# DEVELOPMENT OF LOW-COST GREEN ABSORBENTS FOR CARBON DIOXIDE ABSORPTION FROM A POST-COMBUSTION SYSTEM

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**by**

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***Submitted***

***in fulfillment of the requirements of the degree of Doctor of Philosophy***

***to the***

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DEDICATED TO

MY PARENTS

&

MY IN-LAWS

# CERTIFICATE

This is to certify that the thesis entitled “**Development of Low-Cost Green Absorbents for Carbon Dioxide Absorption From a Post-Combustion System”** being submitted by **Amita Chaudhary** to the Department of Chemical Engineering, Indian Institute of Technology, New Delhi, in fulfillment of the requirements for the award of the degree of **Doctor of Philosophy** in Chemical Engineering, is a record of bonafide work carried out by her. She has worked under my guidance and supervision and has fulfilled the requirements, which to my knowledge have reached the requisite standard for the submission of the thesis.

The research report and results presented in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree or diploma.

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# Abstract

This research presents the development of a series of low-cost Protic Ionic Liquids (PILs) for $CO_2$ gas absorption from a post-combustion system. The PILs were synthesized by proton transfer from Bronsted acid to Bronsted base. The structures of the synthesized protic ionic liquids were elucidated using FT-IR, $^1$H NMR, $^{13}$C NMR, and mass spectroscopy. Experimentally physico-chemical properties of pure Triethylenetetrammonium lactate ([TETA] [Lactate]) were evaluated at different temperatures ranging from 298K to 363K.

Studies of $CO_2$ -absorption capacity were carried at ambient conditions in 0.5 M aqueous solution of [TETA] [Lactate]. The experiment proved a very good efficiency of 1.92 mol mol$^{-1}$ of $CO_2$ when the $CO_2$ was bubbled discontinuously, whereas in continuous bubbling it showed only 1.57 mol of $CO_2$ absorbed per mol of [TETA] [Lactate].

The kinetics of $CO_2$-absorption in aqueous solutions of [TETA] [Lactate] was studied in a stirred-tank contactor with a plane interface. The operating variables considered in this study were the initial concentration of [TETA] [Lactate] and the temperature of the absorbing solution. Specific absorption rates were determined under different experimental conditions. Results indicate that the absorption process takes place in a fast reaction regime and the reaction exhibited pseudo first-order kinetics. The reaction rate constant was determined by performing the measurement of the kinetics at different temperatures and by making the Arrhenius plot for the $CO_2$-absorption in [TETA] [Lactate] solutions. The consequence of variance in lean-$CO_2$ gas flow-rate and [TETA] [Lactate] concentration in the liquid phase were also analyzed in detail for the $CO_2$-absorption.

The present work also examined the $CO_2$-absorption in aqueous solutions of [TETA] [Lactate] in a foam-bed reactor (FBR). Experimental results show that in foam-bed reactor the synthesized PIL, i.e. [TETA] [Lactate], shows higher $CO_2$-absorption rate. The effect of surfactant used on the overall mass-transfer coefficient in absorption process was also determined experimentally. In addition, the effect of different operating variables like types of surfactant, surfactant concentration, lean gas flow-rate, $CO_2$ flow-rate, height of foam-bed, and initial concentration of [TETA] [Lactate] upon the volumetric mass-transfer coefficient and subsequently, on carbon-dioxide absorption rate were studied.

The carbon-dioxide absorption rate obtained in a bubble-column reactor has been compared with that of a foam-bed reactor. Up to 18% higher absorption rate are obtained in a foam-bed reactor.

Further, regeneration of $CO_2$-saturated [TETA] [Lactate] solutions was done thermally with continuous bubbling of $N_2$ gas in a semi-batch process. The regeneration rate was measured as a function of temperature and flow rate of $N_2$ gas through the solution in a semi-batch process. The studies reveal that regeneration rate increased with increase in temperature from 343 K to 383K and then it is leveled off. The increased flow-rate of $N_2$ gas further enhanced the regeneration rate at the given temperature. In the recycling studies, it was proved that [TETA] [Lactate] could be reused with simultaneous absorption and desorption for continuous three cycles with the same capacity and then the $CO_2$-absorption capacity slightly decreased from 0.65 to 0.59 mol $mol^{-1}$ in next five cycles. Later, in the ninth cycles, its capacity was coming to 0.46 mol $mol^{-1}$ which is comparable to first cycle $CO_2$-absorption of 30% MEA (0.55 mol $mol^{-1}$ ).

The corrosion studies were done on different metals using two standard methods, viz. Electrochemical and Weight-loss method. The results were interpreted using polarization curves, SEM, and EDX techniques. Linear polarization plots showed that an increasing the concentration of [TETA] [Lactate] from 0.1 to 0.5 kmol $m^{-3}$ in 4. kmol $m^{-3}$ MEA solutions the corrosion rate decreased from 3.98 mmpy to 0.086 mmpy which further supported by the

polarization resistance calculations. There was an increment in polarization resistance with an increase [TETA] [Lactate] concentration in $CO_2$-loaded solution. The anodic Tafel slope ($\beta_a$) and cathodic Tafel slope (($\beta_b$) of $CO_2$ loaded 4.0 kmol $m^{-3}$ MEA decreased with increasing [TETA] [Lactate] concentration, indicating that the [TETA] [Lactate] inhibited the corrosion. At last, the experimental results were compared with the predictions of the theoretical model of a foam - bed reactor. The comparison of the experimental data with theory showed that the conversions obtained experimentally were higher than those predicted by the model. Due to the increase in viscosity of the solution of ionic liquid with reaction, the model failed to predict the experimental data beyond 5 minutes of the reactor operation, because the single stage model is valid only for absorbing liquids having constant low viscosities.

Lastly, the precursors cost of synthesized [TETA] [Lactate] was compared with the conventional ionic liquids precursors cost from Sigma Aldrich. [TETA] [Lactate] is comparably of low-cost and less toxic in terms of negligible vapor pressure and solvent lose.

# सार

यह शोध दहन के बाद के सिस्टम से $CO_2$ गैस के अवशोषण के लिए कम लागत वाली प्रोटोनिक आयोनिक तरल पदार्थ (PIL) की एक श्रृंखला के विकास को प्रस्तुत करता है। जनहित याचिका को ब्रोंस्टेड एसिड से ब्रोंस्टेड बेस में प्रोटॉन ट्रांसफर द्वारा संश्लेषित किया गया था। संश्लेषित प्रोटी आयनिक तरल पदार्थों की संरचनाओं को एफटी-आईआर, 1 एच -एनएमआर, 13 सी- एनएमआर, और मास स्पेक्ट्रोस्कोपी का उपयोग करके अलग किया गया था। प्रायोगिक तौर पर शुद्ध ट्राइएथिलनेटेट्रामोनियम लैक्टेट (टेटा [लैक्टेट]) के भौतिक-रासायनिक गुणों का मूल्यांकन अलग-अलग तापमान पर किया गया था।

$CO_2$ के अभिसरण क्षमता के अध्ययनों को परिवेशीय परिस्थितियों में [TETA] [लैक्टेट] के 0.5 M जलीय घोल में किया गया। $CO_2$ को 1.92 mol mol$^{-1}$ की बहुत अच्छी दक्षता साबित हुई जब $CO_2$ को बंद कर दिया गया, जबकि लगातार बुदबुदाहट में यह केवल 1.57 mol $CO_2$ को अवशोषित करता है जो कि टेटा [लैक्टेट] के प्रति मोल को अवशोषित करता है।

टेटा [लैक्टेट] के जलीय घोल में $CO_2$-अवशोषण के कैनेटीक्स को एक जानने वाला इंटरफ़ेस के साथ एक हलचल-टैंक संपर्ककर्ता में अध्ययन किया गया था। इस अध्ययन में विचार किए गए ऑपरेटिंग चर टेटा [लैक्टेट] की प्रारंभिक एकाग्रता और अवशोषित समाधान का तापमान थे। विशिष्ट प्रयोगात्मक दरों के तहत विशिष्ट अवशोषण दर निर्धारित की गई थी। परिणाम बताते हैं कि अवशोषण प्रक्रिया एक तेज प्रतिक्रिया शासन में होती है और प्रतिक्रिया ने छद्म प्रथम-क्रम कैनेटीक्स का प्रदर्शन किया। विभिन्न तापमानों पर कैनेटीक्स का मापन करके और टेटा [लैक्टेट] समाधानों में $CO_2$-अवशोषण के लिए ऐरहेनियस प्लॉट बनाकर प्रतिक्रिया दर स्थिर निर्धारित की गई थी। $CO_2$ गैस प्रवाह-दर और टेटा [लैक्टेट] में विचरण में तरल चरण में सांद्रता का भी $CO_2$-अवशोषण के लिए विस्तार से विश्लेषण किया गया।

वर्तमान कार्य ने फोम-बेड रिएक्टर (FBR) में टेटा [लैक्टेट] के जलीय घोलों में $CO_2$ के अवशोषण की जांच की। प्रायोगिक परिणाम बताते हैं कि फोम-बेड रिएक्टर संश्लेषित जनहित याचिका, यानी टेटा [लैक्टेट], उच्च $CO_2$-अवशोषण दर को दर्शाता है। अवशोषण प्रक्रिया में समग्र द्रव्यमान-स्थानांतरण गुणांक पर प्रयुक्त सर्फेक्टेंट का प्रभाव भी प्रयोगात्मक रूप से निर्धारित किया गया था। इसके अलावा, अलग-अलग ऑपरेटिंग चर जैसे सर्फेक्टेंट, सर्फैक्टेंट एकाग्रता, लीन गैस प्रवाह-दर, $CO_2$ प्रवाह-दर, फोम-बिस्तर की ऊंचाई, और टेटा [लैक्टेट] की प्रारंभिक सांद्रता पर बड़े पैमाने पर-स्थानांतरण गुणांक और बाद में, कार्बन-डाइऑक्साइड अवशोषण दर का अध्ययन किया गया।

बबल-कॉलम रिएक्टर में प्राप्त कार्बन-डाइऑक्साइड अवशोषण दर की तुलना फोम-बेड रिएक्टर से की गई है। फोम-बेड रिएक्टर में 18% तक उच्च अवशोषण दर प्राप्त की जाती है।

इसके अलावा, $CO_2$-संतृप्त टेटा [लैक्टेट] के उत्थान को अर्ध-बैच प्रक्रिया में N2 गैस के निरंतर बुदबुदाहट के साथ थर्मल रूप से किया गया था। पुनर्जनन दर को सेमी-बैच प्रक्रिया में समाधान के माध्यम से एन 2 गैस के तापमान और प्रवाह दर के एक फ़ंक्शन के रूप में मापा गया था। अध्ययनों से पता चलता है कि पुनर्जनन दर 343 K से 383K तक तापमान में वृद्धि के साथ बढ़ी और फिर इसे बंद कर दिया गया। नाइट्रोजन गैस की बढ़ी हुई प्रवाह दर ने दिए गए तापमान पर पुनर्जनन दर को और बढ़ा दिया। पुनर्चक्रण अध्ययनों में, यह साबित हुआ कि टेटा [लैक्टेट] को एक ही क्षमता के साथ लगातार तीन चक्रों के लिए एक साथ अवशोषण और वियोजन के साथ पुन: उपयोग किया जा सकता है और फिर $CO_2$-अवशोषण की क्षमता अगले में 0.65 से 0.59 mol $mol^{-1}$ से थोड़ी कम हो गई पाँच चक्र। बाद में, नौवें चक्र में, इसकी क्षमता 0.46 mol $mol^{-1}$ थी जो कि पहले चक्र $CO_2$ अवशोषण 30% एम ई ए (0.55 mol $mol^{-1}$) के बराबर है।

संक्षारण अध्ययन दो मानक विधियों, अर्थात का उपयोग करके विभिन्न धातुओं पर किया गया था। विद्युत और वजन घटाने की विधि। परिणाम ध्रुवीकरण घटता, एस ई एम, और ई डी एक्स तकनीक का उपयोग कर व्याख्या की गई। रैखिक ध्रुवीकरण भूखंडों से पता चला है कि बढ़ते हुए टेटा [लैक्टेट] की सघनता 0.1 से 0.5 kmol $m^{-3}$ में 4. kmol $m^{-3}$ एम ई ए घोल में संक्षारण दर 3.98 mmpy से घटकर 0.086 mmpy हो गई है - जो ध्रुवीकरण प्रतिरोध द्वारा समर्थित है। सीओ 2-लोड समाधान में वृद्धि टेटा [लैक्टेट] एकाग्रता के साथ ध्रुवीकरण प्रतिरोध में वृद्धि हुई थी। एनोडिक Tafel slope ($\beta_a$) और $CO_2$ का कैथोडिक Tafel ढलान ($\beta_b$) 4.0 kmol $m^{-3}$ MEA लोड होने के साथ टेटा [लैक्टेट] एकाग्रता में वृद्धि के साथ कम हो गया, यह दर्शाता है कि टेटा [लैक्टेट] ने संक्षारण को रोक दिया है।

अंत में, प्रयोगात्मक परिणामों की तुलना एक फोम-बेड रिएक्टर के सैद्धांतिक मॉडल की भविष्यवाणियों के साथ की गई थी। सिद्धांत के साथ प्रयोगात्मक डेटा की तुलना ने दिखाया कि प्रयोगात्मक रूप से प्राप्त रूपांतरण मॉडल द्वारा भविष्यवाणी की गई तुलना में अधिक थे। प्रतिक्रिया के साथ आयनिक तरल के समाधान की चिपचिपाहट में वृद्धि के कारण, मॉडल रिएक्टर ऑपरेशन के 5 मिनट से परे प्रयोगात्मक डेटा की भविष्यवाणी करने में विफल रहा, क्योंकि एकल चरण मॉडल केवल निरंतर कम चिपचिपाहट वाले तरल पदार्थों को अवशोषित करने के लिए मान्य है।

अन्त में, संश्लेषित टेटा [लैक्टेट] की पूर्ववर्ती लागत की तुलना सिग्मा एल्डरिच के पारंपरिक आयनिक तरल अग्रदूतों की लागत से की गई थी। टेटा [लैक्टेट] नगण्य वाष्प दबाव और विलायक खो के संदर्भ में तुलनात्मक रूप से कम लागत और कम विषाक्त है।

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| | |
|---|---|
| A | Arrhenius Pre-exponential factor, $m^3 mol^{-1} s^{-1}$ |
| a | Volumetric Gas-Liquid Interfacial Area, $m^{-1}$ |
| 2a | Thickness of liquid film, m |
| B | Base (water) |
| $C_A$ | Concentration of species A in the liquid phase in the foam film, kmol $m^{-3}$ |
| $C_{Ag}$ | Concentration of A in the gas pockets surrounding the liquid films, kmol $m^{-3}$ |
| $C_B$ | Concentration of reactant B in the liquid phase in the storage section at time t, kmol $m^{-3}$ |
| $C_{B0}$ | Initial concentration of reactant B in the liquid stream entering the storage section, kmol $m^{-3}$ |
| $C_{B1}$ | Concentration of liquid phase reactant B in the liquid draining into the foam section, kmol $m^{-3}$ |
| $C_{TETAL}$ | Initial Concentration of [TETA] [Lactate], kmol $m^{-3}$ |
| $CO_2$ | Carbon-dioxide gas |
| $C_{2,i}$ | $CO_2$ concentration at G-L interface, kmol $m^{-3}$ |

| | |
|---|---|
| CTAB | Cetyltrimethylammonium bromide ($[(C_{16}H_{33})N(CH_3)_3]Br$) |
| CS | Carbon Steel |
| CMC | Critical Micelle Concentration, mM |
| $D_A$ | Diffusion coefficient of reactant A in the liquid phase, $m^2s^{-1}$ |
| $D_{CO_2}$ | Diffusion coefficient of carbon dioxide in the [TETA] [Lactate] solution, $m^2s^{-1}$ |
| $D_{CO_2}^{H_2O}$ | Diffusivity of $CO_2$ in water, $m^2s^{-1}$ |
| $D_S$ | Diameter of impeller blades in the liquid-phase, m |
| $D_{Stirred-cel}$ | Inner diameter of stirred tank reactor, m |
| $E_a$ | Activation energy, kJ $mol^{-1}$ |
| $E_A$ | Enhancement Factor |
| $E_i$ | Instantaneous enhancement factor |
| EDX | Energy-dispersive X-ray spectroscopy |
| FT-IR | Fourier Transform Infrared Spectroscopy |
| G-L | Gas-Liquid Interface |
| $H_{CO_2}$ | Henry’s constant for carbon-dioxide in [TETA] [Lactate] solution |
| Ha | Hatta Number |
| ILs | Ionic Liquids |

| | |
|---|---|
| $k_{l}a$ | Volumetric mass-transfer coefficient, ms$^{-1}$ |
| $k_{-1}$ | Backward first-order reaction rate constant, s |
| $k_2$ | Forward second-order reaction rate constant for the formation of the zwitterion, m$^{3}$mol$^{-1}$ s$^{-1}$ |
| $k_{ov}$ | Overall pseudo-first order reaction rate constant, s$^{-1}$ |
| $k_B$ | Rate constant for the de-protonation of the zwitterion by a base, m$^{3}$ mol$^{-1}$ s$^{-1}$ |
| $k_n^2$ | Equals $\left[-\left(p_n+\lambda\right)/D_A\right]$, m$^{-1}$ |
| $K_e$ | Equilibrium distribution factor, dimensionless |
| $l$ | Representative length of an idealized gas pocket for absorption, equals $\frac{V_B}{12K_eS}$, m |
| M | Total amount of reactant A, both free to diffuse and immobilized, in half the liquid film of surface area S at contact time $t_c^*$ , k mol |
| $M_\infty$ | Total amount of reactant A, both free to diffuse and immobilized, in half the liquid film of surface area S after infinite time $t_c^*$ , k mol |
| n | Number of moles, k mol |
| $p_n$ | Equals $D_A k_n[tan(k_n a)]/l$, s$^{-1}$ |

| | |
|---|---|
| $P_1$ | Equals $\frac{Q_1}{V}$, s$^{-1}$ |
| $P_2$ | Equals $\frac{Q_1 C_{B1}}{V}$, k mol m$^{-3}$s$^{-1}$ |
| $Q_1$ | Flow rate of liquid entering the foam section, m$^3$s |
| S | Surface area of a liquid film, m$^2$ |
| t | Time of operation of the foam-bed reactor, s |
| $t_c$ | Time of contact between the liquid film and gas pockets in the foam section, s |
| $t_c^*$ | Total time of contact in the foam section, s |
| $t_i$ | Time node corresponding to the ith interval, s |
| V | Volume of the liquid in the storage section, m$^3$ |
| $V_l$ | Volume of the liquid film in the foam section, m$^3$ |
| $V_B$ | Volume of a foam bubble, m$^3$ |
| x | Spatial coordinate of a system with origin placed at the centre of the foam film, m |
| Y | Stoichiometric factor for B (moles of aqueous phase reactant B consumed per mole of A), dimensionless |