



Bayesian Analysis of a CFD Model to the Absorption of Ammonium Concentrations in Zeolite

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Abstract In recent years it has been considered absorption ammonium zeolite for obtaining hydrogen. For which it is important to know the best gravimetry and optimal concentration of ammonium used in zeolite-based devices. In this research, ammonio at 5, 10 and 15 g/l through three different gravimetries of zeolite were simulated by Computational Fluid Dynamics, to measure its performance as ammonium remover. The zeolite was activated with NaCl at 200 °C with the aim of presented better physical and chemical characteristics. The laboratory results allowed us to obtain the initial values and to develop the calibration computer models. The results obtained by the models showed that the concentration of 10 g/L and particle zeolite size between 1.00 mm to 1.55 mm, were the most effective values in absorbing ammonium. To increase the performance to ammonium absorption process, we apply a multivariate analysis method based in Bayesian networks, in order to obtain inferences and determine the variables of greatest significance in the absorption of ammonia process. Analysis by Bayesian networks, using Naïves Bayes determined that the height of the device simulated had influencia to absorption.

Keywords Bayesian networks, heuristic models, CFD, ammonium

Introduction

Natural zeolites are used in the treatment of wastewater from urban areas, industrial and agriculture areas, and circulating water systems for ammonia removal. The large cation exchange capacity of zeolites is due to unbalanced loads that will attract the nearest to maintain neutrality cation. The catalytic property is related mainly with the active surfaces of the structure of zeolites with internal passages and vacuum system, the size of the internal cavities and cation exchange properties. Several industrial plants use zeolite: what the ammonium concentration in the effluent is reduced from 15 ppm to 2 ppm [1].

Rezazakemi *et al.*, [2] simulated by a stationary 2D CFD model, a hollow membrane for removing ammonia in aqueous solution, estimating the concentration distribution. They were considering parameters such as feed rate, feed concentration and pH on the elimination of amñaco. The simulation results showed that the model developed can be used to evaluate the effective parameters involving the removal of ammonia by means of membrane contactors.

Other studies were performed by Mandowara and Bhattacharya [3] for removing ammonia water through a selective membrane. They obtained correlation between simulation results and experimental data for a contactor



75 fibers. They obtained correlation between the simulation results and data generated in the laboratory from a contactor containing 10,200 fibers was also observed. The model predicts the free fraction of ammonia.

A novel model was developed to simulate ion transport through porous media by Ghadiri *et al.* [4]. The model is based on equations derived mass transfer and momentum of solute in all phases, including food, solvent and membrane by CFD. The simulation results showed the velocity profile, pressure and solute concentration.

In a study by Tahvildari *et al.*, [5] on the modeling and simulation of a membrane that absorbs CO₂ by aqueous 2-amino-2-methyl-1-propanol (AMP) as an absorbent, the results revealed that the increase speed of solvent improves the removal of CO₂ in the contactor hollow fiber membrane. Moreover, it was found that the mode of counter-current process is more favorable to achieve the highest efficiency of separation.

A VOF (volume of fluid) method was presented by Liu *et al.*, [6], for predicting the flowing process of two-phase countercurrent falling film. Three important momentum source terms, including interface shear stress, surface tension and porous medium source term, are considered. On the basis of using a CFD model to simulate the influence of viscosity, surface tension and flow resistance, the results show that the viscosity and the surface tension have great influence on the thickness and the fluctuation of liquid film which further affect the mass transfer coefficient, and that high flow resistance will cause liquid membrane rupture which interferes with the mass transfer.

In general have been enormous efforts devoted to the analysis of ammonium absorption using CFD, however, CFD models are not allowing us to understand the relationships of variables involved and therefore a total process optimization. Thus the aim of this study was to evaluate the particle size of zeolite as a filter at three different concentrations of NH₃, using Bayesian analysis of a stationary CFD model developed and validated using laboratory data; to determine the best features for the design of a hydrogen generating device.

Theory

Expected probability distribution of output variables (eq. 1) is determined by the algorithm of solution of the BN. This technique has been used to identify relationships between seemingly indeterminate variables, describing and quantifying these relationships even with a set of missing data [7, 8].

$$P(x_1, \dots, x_n) = \prod_{i=1}^n P(x_i | \text{parents}(x_i)) \quad (1)$$

The result of this calculation (eq. 2) depends on the probability distribution of the input variables. BN is a joint probabilities distribution of a collection of discrete random variables [9].

$$P(c_j | x_i) = P(x_i | c_j) P(c_j) / \sum_k P(x_i | c_k) P(c_k) \quad (2)$$

The aim of BN structure learning is to find a configuration that best describes the observed data. Statistical machine learning methods have been applied in the Bayesian statistics; however, machine learning can employ a variety of classification techniques to produce models other than BN. The number of possible structures of direct acyclic graph for searching is exponential in the number of variables in the domain (eq.3). Machine learning can be seen as an attempt to automate some parts of the scientific method by mathematical methods.

$$f(n) = \sum_{i=1}^n (-1)^{i+1} C_i^n 2^{i(n-i)} f(n-i) \quad (3)$$

In supervised learning algorithm produces a function that establishes a correspondence between inputs and desired outputs of the system, using a node class. In unsupervised learning all the modeling process is carried out on a set of examples formed as just by logging into the system. The simple Bayesian classifier (Naive Bayes classifier, NBC) assumes that attributes are independent of each other given the class and the probability. We can be obtained by the product of the individual conditional probabilities each attribute given the class node.

When we have complete and sufficient data for all variables in the model, is relatively easy to obtain parameters, assuming the structure is given. The most common method is called maximum likelihood estimator (EM) under which the probabilities based on the frequency data are estimated.



The most representative method of the score-and search based approach is the K2 algorithm. The algorithm starts by assigning each variable without dependent relationships (parents). It then incrementally adds a parent to the current variable which mostly increases the score of the resulting structure. When any addition of a single parent cannot increase the score, it stops adding parents to the variable. Since an ordering of the variables is known beforehand, the search space under this constraint is much smaller than the entire structure space, and there is no need to check cycles in the learning process. If the ordering of the variables is unknown, we can search over orderings [10, 11].

Materials and Methods

Laboratory work was consisted to evaluate the removal of ammonium ion exchange zeolite clinoptilolite type used for wastewater treatment. We conducted the experiment concerns in a device formed by two columns ammonia solution to three different concentrations: 5, 10 and 15 g / l. The activation process of the zeolite was carried out in the device sonochemistry ULTRA-sonik, where three different concentrations of NH_4Cl were mixed: 5, 10 and 15 g / l in distilled water and mixed 5 g of Zeolite different gradings:

- Mesh 4-6: (3.05 - 4.75 mm)
- Mesh 6-12: (1.55 - 3.05 mm)
- Mesh 12-30: (1.00- 1.55 mm)

The effluent was treated by ion exchange with natural zeolite clinoptilolite type of the San Francisco mine in San Luis Potosi, Mexico. The zeolite was preconditioned with sodium chloride (NaCl) to transform its homoionic sodium form, in order to increase the ion exchange capacity [1].The washed about 928 g of zeolite, corresponding to the two columns of PVC (Figure 1), subsequently sonicated (ULTRA-sonik) with a 1 M NaCl solution for 30 minutes. After washed three times samples with deionized water, and heated at 200 °C for one hour to the final drying process.

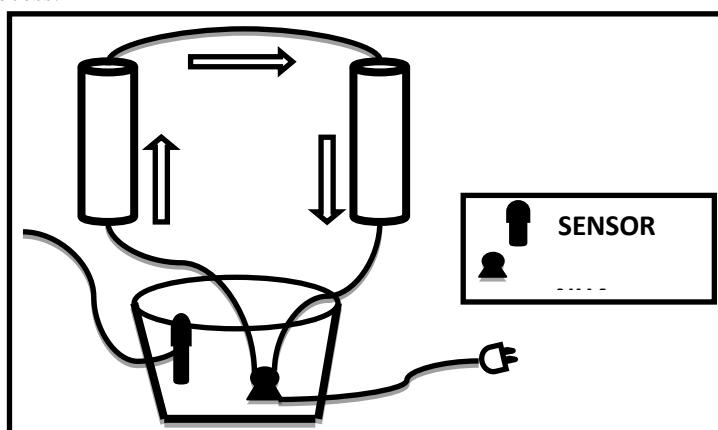


Figure 1: Two columns of PVC device of zeolite

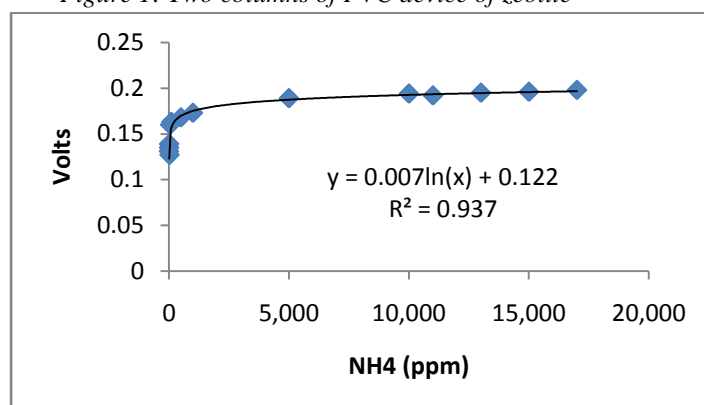


Figure 2: Calibration curve ammonia sensor



For measurements of ammonium, we employ an electrode Ammonium ion selective membrane made of a PVC, which measures ammonium ions in aqueous solutions in a range concentration of 1 M to 5×10^{-6} or 0.1 ppm to 18,000 ppm, with resolution (12 bits) equal to 0.15 mV, pH 4 – 10, 0 – 50°C of temperature, and reproducibility $\pm 4\%$.

Once the solutions for the calibration curve (Figure 2) was obtained, we began to take reading with the sensor, ISA (NaCl) solution to all solutions to ensure that samples and standards have the same ionic strength is added, it was performed repeatedly until data were repetitive.

To analyzing the relationship between variables, we used ELVIRA system v 0.162 in three stages, suggested by Ortiz-Vazquez [12]:

- It is carried out using the algorithm of allocation "to mean" to complete the series of partial data. This algorithm replaces lost or unknown values, the mean values for each variable. This method requires no limits and involves discretizing the massive data by the algorithm using six intervals with the same frequency.
- According to De la Torre-Gea *et al* [13], the best Bayesian network structure is developed using K2 algorithm with 5 parents and without restrictions.
- We performed dependency analysis to get the topological structure of the network, which represents the causal variables and their dependencies. After obtaining a parametric learning network, we calculated the conditional probabilities variables that show the relationship or dependence.

Results and Discussion

The results of the work done in the laboratory indicate that the amount of NH_4 absorbed by the zeolite increases exponentially with decreasing size of the particles form; to reason expressed in the equation 4.

$$y = 663650e^{-1.679x} \quad (4)$$

The catalytic property is related mainly with the active surfaces of the structure of zeolites with internal passages and vacuum system, the size of the internal cavities and cation exchange properties, as shown in Fig 4. These findings are consistent with the results obtained by Leyva *et al.* [14].

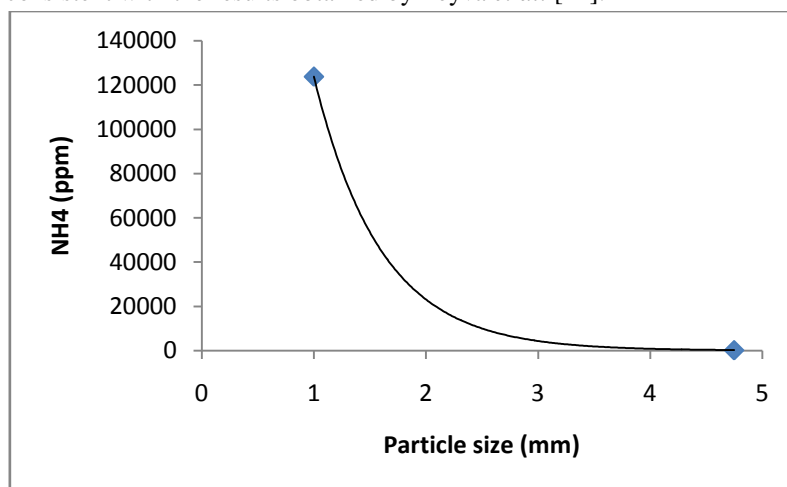


Figure 3: Evaluation of granulometry about absorption of ammonia in 100 minutes

The zeolite particle size equal to 1.0 mm absorbed NH_4 an amount from a urea solution at different concentrations, relative to equation 5.

$$y = -0.233x^2 + 5.495x - 11.65 \quad (5)$$

Ammonium absorption obtained from the zeolite, consistent with studies by Prajapathi *et al.* [1], and whose values are shown in Figure 4.



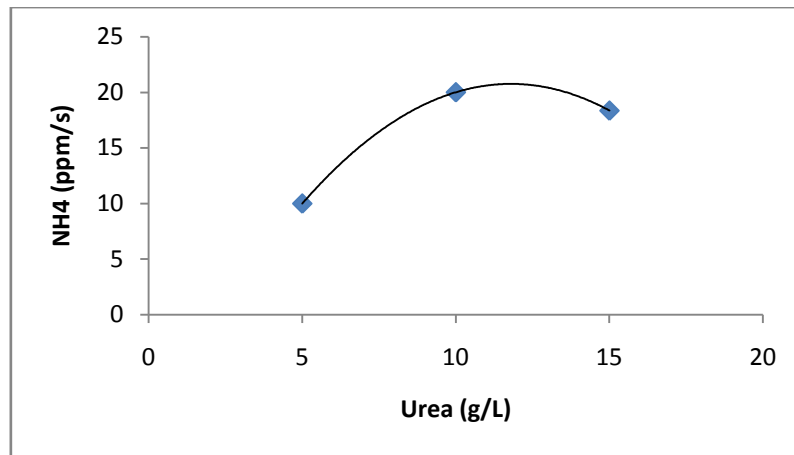


Figure 4: Evaluation of the urea concentration about absorption of ammonium

By the results obtained in the laboratory, we enhance the calculations to obtain the data shown in Table 1, which served for use as initial values for the CFD model.

Table 1: Velocity absorption.

	Zeolite size (mm)	
	4.75	1.0
Velocity absorption (ppm/s)	0.038	20.0

We perform numerical approximation using CFD for a prediction model of the physical conditions present in the ammonia absorption process. Table 2 shows a summary of the boundary conditions and initial values CFD model. The results of the CFD approach are shown in Figure 5.

Table 2: Summary of configuration to the CFD model

	Description	Magnitude
Solver	3D Simulation	
	Double Precision	
Type of model	Steady state	
Type of mesh	Automatic	Patch
	Conforming/Sweeping	
	Minimum size of elements	0.15 m
	Number of elements	650,801
Viscosity	K-ε with buoyancy (2ecuaciones)	
	C1-Epsilon	1.44
	C2-Epsilon	1.92
Energy equation	Active	
Zeolite simulation	Porous media	0.1, 0.5 and 1.0
Domain inlet	Inlet velocity	0.1 m s ⁻¹
	Kinetic energy Turbulence	1.0 m ² /s ²
	Dissipation rate Turbulence	1.0 m ² /s ²
	Temperature	300°K
	NH ₃ Concentration	0.02 g/L
	Urea CO ₂ (NH ₂) ₂	0.03g/L
Domain outlet	Outlet presion	2.015e ⁻⁶ Pa
	Kinetic energy turbulent	1.0 m ² /s ²
Physical properties of materials		
	Air	Aluminium



Density (kg m ³)	1.22	1400
Specific heat (J K ⁻¹ °K ⁻¹)	1006.43	1738
Thermal conductivity (W m ⁻² k ^{o-1})	24.2 e ⁻³	1.5
Thermal Expansion coefficient °k ⁻¹	3.389 e ⁻³	
Species transported	Urea water	
Thermal conductivity	0.0454 w/m-k	
Viscosity	1.72 e-05 kg/m-s	
Mass diffusivity	2.88 e-5 kg/m-s	
Thermal diffusion coefficient	-8e-06 t + 6 e-05 kg/m-s	

The CFD model is divided into three columns; the first from top to bottom represents the fluid inlet to the system, the second section represents a porous medium with the characteristics of the zeolite determined by equations 4 and 5, and the third column representing the fluid outlet domain. In Figure 5 we show the graphical results of the CFD model. In Figure 5 we show the graphic results of the CFD model of interest according to Bayesian analysis described below. The figures show that the column constituting the zeolite filter influences the dynamics of the system in the first 10 cm of its length.

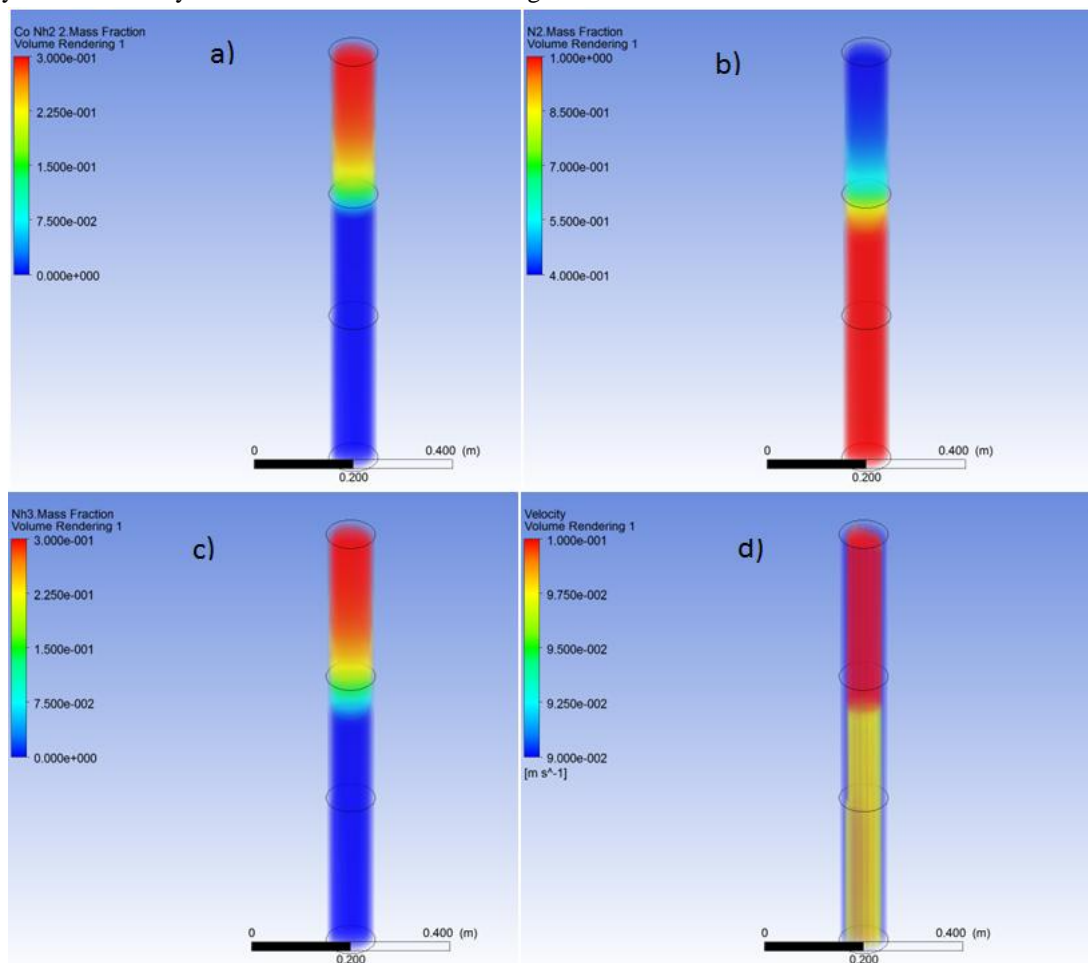


Figure 5: Results of CFD model: a) Urea, b) N₂, c) NH₃, and d) Velocity

The numerical results of the CFD model were employed to perform Bayesian analysis; the results are shown in Figure 6. We built a model classic naïve Bayes with all predictor variables, ie, it is assumed that the predictor variables are conditionally independent given the class. With this results, we proceeded to the analizys used the software Elvira to determine the BN model structure. This proccess was made with *non-supervised classification* method (6-a); we show the result of unsupervised clustering or classification, where the class node establishes a bridge between the variables relating them according to Bayes' theorem. The tables indicate the



variables and vectors dependency ratios; red are direct relationships, and blue color is inverse relationships. Vectors black color indicates independence.

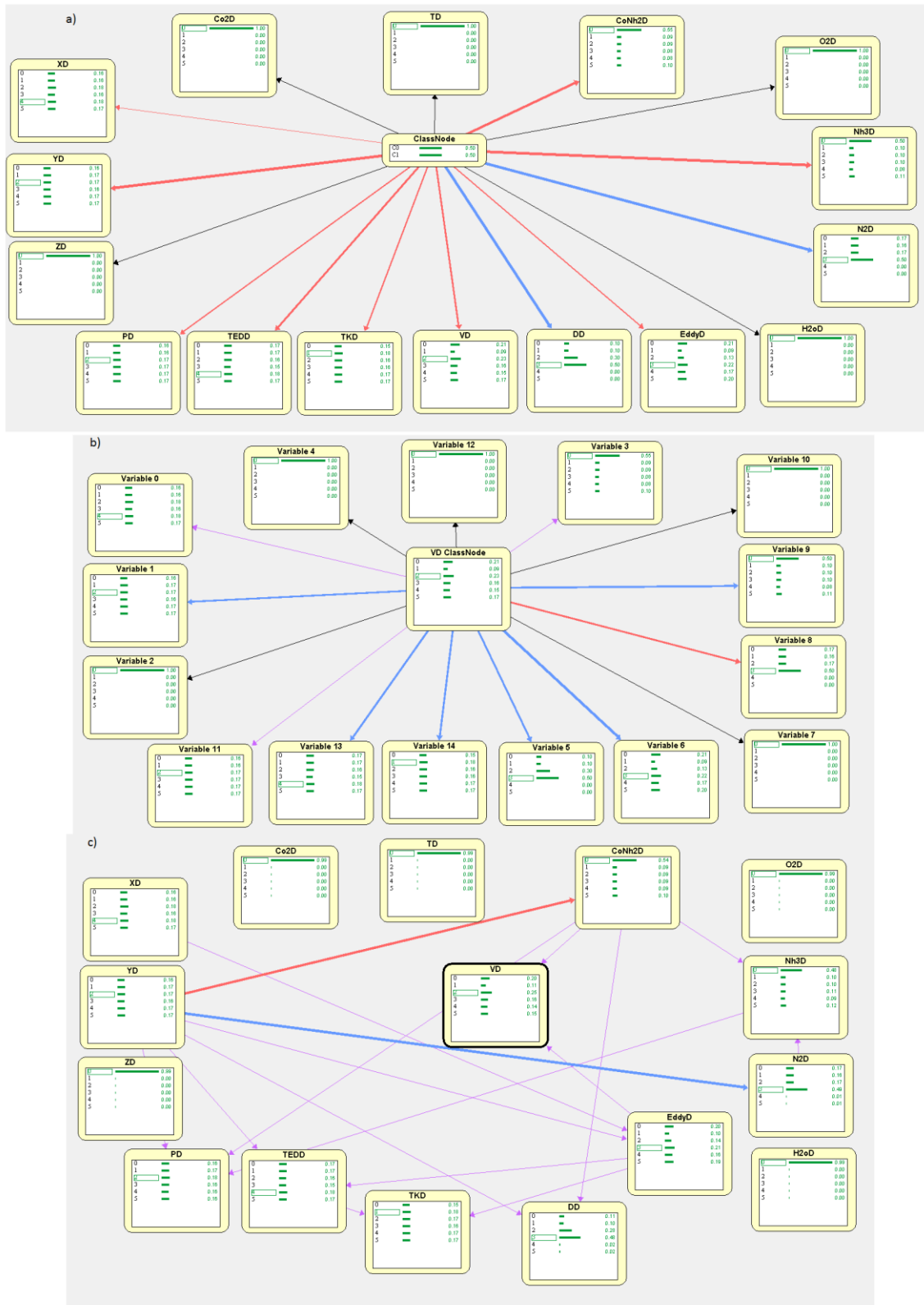


Figure 6: Bayesian networ: a) supervised model b) non-supervised model and c) K2 algorithm



Urea concentrations (Co NH_2) and ammonium (NH_4) are intrinsically related to the process and the filter length where attachment takes place. Other variables such as pressure (P), turbulence (TED), turbulence kinetic (TK), dissipation of turbulence (Eddy) and velocity (V) have less dependence. The variables gaseous nitrogen (N_2) and temperature (T) are related inversely with the above variables.

Figure 6-b, which corresponds to a supervised classification Naïve Bayes model EM, we show that the variable V is the susceptible to changes in the values of the other variables. However, when the input speed is large, the absorption decreases and ammonium nitrogen is released as N_2 .

Figure 6-b, which corresponds to a supervised classification Naïve Bayes model EM, we show that the variable V is the susceptible to changes in the values of the other variables. However, when the input speed is large, the absorption decreases and ammonium nitrogen is released as N_2 . Other variables such as density (D) and turbulence tend to decrease with increasing speed; so this variable is critical in the process of absorption of ammonium and can be monitored by measuring and density.

When we use the Bayesian classifier by factorization, using the K2 algorithm (Figure 6-c), we note that the length of the zeolite filter sets the inversely proportional relationship between the released nitrogen (N_2) and Urea (CONH_2); It is indicating that absorption ammonium performed in the first 10 centimeters of the filter.

It is important to consider that the scope of this work involves a stationary model, based on the characteristics of the zeolite in a maximum time of 100 minutes. Therefore, we recommend performing dynamic models that consider a longer interval of time.

Conclusion

We concluded that the concentration of 10 g / l activated with NaCl has good absorption and can be used by removing ammonium commonly found in wastewater. The CFD model helped us to establish physical conditions that we could not be measured by sensors and are important in determining the critical variables that can define the design of devices that absorb ammonia. The size of the particles of the zeolite used as a filter can be increased more than 500 times the absorption ammonium. The input speed is a critical variable that must be maintained to optimize the absorption process ammonium. Bayesian Network method permit us determine relationships between variables considered independent with classic statistical methods. We recommend that further studies should be performed with dynamic models that consider a larger time interval for the design of new sensors ammonium devices.

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References

- [1]. Prajapati, J.C., Syed, H. S. Jagdiah Chahuan, J. (2014). Removal of Ammonia from wastewater by ion exchange technology. *International Journal of Innovative Research in Technology*. 1(9):6–11.
- [2]. Rezakazemi, M., Shirazian, S., Ashrafizadeh, S.N. (2012). Simulation of ammonia removal from industrial wastewater streams by means of a hollow-fiber membrane contactor, *Desalination*, Volume 285 (31): 383-392.
- [3]. Mandowara, A., Bhattacharya, P.T. (2011). Simulation studies of ammonia removal from water in a membrane contactor under liquid–liquid extraction mode. *Journal of Environmental Management*. Volume 92 (1): 121-130. ISSN 0301-4797.
- [4]. Ghadiri, M., Asadollahzadeh, M., Hemmati, A. (2015). CFD simulation for separation of ion from wastewater in a membrane contactor. *Journal of Water Process Engineering*. Volume 6: 144-150.
- [5]. Tahvildari, K., Reza Razavi S.M., Tavakoli, H., Mashayekhi, A., Reza Golmohammadzadeh. (2016). Modeling and simulation of membrane separation process using computational fluid dynamics. *Arabian Journal of Chemistry*. Volume 9, (1): 72-78.
- [6]. Liu, C., Xiao, J., Wang, H., Qiu, T. (2013). CFD simulation of cyclohexene hydration process with two-phase flow. College of Chemistry and Chemical Engineering, Fuzhou University.



- [7]. Hruschka E, Hruschka E, Ebecken N F F, Bayesian networks for imputation in classification Problems, *J Intell Inform Syst*, 29 (2007) 231.
- [8]. Reyes P, Bayesian networks for setting genetic algorithm parameters used in problems of geometric constraint satisfaction, *Intel. Artificial*, 45 (2010) 5.
- [9]. Garrote L, Molina M, and Mediero L. Probabilistic Forecasts Using Bayesian Networks Calibrated with Deterministic Rainfall- Runoff Models, in Vasiliev *et al.* edited by *Extreme Hydrological Events: New Concepts for Security* (Springer) 2007, 173.
- [10]. Borunda, M., Jaramillo, O. A., Reyes, A., Ibargüengoytia, P.H. (2016). Bayesian Networks in Renewable Energy Systems: A Bibliographical Survey. *Renewable and Sustainable Energy Reviews*, 62; 32–45.
- [11]. Guoian, L. Knowledge Discovery with Bayesian Networks, Ph. D. thesis, National University of Singapore, Singapore, 2009.
- [12]. Ortiz-Vazquez, I.C., Pérez-Robles, J.F., Fernandez-Loyola, R., Pérez-Brito, J.F., and De La Torre-Gea, G.A. (2015). A Multivariable Computational Fluid Dynamics Analysis Method based in Bayesian Networks Applied in a Bioreactor. *Journal of Applied Chemical Science International*, 6(1), 10 – 17.
- [13]. De la torre-Gea, G., García-Manzo, G., De la Vega-Flatow J.N., Martínez-Alcaráz S. L., Quijada-López, R.M., Rodríguez-Reyes, C.S. (2016). Determination of relationship patterns in EEG and BVP signals using the K2 learning algorithm. *Ponte Journal*, 72 (3): 22 – 32.
- [14]. Leyva-Ramos, R., Berber-Mendoza, M.S., Mendoza-Barrón, J., Aragón-Piña, A. (2004). Pb ion exchange (ii) in aqueous solution on cation exchange modified clinoptilolite. *Journal of the Mexican Chemical Society*. 48(2); 130-136.

