ADSORPTION OF AMMONIA IONS AND AMMONIUM FROM AQUEOUS SOLUTIONS ON MODIFIED ACTIVATED CARBONS

T. Lupashcu*, M. Ciobanu

Institute of Chemistry of the Academy of Sciences of Moldova
Email: lupascut@gmail.com

Abstract: The adsorption process of ammonia ions and ammonium from aqueous solutions on the intact activated carbon obtained from nutshells through activation with phosphoric acid and oxidized with H_2O_2 and later impregnated with salt containing Co^{2+}, Ag^+, Ni^{2+}, Cu^{2+}, has been investigated. The efficiency of ammonia ions and ammonium elimination from various water categories, using both activated carbon (the intact CAN-7 and CAN-7 oxidized with H_2O_2 and impregnated with Co^{2+}, Ag^+, Ni^{2+}, Cu^{2+} ions) has been demonstrated.

Keywords: adsorption, ammonia ion, ammonia and activated carbon.

Introduction

Adsorption of ammonium vapors on activated carbons has been studied using adsorption technique [1-10] or those of calorimetry technique [11-14]. In literature, one can find few data regarding the adsorption of ammonia ions from aqueous solutions on modified activated carbons.

We have studied the adsorption of ammonia ions from aqueous solutions on activated carbons CAN-7 and CANO-7 obtained from nutshells, activated with phosphoric acid and oxidized with H_2O_2.

As the result of activated carbon CAN-7 oxidation, the content of acid functional groups has increased from 1.4 to 1.62 mg-echiv/g.

The oxidized activated carbons have been treated with aqueous solutions of Co^{2+}, Ag^+, Ni^{2+} and Cu^{2+} salts.

Results and discussions

The percentage of NH_3 in the solutions formed from ammonium salts varies significantly depending on the solution's pH and temperature [15]. Analytical determination of NH_4^+ content [15] is actually reduced to the determination of ammonia ions and ammonium total quantity.

Fig.1 shows the adsorption isotherms of NH_4^+ ions and NH_3 from aqueous solutions on CAN-7, CANO-7 + Co^{2+}, CANO-7 + Cu^{2+}, CANO-7 + Ag^+, CANO-7 + Ni^{2+} on initial pH 6,13 and temperature 20^0C.
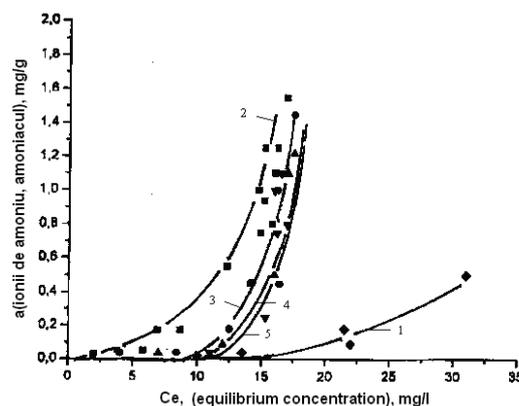

Fig.1. Adsorption isotherms of NH_4^+ ions and NH_3 from aqueous solution on intact CAN-7 (1) , CANO-7 + Co^{2+} (2), CANO-7 + Cu^{2+} (3),CANO-7 + Ag^+ (4),CANO-7 + Ni^{2+} (5) on initial pH 6,13 and temperature 20^0C.

Data shown in fig.1 demonstrate that the oxidation of activated carbon CAN-7, followed by impregnation with various metal cations, modify substantially both form of NH_4^+ and NH_3 adsorption isotherms. Also the adsorption capacity of CAN-7 increases. It should be noted that impregnation of activated carbon CANO-7 with Co^{2+} greatly increases (compared with other samples of investigated activated carbons) the adsorption capacity of NH_4^+ ions and NH_3. It is also worth mentioning that the content of metals in the samples of modified activated carbon is of: Co – 0.2%, Ag – 1%, Ni – 0.04%, Cu – 0.16%.

The high value of ammonia ions and ammonium adsorption on CANO-7 +Co^{2+} activated carbon samples can be explained by the increased capacity of Co^{2+} to form coordinative compounds with NH_3. In the solution, Co^{2+} forms five coordinative compounds with NH_3. For $[Co(NH_3)_6]^{2+}$ $pK_{1,2,3,4,5} = 5,13$. $K_{1,2,3,4,5} = 7,4 \cdot 10^{-6}$ [16].

Fig. 2 shows the dependence of adsorption values of ammonia ions and of ammonium on the pH of equilibrium concentrations solutions on CANO-7 +Co^{2+} and CAN-7 at t = 20^{0}C.

The data show a considerable increase of adsorption values, starting with certain values of pH. At relatively high values of pH (in the alkaline medium), the adsorption of ammonium formed in these conditions becomes significant.
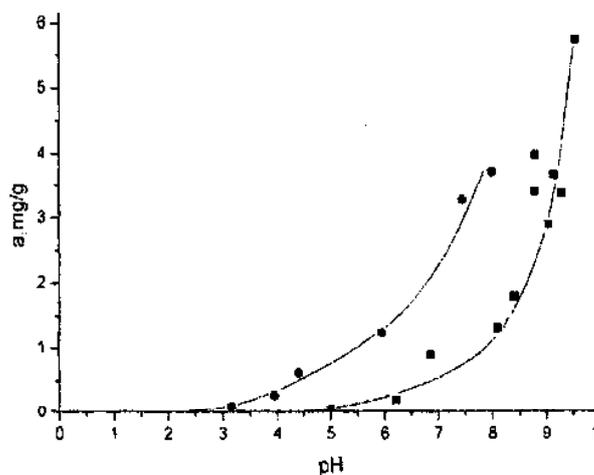

Fig.2. Dependence of adsorption NH$_3$ and NH$_4^+$ ions upon the pH of equilibrium concentrations solutions on activated carbon CAN-7 (●) and CANO-7 + Co^{2+} (■). t= 20^{0}C.

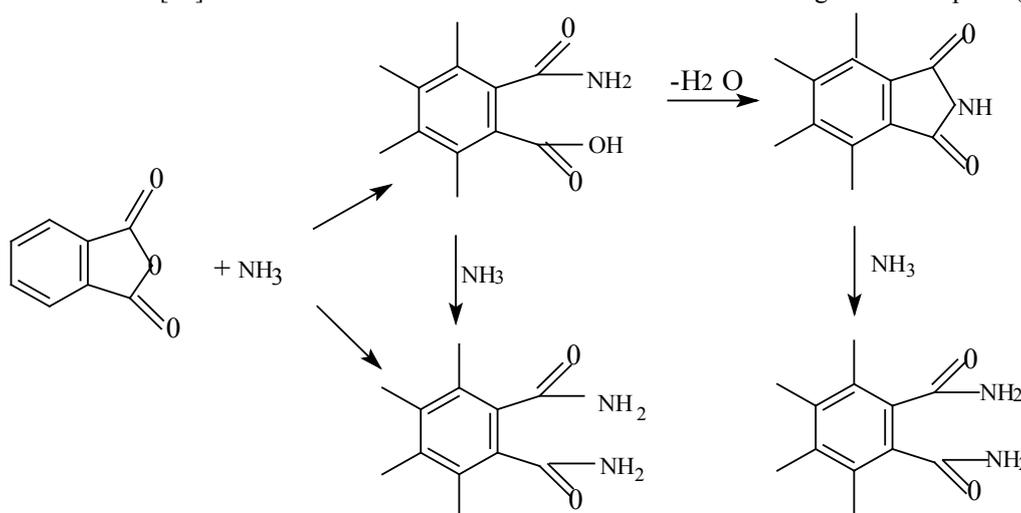It has been found [17] that ammonium is adsorbed on the carbon surface through chemosorption (fig.3).

Fig. 3. Interaction of ammonium with the surface of the adsorbent [17].

The maximum value of ammonia ions adsorption on intact CAN-7 and CANO-7 + Co^{2+} activated carbon can be calculated on the basis of Dubinin-Serpinschi equation (DS-1) inferred for the process of water vapors adsorption on the active centers from the surface of the adsorbent. Its linear form has been utilized:

$$Ce/Cs/a = 1/amC - 1/am \; Ce/Cs,$$

where Ce is the equilibrium concentration of NH$_4^+$ and NH$_3$ (mmol/l); Cs is the solubility of NH$_3$ (mmol/l); a is the adsorption value of NH$_4^+$ ions and NH$_3$ (mmol/g). Substitution, in equation DS-1, of P/Ps for Ce/Cs (to be applied in solutions) is, in our opinion, totally justified taking into consideration the applicability of Dubinin-Radushchievichi equation for solutions [18].

Fig. 4 shows the dependence Ce/Cs/a on Ce/Cs of the isotherm of ammonia ions and of the ammonium on intact CAN-7 (1) and CANO-7+ Co^{2+} activated carbon.
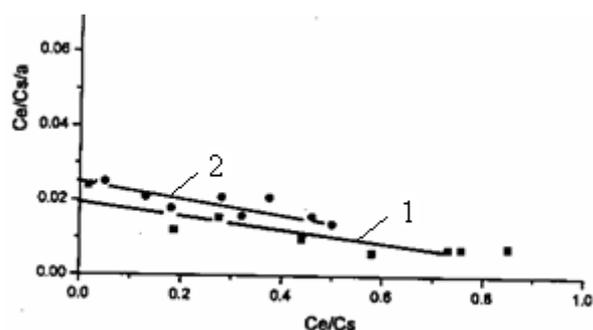
Fig.4. Adsorption isotherm of NH_4^+ and NH_3 from aqueous solutions on intact CAN-7 (1) and CANO-7+ Co $^{2+}$ (2) in the coordinates of DS-1 equation.

The adsorption value (a_m) on intact CAN-7 is about 50 mmol/g and on CANO-7+ Co $^{2+}$ is 66 mmol/g. Considering this supposition, the result of the present investigation must be taken into account as a possibility of purifying the water containing ammonia ions and ammonium in significant quantities.

Conclusions

1. It was established that at high pH values (10,6), the value of NH_4^+ and NH_3 adsorption increases considerably due to the formation, in the alkaline medium, of ammonium which exhibits a mechanism and adsorption capacity totally different from that of ammonia ions.
2. The possibility of water purifying from ammonia ions utilizing activated carbon, oxidized and impregnated with Co^{2+}, Ni^{2+} and Cu^{2+} ions, has been found.

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