green, Ammonium removal using ion exchange and biological regeneration. Water Res. 32 (7) (1998) 2019–2028.