Preparation of a Locally Produced Activated Carbon from Coconut Shells and Its Use in Reducing Hexamine Cobalt (III)

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Abstract-Coconut is produced in large quantities in South Western part of Nigeria especially in Badagry area of Lagos State. The fleshy part (mesocarp) is either eaten of used to process oil while the husks is usually discharged and constitute a waste. In this work the coconut husks were carbonated and used to produce activated carbon using Zinc Chloride as the activating agent. The resulting activated carbon was used to catalyze the reduction of hexamine cobalt (III) to hexamine cobalt (II). Hexamine cobalt (II) is used for retrofitting the simulation removal of SO2 and NO from flue gases released from power plants. The factors studied in this paper include the effects of the following factors on the kinetics of the reaction: stirring speed, particle size distribution, mass of activation carbon, initial concentration of hexamine cobalt (III), temperature and pH. The results indicate that optimum condition for the conversion of the reduction reaction are for pH of 2.6, stirring speed of 400rpm particle size distribution of 150-200 mesh size. However, the rate of reaction was found to first order with respect to hexamine Cobalt (III) and increases with concentration of carbon mass, initial concentration of the feed and temperature.

Index Terms—Activated carbon, coconut, hexamine cobalt, kinetics.

I. INTRODUCTION

Power plants usually generate flue gases such as NO, NO₂, SO₂, SO₃ and CO. These gases have serious consequences on the environment including global warming, acid rain and depletion of the ozone layer. Efforts are being made worldwide to minimize or eliminate the release of these gases to the atmosphere to comply with environmental regulations and standards [1]-[10]. One method which has been developed by Long, Xin, Wang, Xiao, and Yuan [8] is the simultaneous removal of NO and SO2 by the adsorption of the gases on hexamine cobalt (II). This reaction(s) usually involve the oxidation of hexamine cobalt (11) to hexamine cobalt (III). The activated carbon catalyzes the reduction of the hexamine cobalt (III) to hexamine cobalt (II) thereby sustaining the continuous removal of the concerned flue gas. The reduction does not proceed appreciably in the absence of a catalyst. [12]. the electrochemical half-cell reduction potential is low and cannot proceed spontaneously. Activated carbon has been found to catalyze many reactions successfully [13]-[19]. The adsorption of the $CO(NH_3)_6^{3+}$ on activated carbon is based on the Langmuir isotherm model which assumes that maximum adsorption corresponds to a monolayer saturated with the adsorbate molecules on the adsorbent surface that is energetically homogenous. Langmuir constants are calculated from the following linearized form.

$$C_e q_e = \frac{1}{bQ} + \frac{C_e}{Q}$$

where Q and b are Langmuir constants derived from the slope and intercept indicative of the maximum adsorptive capacity (mg/g) of adsorbent and energy of adsorption respectively, while Ce is the remaining concentration of the adsorbate after equilibrium (mg/l) and q_e is the amount adsorbed at equilibrium (mg/g).

A. The Mechanism of Activated Carbon Reduction of Hexamine Cobalt (III)

The mechanism of activated carbon catalyzing the reduction of $CO(NH_3)_6^{3+}$ can be expressed as follows [20]

$$AC + C_o(NH_3)_6^{3+} \leftrightarrow AC \dots C_o(NH_3)_6^{3+}$$
 (1)

The NH₃ molecules may react with the acidic part of the carboxylic groups and phenolic hydroxyl groups to form $C_o(NH_4)^{2+}$ complexes on carbon surface. The formation of these complexes may accelerate $C_o(NH_3)^{3+}$ ions disintegrate to cobalt (III), as shown below;

$$C \dots C_0 (NH_3)_6^{3+} \leftrightarrow C_0^{3+} + 6NH_3 + C$$

$$(2)$$

II. EXPERIMENTAL

A. Preparation and Activation of Carbon

The coconut shell samples were obtained from mile 12 market in Lagos. Dirt was removed from samples after which they were washed and sun dried for 24hrs. The samples were crushed in order to be processed further in the furnace.

B. Production of Activated Carbon

Carbonization of the precursor was carried out at a temperature of 650°C, the carbonization was achieved in a muffle furnace for 2hrs. The method is as follows:

- 1) The coconut shell was cleaned from other materials such as coconut fiber or soil.
- 2) It was then sun dried
- The dried shell was burned in the furnace at 650°C for 2hours.
- 4) The carbonized coconut shell was then crushed and separated into different mesh sizes
- The charcoal was soaked in chemical solution of ZnCl₂ for 8 hours, to become activated carbon.
- 6) The activated carbon was further treated by HCl

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(0.1M) and NaOH (1M) and Ammonia solution.

- 7) Then the moist activated carbon was kept in the furnace at 700° C (activated temperature) to increase the porosity of the activated carbon.
- The resulting activated carbon was washed with distilled water and dried in the furnace at 110°C for 2hrs.
- 9) It was then packed in the dry container.

C. Procedure for the reduction of Hexamine Cobalt (iii) The Experimental set up is Available Elsewhere [20]

A turbine impeller of diameter 3cm was mounted on the bottom of the stirring rod. Measured liquid ammonia was put into a volumetric bottle of 1000ml to make up hexamine cobalt (III) aqueous solution. Two hundred milliliter hexamine cobalt (III) aqueous solution and appropriate dose of activated carbon was introduced into the glass flask. The coconut activated carbon produced was used. The contents of acidic surface groups were examined according to the method of Boehm. The pH values of the solutions were adjusted before addition of activated carbon by adding appropriate amounts of H₂SO₄ or NaOH. The liquid samples were withdrawn periodically to determine the changes of hexamine cobalt (II) concentration in the aqueous solution during the experiments. Cobalt (II) was determined spectrophotometrically. The effects of the following factors on the rate of the reaction were examined:

D. The effect of pH

Stirring Speed = 500rpm; Particle size = 120-140mesh; $C_o(NH_3)_6^{3+}$ =0.01mol/l; Activated carbon = 5g/l; Temperature = 60^oC

E. Effect of Stirring Speed on Hexamine cobalt (III) reduction.

pH = 2.6; $C_o(NH_3)_6^{3+}$ = 0.01mol/l; Particle size = 120 - 140 mesh; Activated Carbon = 5 g/l

F. Effect of activated carbon particle size on hexamine cobalt (III) reduction.

pH = 2.6; 60^oC; Stirring Speed = 500(rpm) $C_o(NH_3)_6^{3+}$ = 0.01mol/l; Activated carbon = 5g/l

G. Effect of temperature on hexamine cobalt (III) reduction.

pH = 2.6; Stirring Speed = 500rpm; $C_o(NH_3)_6^{3+}= 0.01 \text{ mol/l}$; Activated carbon = 5g/l

H. The effect of concentration on hexamine cobalt (III) reduction

pH=2.6; Stirring Speed = 500rpm; $C_o(NH_3)_6^{3+} = 0.01$ mol/l; Activated carbon = 5g/l

I. Effect of Initial pH





The $C_o(NH_3)_6^{3+}$ conversions for a reaction of 1h are depicted in Figure1. It can be seen from Figure 1 that pH of the solution affects this catalytic reduction greatly. The highest $C_o(NH_3)_6^{3+}$ conversion is obtained at pH 2.6. The conversion decreases as pH is lower or higher. Therefore, it can be concluded that the optimal pH for $C_0(NH_3)_6^{3+}$ Reduction is 2.6. pH affects not only the surface charge of the activated carbon, but also the degree of ionization and speciation of adsorbate during reaction. The disintegration of the $C_o(NH_3)_6^{3+}$ is essential to the regeneration of cobalt (II). In acidic solutions $C_{\rho}(NH_3)_6^{3+}$ is liable to disintegrate due to the formation of NH4⁺ ions. According to the equilibrium between NH3 and NH4 + NH4 ions become fewer with increasing pH. Disintegration of $C_o(NH_3)_6^{3+}$ is therefore inhibited as the basicity of the solution becomes stronger. On the other hand, the adsorption of $C_o(NH_3)_6^{3+}$ ions on activated carbons is greatly influenced by the pH of the solution, because the mean surface charge density of the carbon is determined by the pH. Thus it can be concluded that the higher the pH, the greater negative charge density on the surface of activated carbon, the easier the cationic $C_o(NH_3)_6^{3+}$ ions absorbed. It is very difficult for $C_o(NH_3)_6^{3+}$ ions to be adsorbed on the activated carbon surface when the pH of the solution is lower. Hence, the reduction of $C_o(NH_3)_6^{3+}$ will be affected detrimentally when pH is lowered. Therefore, there is an optimal pH range for $C_o(NH_3)_6^{3+}$ reduction catalyzed by activated carbon in aqueous solutions.

J. Effect of Stirring Speed on Hexamine Cobalt (III) Reduction



Fig. 2. Showing the effect of rotation speed, pH =2.6, 60° C, 0.01 mol/l, activated carbon = 5g/l

It can be seen from the Fig. 2 that the $C_o(NH_3)_6^3$ conversion may increase with the stirring speed. As the stirring speed is below 400 rpm After 1 h operation, the $C_o(NH_3)_6^{3+}$ conversion increases from 70% to 82.12% as the stirring speed increases from 200 to 400 rpm, However, the $C_o(NH_3)_6^{3+}$ conversion at 400 rpm is equal to that at 500 rpm and 600rpm. There exists a viscous flow coat about the exterior of solid catalyst in the liquid-solid catalytic reaction. The reaction only takes place after the reactants get through the liquid film to the surface of the catalyst. The thickness of the liquid film and the resistance of mass transfer will be reduced at the increase of stirring speed. Therefore, the reaction rate may be accelerated with the stirring speed. However, the external mass transfer

limitation is eliminated as the stirring speed is above 400 rpm hence, the reaction rate may not increase further as the stirring speed rises.

K. Effect of Activated Carbon Particle Size



Fig. 3 depicts that the $C_o(NH_3)_6^{3+}$ conversion increases as the activated carbon particle size reduces. For example, after 2h operation, the $C_o(NH_3)_6^{3+}$ conversion is 71.31% catalyzed with 40-80 mesh activated carbon while the $C_o(NH_3)_6^{3+}$ conversion gets to 83.2% catalyzed with 80-100 mesh activated carbon. However, the $C_o(NH_3)_6^{3+}$ conversions don't increase further as the activated carbon particle size reduces below 120mesh. The $C_o(NH_3)_6^{3+}$ conversions catalyzed with 100-120 mesh activated carbon is almost equal to that catalyzed with 150-200 mesh activated carbon. It can be concluded that the internal mass transfer is negligible as the particle size is below 100-120 mesh. In heterogeneous catalysis, the conversion of one reactant is very often affected by mass transfer limitations, so apparent kinetics are actually governed by external or internal mass transfer resistances. Intrinsic kinetics can only be evaluated if the above effects are minimized. According to the experimental results discussed previously, the mass transfer resistances can be eliminated under the conditions with stirring speed greater than 400rpm and activated carbon particle size less than 120mesh. The run was s carried out under the condition without mass transfer resistances.

L. Effect of Activated Carbon Mass



Fig. 4. Effect of carbon mass on the reduction of $C_o(NH_3)_6^{3+}$, pH = 2.6, 60°C, 0.01mol/l

After 1h operation, the $C_o(NH_3)_6^{3+}$ conversion is only 12% with the catalysis of activated carbon 0f 1.5g but the

 $C_o(NH_3)_6^{3+}$ conversion goes up to 34.5% catalyzed with activated carbon of 1.5 g/l. Fig. 4 also manifests that the $C_o(NH_3)_6^{3+}$ conversion increases markedly with activated carbon mass. For example, after 1h operation, the $C_o(NH_3)_6^{3+}$ conversion increases from 12.0% to 75.0% as the activated carbon mass increases from 1.5 to 6.0 g/l. This can be attributed to more carbon surface area and availability of more active sites at higher activated carbon dosage.

M. Effect of $C_o(NH_3)_6^{3+}$ Concentrations



Fig. 5(a). The effect of concentration on $C_o(NH_3)_6^{3+}$, pH=2.6, 60°C, activated carbon = 5g/l



Fig. 5(b). The plot of concentration vs. Time, pH = 2.6, 60°C, activated carbon = 5g/l

The experimental results shown in figures 5a,b, demonstrate that the $C_o(NH_3)_6^{3+}$ conversion rate increases with its initial concentration. The $C_o(NH_3)_6^{3+}$ conversion equation can be written as;

$$-\frac{dC_{C_0(NH_3)_6^{3+}}}{dt} = kC_{C_0(NH_3)_6^{3+}}^n$$

According to the experimental data depicted in Figure 5a,b, the n in this equation can calculated with matlab software. The n values calculated are listed in Table I. It can be concluded that the redox reaction is first order in respect to $C_o(NH_3)_6^{3+}$. The slope of the curve of $-InC_{C_o(NH_3)_6^{3+}}$ Vs. *t* is the value of *k*. The value of *k* at 60°C is obtained as 0.1129min⁻¹.

TABLE I: SHOWING CONCENTRATION AND THE ORDER OF REACTION USING MATLAB SOFTWARE

$C_o(NH_3)_6^{3+} mol/l$	0.004	0.006	0.008	0.01
Value of n	1.0453	0.9607	1.1149	0.9784

N. Effect of Temperature



THE EFFECT OF TEMPERATURE ON THE

Fig. 6. Effect of temperature on the reduction of $C_o(NH_3)_{6}^{3+}$, pH = 2.6, activated carbon = 5g/l

A conclusion can be drawn from the experimental results shown in Fig. 7 that the hexamine cobalt (III) conversion increases with temperature. For instance, after twenty minutes' operation, the $C_o(NH_3)_6^{3+}$ conversion increases from 18.81 to 89.96% when the temperature rises from 60° C to 100° C. The explanation can be explained as follows. Firstly, high temperature is liable to make hexamine cobalt (III) decompose into Co^{3+} and NH₃ easily. Secondly, dynamically, the redox reaction rate increases as temperature rises. Thirdly, oxygen solubility decreases with temperature, causing the oxygen produced by reaction to stripe much more quickly from the activated carbon. All of these factors contribute to the acceleration of hexamine cobalt (III) reduction.

O. Effect of Temperature on Rate Constant



Fig. 7. Effect of Temperature on Rate Constant, pH=2.6, 60°C, activated carbon = 5g/l

III. CONCLUSION

The reduction of hexamine cobalt (III) catalyzed by coconut activated carbon has been studied in a batch stirred tank. It can be concluded that activated carbon catalyzes the $C_o(NH_3)_6^{3+}$ reductions. The $C_o(NH_3)_6^{3+}$ conversion increases markedly with activated carbon mass. This catalytic reduction reaction is first order in respect to $C_o(NH_3)_6^{3+}$. Temperature speeds up the $C_o(NH_3)_6^{3+}$ reduction. pH affects this catalytic reduction reaction greatly. There is an optimal pH of 2.6 for this reaction. The $C_o(NH_3)_6^{3+}$ conversion decreases as pH is lower or higher. The results compare favorably with the work of Long, Chang and Yuan [20] which uses a commercial activated carbon. However, since this work uses the optimal pH for the experiments it has a lower

activation energy of 17.60 ± 1.66 kJ/mol. compared with 56.7 ± 1.86 kJ/mol obtained by long et al. The use of the coconut shell for producing activated carbon will minimize the wastes generated and generate more revenue

REFERENCES

- T. W. Chu, H and H.T. Hsueh, "Kinetic study of absorption of SO₂ and NO, with aicide NaClO₂ solutions using the sparying column." *Journal of Environmental Engineering*, Vol. 129, pp. 967 – 974, 2003.
- [2] M. Sakai, C. Su, and E. Sasaoka, "Simultaneous removal of SOX and NOX using slaked lime at low temperature" Industrial and Engineering Chemistry Research, Vol. 41, pp. 5029 – 5033, 2002.
- [3] H. T, Chu, W. Chien, and Li, S.Y. "Simultaneous absorption of SO₂ and NO from flue gas with KMnO₄ / NaOH solutions," *the Science of the total environment*, vol. 275, pp. 127–135, 2001.
- [4] C.L., Yang, and H. Shaw, "Aqueous absorption of nitric oxide induced by sodium chlorite oxidation in the presence of sulfur dioxide", *Environmental Progress*, vol. 17, pp. 80–85, 1998.
- [5] H. Chu, T.W. Chien, and B.W. Twu, "The absorption kinetics of NO in NaClO₂ / NaOH solutions," *Journal of Hazardous Materials B*, vol. 84, pp. 241–252, 2001.
- [6] D. S. Jin, B.R. Deshwal, Y.S. Park, and H.K. Lee, "Simultaneous removal of SO₂ and NO by wet scrubbing using aqueous chlorine dioxide solution", *Journal of Hazardous Materials B*, vol. 135, pp. 412–417. 2006.
- [7] L. Wang, W. R. Zhao, and Z. B. Wu, "Simultaneous absorption of NO and SO₂ by Fe (II) EDTA combined with Na₂SO₃ solution," *Chemical Engineering Journal*, vol. 132, pp. 227–232, 2007.
- [8] X. L. Long, Z. L. Xin, H. X. Wang, W. D. Xiao, and W. K. Yuan, "Simultaneous removal of NO and SO₂ with Hexammine Cobalt (III) solution coupled with the Hexammine Cobalt (III) regeneration catalyzed by activated carbon," *Applied Catalysis B: Environmental*, vol. 54, pp. 25–32. 2004.
- [9] H. Teng, Y.T. Tu, Y.C. Lai, and C.C. Lin, "Reduction of NO with NH₃ over carbon catalysts," *the effects of treating carbon with H₂SO₄ and HNO₃, Carbon*, vol. 39, pp. 573–582. 2001.
- [10] L. R. Radovic, C. Moreno-Castilla, and J. Rivera-Utrilla, "Carbon materials as adsorbents in aqueous solutions," *Chemistry and Physics* of Carbon, vol. 27, pp. 227–403, 2001.
- [11] S. Bashkova, A. Bagreev, and T.J. Bandosz, "Catalytic properties of activated carbon surface in the process of adsorption / oxidation of methyl mercaptan," *Catalysis Today*, vol. 99, pp. 323–328. 2005.
- [12] A. Eftaxias, J. Font, A. Fortuny, A. Fabregat, and F. Stuber, "Kinetics of phenol oxidation in a trickle bed reactor over active carbon catalyst", *Journal of Chemical Technology and Biotechnology*, vol. 80, pp. 677–687, 2005.
- [13] E. Auer, J. Freund, and T. Tacke, "Carbon as supports for Industrial Process Metals", *Applied Catalysis; A General*, vol. 173, pp. 259-271. 1998.
- [14] P. Roisson, J.-P. Brunelle, P. Nortier, in: A.B. Stiles (Ed.), Catalyst Supports and Supported Catalysts, Butterworth, Boston, 1987, p. 11.
- [15] H. P. Boehm, C. Morterra, A. Zecchina, and G. Costa (Eds.), *Structure and Reactivity of Surfaces*, Elsevier, Amsterdam, 1989, pp.145.
- [16] L. R. Rubivic, F. A. Roubrigues, and P. A. Thowler, Ed., "Chemistry, Physics and Carbon," vol. 25, Mezzel Dekker, New York, 1997, pp. 243.
- [17] C.A. Leon, Y. Leon, I.M. Solar, and L.R. Calenman Radvic, "Carbon" pp. 797, 1992.
- [18] R. C. Bamsal, J.B. Donnet, and F. Stocheti, "Active Carbon" Mezzel Dekker, New York, 1998, pp. 245.
- [19] F. Rodriguez-Reinoso, M. Molina-Sabio, "Textural and chemical characterization of micro-porous carbons: Adv Colloid Interface Sci." vol. 76-77, pp. 271-294, 1998.
- [20] X. Long, H. Chang and W. Yuan, "Reduction of Hexammine cobalt (III) Catalyzed by Coconut Activated Carbon", *Environmental Bryrer* and Sustainable Energy, Vol. 29 No.1, pp. 85-92, 2010.



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