Indian Journal of Chemical Technology
Vol. 29, September 2022, pp. 560-565
DOI: 10.56042/ijct.v29i5.61187

Carbon monoxide absorption with iron and alcohol solutions via design expert method

Hava Gizem Kandilci, Hediye İrem Özgündüz, Nil Acaralı & Jale Gülen*

Yildiz Technical University, Department of Chemical Engineering, Davutpasa St., N.127, Esenler, Istanbul, Turkey

E-mail: gulenj@yildiz.edu.tr

Received 7 March 2022; accepted 5 May 2022

In this study, effective parameters on CO absorption using ethyl alcohol and iron solutions [time (15-75 min), temperature (36-40°C), concentration (0-40% v/v, of ethyl alcohol, 0-8%w/v, of iron solution), stirring rate (0-400 rpm)] and interactions of parameters with each other have been examined as the optimization method by using Design Expert method, 4 parameters and 5 levels. Mathematical optimization results are evaluated by finding the optimum points. As a result, the effects of parameters on CO absorption are comparatively investigated. It is observed that the parameters could interact binary and also influence CO absorption (R1). According to ANOVA analysis, the value of the quadratic model ($p<0.0001$) is found to be less than 0.05 and indicates that the model is meaningful for ethyl alcohol solution. The experimental data of the model is well represented for ethyl alcohol solution (R^2=0.9426) and iron solution (R^2=0.9384) as can be seen from correlation coefficients. The data are furnished via FT-IR spectra.

Keywords: Absorption, Carbon monoxide, Design Expert, Optimization

Industry has been developing day by day for the welfare of human being but many various effluents are discharged to the environment. Environment is under the threat of pollution in the form of solid, liquid and gaseous. Among the gas pollutants, carbon monoxide promising agent for triggering the greenhouse gas emission[1,2].

Carbon monoxide (CO) is one of the main agents among the other eminent gaseous pollutants that can be evolved due to the unburned fuels of the vehicles or industrial systems[3]. Once upon a time, CO and CH_4poisonings were especially tested by the effect on canaries in mining[4]. In our country, CO poisoning, which are seen in winter especially owing to social, economic and climatic reasons, constitute more than half of the poisonings that cause death due to haemoglobin affinity. Several effects on human being can be determined from the blood plasma[5]. CO intoxication is the first place among the most common poisonings in the social and especially mining operations[6]. The death after CO poisoning is common in our country and in the World[7]. CO is a colourless, odourless, tasteless gas which is formed as a result of the carbon-having fuels burning inadequate oxygen conditions[8]. When the human beings expose to CO emissions, it rapidly passes into the bloodstream with uniting haemoglobin; by forming carboxyhaemoglobin (COHb) spontaneously, and affects different parts of the body. High metabolic functions (cardiac and nervous system) are particularly affected due to intoxication CO[9,10]. The main sources of carbon monoxide are exhaust fumes of motor vehicles and generators of wood, coal, natural gas, gasoline[11] and propane-fueled heating systems, fires, paint solvents containing methylene chloride and cigarette smoke[10]. CO inhalation was demonstrated in various models[12]. An experimental study was performed but it was not confirmed in a clinical trial exposing healthy volunteers up to 500 ppm CO resulting in 7% CO-Hb[13]. A confidence study by using inhaled CO on kidney transplant patients gave some preclinical results[14,15]. Other trials were focused on local exposure of the lungs through inhaling CO. Another study on chronic pulmonary disease showed a trend on inhalation of 100 ppm CO (2.6% CO-Hb in term of total Hb[16]. Systemic CO levels can be checked against among clinical studies using CO-Hb formation[17]. Because of toxicity, CO was limited to CO-Hb levels of <10%. Some preclinical trials have been carried out between 250–500 ppm CO resulting in CO-Hb levels up to 20%[18-20]. Pharmacological differences about therapeutic gas delivery revealed major challenges in health[21,22]. As a result, differences in absorption and

kinetics among species were a significant issue for studies[23,24] (Fig. 1).

Optimization with factorial designs is an effective and systematic tool that cuts down the time required for the development of pharmaceutical forms. It improves research and development work by decreasing the number of experimental trials to evaluate multiple parameters and interactions by making the process less laborious. Factorial designs which entail working all the factors in all possible combinations, are considered to be the most efficient in estimating the effect of individual variables and interactions with usage of minimum experiments[25]. They have played an important role in understanding the relationship between the independent variables and the responses to them in pharmaceutical formulations improvement[26]. The independent variables or parameters or factors are controllable, whereas responses are dependent. The contour plot gives a 2-D visual whereas the responses surface gives a 3-D visual of the representation values of responses and maintains the process of optimization by providing an empirical model equation for the response as a function of the various variables[27,28,29].

In this study, parameters on CO absorption using ethyl alcohol and iron solutions were investigated by using the Design Expert method for 4 parameters and 5 levels. It was observed that the parameters could interact with each other and also influence CO absorption. The results indicated that the model was meaningful and parameters had a statistically significant effect on CO absorption.

Experimental Section

Materials

The Design of experiment (DoE) was constructed in this study using Design Expert® Software (Version 7.0.0, Stat-Ease Inc.). Ethyl alcohol (96%) and iron solution ($FeCl_2.6H_2O$) (234,751 g/mol) were purchased from Merck. CO gas (40 L) was supplied from Habas A.Ş. All other solvents and chemicals are of analytical grade.

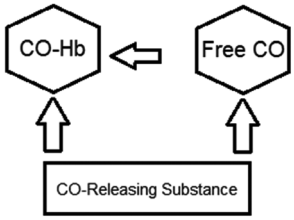

Fig. 1 — Interaction of CO-Hb mechanism

Method

Iron solution was prepared as 1 M for stock solution and later diluted with distilled water for the composition of 0 to 0.08 M with 0.02 M increments. Pure ethyl alcohol was diluted with distilled water for the composition of 0-40% (v/v) with 10% increments. The experiments were carried out in glass beaker containing solutions (iron or ethyl alcohol) by passing CO gas (5 mL/min) (Cole-Parmer Flowmeter).The present study consists of five full level central composite design (total 29 runs) for optimization. Statistical experimental design was performed by making use of Design-Expert 7.0.0. Response surface graphs were used to evaluate the factor interaction between the variables (Table 1). Selected independent variables studied were time (A); temperature (B); concentration (C) and stirring rate (D).The five levels for these variables were coded as 2, 1, 0, -1 and -2 for levels, respectively (Table 2). CO absorption (R1) was selected as dependent variable. A total of 29 experimental runs were required for analyzing the

Table 1 — Design Expert Method

Run	Factor 1 A:A	Factor 2 B:B	Factor 3 C:C	Factor 4 D:D
1	-1.00	+1.00	+1.00	-1.00
2	+2.00	0.00	0.00	0.00
3	-1.00	+1.00	+1.00	+1.00
4	0.00	0.00	0.00	0.00
5	-1.00	+1.00	-1.00	+1.00
6	-2.00	0.00	0.00	0.00
7	+1.00	+1.00	+1.00	+1.00
8	+1.00	-1.00	-1.00	-1.00
9	+1.00	-1.00	-1.00	+1.00
10	0.00	0.00	0.00	0.00
11	0.00	0.00	0.00	0.00
12	0.00	0.00	0.00	0.00
13	0.00	0.00	+2.00	0.00
14	0.00	0.00	0.00	0.00
15	+1.00	-1.00	+1.00	+1.00
16	0.00	0.00	-2.00	0.00
17	0.00	0.00	0.00	+2.00
18	-1.00	-1.00	+1.00	+1.00
19	-1.00	+1.00	-1.00	-1.00
20	+1.00	+1.00	-1.00	+1.00
21	+1.00	-1.00	+1.00	-1.00
22	-1.00	-1.00	+1.00	-1.00
23	0.00	+2.00	0.00	0.00
24	-1.00	-1.00	-1.00	-1.00
25	+1.00	+1.00	+1.00	-1.00
26	0.00	-2.00	0.00	0.00
27	-1.00	-1.00	-1.00	+1.00
28	+1.00	+1.00	-1.00	-1.00
29	0.00	0.00	0.00	-2.00

interaction of each level. The solutions were prepared not exceeding the toxicity value.CO values of reference (25°C, 0 rpm) and samples were measured by using Flue Gas Analyzer (Optima-7).

Results and Discussion

The optimization of CO absorption was carried out by chosen independent process variables (4) using 29 runs. Responses are given in Table 3 for specified ranges and levels of variables.

The amount of CO absorption was taken as the response to the design experiments. The quadratic equation model was stated to predict the optimal point. The Design Expert (version 7.0.0, StatEase) was used for regression and graphical analyses of the data. R1 and the model equation were used to predict the optimum values and to make clear the interaction between the parameters within the specified range[30].

In this study, the effect of parameters on CO absorption was comparatively investigated for ethyl alcohol and iron solution. As a result, it was observed that the parameters could interact binary and also influence CO absorption (R1). For ethyl alcohol solution, according to ANOVA analysis, the value of the quadratic model ($p<0.0001$) was less than 0.05 and indicated that the model was meaningful. The experimental data of the generated model were represented by a good correlation coefficient ($R^2=0.9426$). It was statistically observed that A, AB, AC, BC, BD, A^2, C^2 were significant model terms (Fig. 2).

The plots Figs. 2, 3 and Tables 1-3 showed that various combinations of independent variables A (time), B (temperature), C (concentration) and D (stirring rate) may satisfy any specific requirement (ie. increased or decreased). For example, as can be seen from Figure 2 and 3, when the stable conditions occurred, A, B and C were in harmony relationships whereas D was not. The physical parameters such as time (A), temperature (B) and concentration (C) were in good harmony as can be seen Figs 2 and 3 but the mechanical effect as stirring rate (D) is not for ethyl alcohol solution. This situation can be attributed to the chelating effect of iron. This similar increasing behaviour was seen for selected parameters of entrapment efficiency of topotecan and thymoquinone whereas the same parameters were inversely affected by the size of topotecan and thymoquinone[31].

A quadratic regression model was made by using coded values from the estimation of data for ethyl alcohol solution as Eq. (1):

$$\text{CO absorption} = +999.00-58.00 *A+14.50*B-12.67*C-15.58*D+74.50*A*B-28.87 *A*C+6.75*A*D+29.13*B*C-38.00*B*D+0.38*C*D-53.71*A^2-4.21*B^2-67.33*C^2+4.42*D^2 \quad ...(1)$$

The other quadratic regression model was made by using coded values for iron solution as Eq.(2):

Table 2 — Coded values with parameters for C1* and C2* solutions

Coded values	Parameters				
	A (min)	B (°C)	C1 (%)	C2 (%)	D (rpm)
+2	75	40	40	8	400
+1	60	39	30	6	300
0	45	38	20	4	200
-1	30	37	10	2	100
-2	15	36	0	0	0

C1* Ethyl alcohol, C2* Iron

Table 3 ─ Responses to CO absorption with C1,C2

Run	Response	Response
	R1-ethyl alcohol (ppm)	R1-iron solution (ppm)
1	989	829
2	621	760
3	860	667
4	1001	1058
5	784	644
6	935	522
7	879	662
8	795	619
9	815	798
10	998	1054
11	1003	1059
12	997	1063
13	693	712
14	996	1068
15	699	700
16	754	759
17	1015	664
18	945	808
19	903	791
20	870	900
21	609	570
22	992	797
23	945	685
24	957	683
25	986	822
26	1007	580
27	1002	569
28	1015	1086
29	1006	712

$$\text{CO absorption} = +1060.40+35.21*A+44.46*B-13.71*C-47.79*D+44.31*A*B-66.44*A*C+23.44*A*D-40.44*B*C-53.81*B*D+5.44*C*D-99.07*A^2-101.19*B^2-75.44*C^2-49.69*D^2 \quad ...(2)$$

For iron solution, according to ANOVA analysis, the value of the quadratic model ($p<0.0001$) was less than 0.05 and indicated that the model was expressive. The experimental data of the generated model were represented by a good correlation coefficient ($R^2=0.9384$). It was observed that A, B, D, AB, AC, BC, BD, A^2, B^2, C^2, D^2 were significant model terms (Fig. 3).

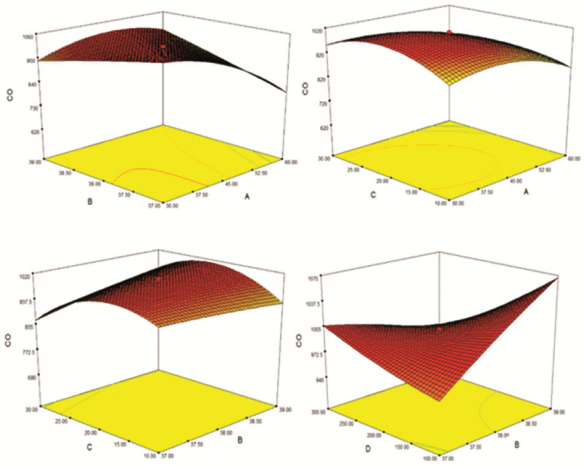

Fig. 2 — 3D Surface response graphs for ethyl alcohol solution

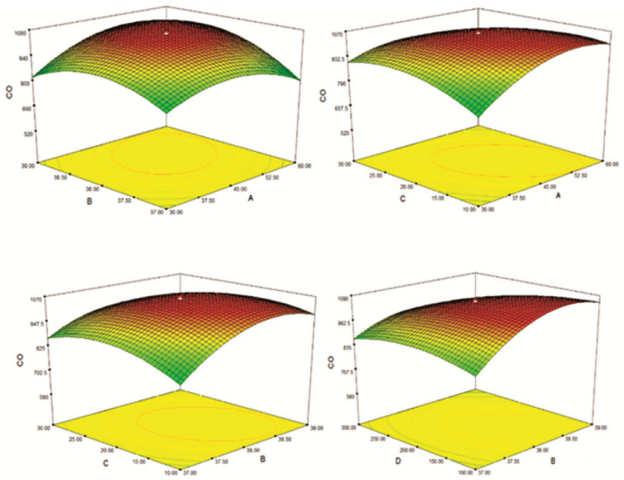

Fig. 3 — 3D Surface response graphs for iron solution

Another approach for materials characterization

CO is a general threat for human being due to the bad habits of cigarette smoking. Cigarettes that are one of the CO sources are used commonly all over the world. Tobacco-burning cigarettes yield smoke through a complex set of processes which occur when tobacco is burned. During smoking, combustion, pyrolysis, distillation, pyro-synthesis, condensation and elution contribute to the formation of a complex chemical mixture denoted as mainstream smoke, that is smoke that exits the mouth end of the cigarette during smoking (Table 4)[32].

TPM is the example of cigarette given in Table 4. The following table shows a severe complex groups that is emitted during the smoking a cigarette (Table 5)[32].

Fourier-transform (FT)-IR spectroscopy is a facile and powerful tool that provides various information regarding chemical and crystal states and bonds [33].

In this study, FT-IR spectra were drawn for a raw (unburned) and a burned cigarette for defining the structural variations of it from this point of view. A Cary 630 FT-IR by Agilent Technology was used to determine the wavelength from 4000 to 800 cm^{-1} (Fig. 4).

The band intensities were shown below:

3312, 3269 cm^{-1}OH stretching

2922, 2920cm^{-1}Aliphatic CH stretching

1874, 1724 cm^{-1}Aromatic carbonyl/carboxyl C=O stretching

1593, 1571 cm^{-1}Aromatic C=C ring stretching

1293 Aromatic CO stretching

1017 cm^{-1}aliphatic ether C-O stretching

777 cm^{-1}Aiphatic CH_2 deformation

Table 4 — Comparison of results from standard FTC measurements

Mainstream smoke yields (*mean* ± *SD*)

Results	IR5F	TOB-HT	IR4F
TPM	2.3 ± 0.2	4.6 ± 0.3	10.7 ± 0.6
"Tar" (mg/cig)	1.8 ± 0.2	2.9 ± 0.2	8.8 ± 0.5
Nicotine (mg/cig)	0.17 ± 0.01	0.19 ± 0.01	0.81 ± 0.04
Carbon monoxide (mg/cig)	2.9 ± 0.2	7.5 ± 0.5	11.1 ± 0.4
Puffs per cigarette	7.1 ± 0.3	15	8.9 ± 0.3

Table 5 — Target compound determination results

Analyte	Average yield IR5F	TOB-HT	IR4F
Acetaldehyde (µg/cig)	134	70	682
Isoprene (µg/cig)	121	9	353
Nitrogen oxides (µg/cig)	107	35	279
Acetone (µg/cig)	62	22	272
HCN (µg/cig)	21	5.1	165
Toluene(µg/cig)	18	6.8	63
Acrolein (µg/cig)	11	20	72
1,3 – Butadiene (µg/cig)	17	1.6	35
Benzene (µg/cig)	13	6.2	38
Ammonia (µg/cig)	7.8	5.5	19.8
Acrylonitrile (µg/cig)	2.8	1.3	11.6
Formaldehyde (µg/cig)	0.7	1.2	11.8
Furfural (µg/cig)	1.3	1.7	1.2
Quinoline (µg/cig)	32	nd	203
NAT (µg/cig)	48	15	97
NNN (µg/cig)	41	11	68
NNK (µg/cig)	21	14	67
Catechol (µg/cig)	8	0.4	45
Hydroquinone (µg/cig)	6	0.7	40
Phenol (µg/cig)	0.7	0.1	11.1
P-and *m*-Cresol (µg/cig)	0.8	0.1	8.1
B[a]P (µg/cig)	1.3	0.6	5.0
2-Aminonaphthalene (µg/cig)	4.0	1.9	12.1
4-Aminobiphenyl (µg/cig)	1.3	nd	3.3

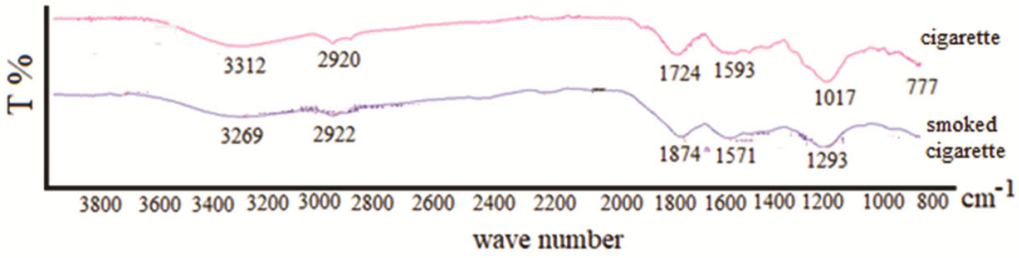

Fig. 4 — FT-IR spectra of burned and unburned cigarette

Conclusion

The response surface methodology of CO absorption modelling has been evaluated for different solutions. The interactions between the factors on the response were comparatively investigated. The optimum conditions of absorption are approximately 60 min, 37°C, 30% (v/v), 100 rpm for ethyl alcohol solution and 32 min, 39°C, 2% (w/v), 289 rpm for iron solution. It is determined that optimum amount of CO absorption was 682 ppm and 504 ppm for ethyl alcohol and iron solution, respectively. The structural effects of different C, H and O groups are explained via FT-IR spectra drawn. This is the indicator how to form the complex groups during the cigarette smoking.

Conflict of interest

The authors declare no conflict of interest.

References

1 Johansson E, Mattisson T, Lyngfelt A & Thunman H, *Chem Eng Res Design*, 84 (2006) 819.
2 Stoica C, Dınu I, Lucacıu I, Nıta-lazar M & Oncu V, *Rev Chım*, 71 (2020) 67.
3 Patrylak L K, Okhrimenko M V, Levterov A M, Konovalov S V, Yakovenko A V & Zubenko S O, *Chem Papers*, 73 (2019) 1823.
4 Remli M A, Mohamad M S, Deris S, Samah A A, Omatu S & Corchado J M, *Exp Syst Appl*, 116 (2019) 131.
5 Amarnath A K S, Suresh C A & Rakshit A, *Indian J Chem Technol*, 28 (2021) 47.
6 Singh K, Shakya H K, Singh A & Biswas B, *Exp Syst*, 35 (2018) 1.

7 Tirosh E & Schnell I, *Environ Sci Pollut Res*, 23 (2016) 21157.
8 Jain K K, *Hyperb Med*, 111 (2004) 133.
9 Hampson N B, Scott K & Zmaeff J L, *J Emerg Med*, 31 (2006) 13.
10 Tintinalli J E, Kelen G D & Stapczynski J S, Carbon Monoxide Poisoning, Emergency Medicine, edited by G Maloney, (2011) 555.
11 Saratwat M & Chauhan N R, *J Sci Indust Res*, 78 (2019) 382.
12 Motterlini R & Otterbein L E, *Nat Rev Drug Discov*, 9 (2010) 728.
13 Mayr F B, Spiel A, Leitner J, Marsik C, Germann P, Ullrich R, Wagner & Jilma B, *Am J Respir Crit Care Med*, 171 (2005) 354.
14 Neto J S, Nakao A, Kimizuka K, Romanosky A J, Stolz D B, Uchiyama T, Nalesnik M A, Otterbein L E & Murase N, *Am J Physiol Renal Physiol*, 28 (2004) F979.
15 Nakao A, Neto J S, Kanno S, Stolz D B, Kimizuka K, Liu F, Bach F H, Billiar T, Choi A M K, Otterbein L & Murase N, *Am J Trans*, 5 (2005) 282.
16 Bathoorn E, Slebos D J, Postma D S, Koeter G H, van Oosterhout A J, van der Toorn M, Boezen H M & Kerstjens H A, *Europ Respir J*, 30 (2007) 1131.
17 Vreman H J, Wong R J, Stevenson D K, Smialek J E, Fowler D R, Li L, Vigorito R D & Zielke H R, *J Forensic Sci*, 51 (2006) 1182.
18 Zeynalov E & Dore S, *Neurotox Res*, 15 (2009) 133.
19 Nakao A, Kimizuka K, Stolz D B, Neto J S, Kaizu T, Choi A M, Uchiyama T, Zuckerbraun B S, Bauer A J, Nalesnik N A, Otterbein L E, Geller D A & Murase N, *Surgery*, 134 (2003) 285.
20 Venditti C C, Casselman R & Smith G N, *BMC Pregnancy Childbirth*, 11 (2011) 101.
21 Romao C C, Blattler W A, Seixas J D & Bernardes G J, *Chem Soc Rev*, 41 (2012) 3571.
22 Knauert M, Vangala S, Haslip M & Lee P J, *Oxid Med Cell Longev*, 3 (2013) 608.
23 Wilson M R, O'Dea K P, Dorr A D, Yamamoto H, Goddard M & Takata M, *PloS One*, 5 (2010) e11565.
24 US National library of Medicine, ClinicalTrials.gov., Carbon monoxide therapy for severe arterial hypertension (CO in PAH), https://clinicaltrials.gov/ct2/show/NCT01523548 , August (2022).
25 Singh B & Ahuja N, *Drug Dev Indust Pharm*, 28 (2002) 431.
26 Vandervoort J & Ludwig A, *Pharmazie*, 56 (2001) 484.
27 Kincl M, Turk S & Vrecer F, *Int J Pharmt*, 291 (2005) 39.
28 Mehta A K, Yadav K S & Sawant K K, *Curr Drug Deliv*, 4 (2007) 185.
29 Patil S B & Sawant K K, *J Microencapsul*, 26 (2009) 432.
30 Elibol M & Ozer D, *Proc Biochem*, 38 (2002) 367.
31 Verma D, Thakur P S, Padhi S, Khuroo T, Talegaonkar S & Iqbal Z, *J Mol Liq*, 242 (2017) 382.
32 Borgerding M F, Bodnar J A, Chung H L, Mangan P P, Morrison, Risner C H, Rogers J C, Simmons D F, Uhrig M S, Wendelbof F N, Wingate D E & Winkler L S, *Food Chem Toxicol*, 36 (1997) 169.
33 Ehiro T, *Chem Pharm Bull*, 69 (2021) 693.