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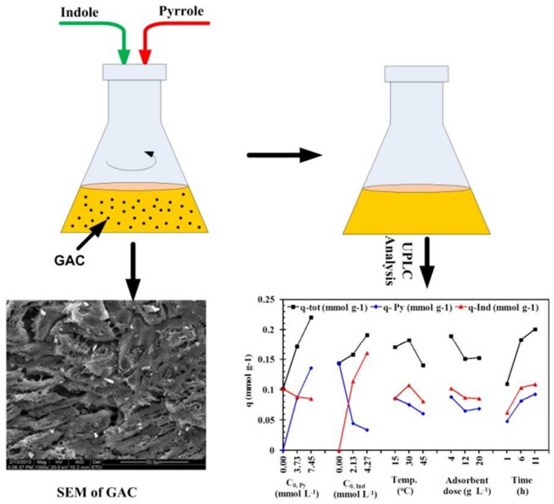
Graphical Abstract

Granular activated carbon used for simultaneous adsorption of pyrrole and indole from aqueous solution.



Simultaneous Adsorption of Nitrogenous Heterocyclic Compounds by Granular Activated Carbon: Parameter Optimization and Multi-Component Isotherm Modeling

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Many industrial aqueous streams contain nitrogenous aromatic compounds which need to be removed by adsorption process for which it is essential to study interactive affects these compounds during their simultaneous adsorption. In the present study, granular activated carbon (GAC) was used for simultaneous adsorption of pyrrole and indole from aqueous solution. First, Taguchi's method (L_{27} orthogonal array) was applied to optimize various parameters like initial adsorbate concentration, adsorbent dose, temperature and contact time for their simultaneous adsorption onto GAC. Adsorbent dose and the interaction between initial concentrations C_o's were found to be the most significant factor. Indole adsorption onto GAC was found to be higher than that of pyrrole. Thereafter, binary adsorption equilibrium data were generated and modeled by various multi-component isotherm models. Extended-Langmuir isotherm best-represented the isotherm data at 30 °C among various multi-component isotherm models used in this study.

Keywords: Adsorption; multi-component adsorption; isotherm modeling.

1. Introduction

Nitrogenous heterocyclic compounds such as pyrrole and indole (which contain fused structure of benzene ring with pyrrole ring) are widely found in natural crude oil, coal tar and bone oil.[1] Coal tar contains nitrogenous compounds such as carbazole (0.9%), quinoline (0.2-0.3%), indole (0.2%), isoquinoline (0.1-0.2%), 2-methylquinoline (0.1-0.2%) and other compounds. Acridine, pyrrole, pyrrolidine, etc. are the major nitrogenous heterocyclic compounds found in creosote which is a distillate of coal tar.[2] Due to higher solubility in water and weak sorption on soil, these heterocyclic compounds readily get transported to subsurface environments contaminating groundwater. Because of toxic and carcinogenic potential, these heterocycles are considered to be priority pollutants by United States Environmental Protection Agency (USEPA).[3-5]

Various physico-chemical methods are available for the treatment of heterocyclic compounds such as thermal catalytic incineration, advanced oxidation processes (AOPs), hydrodenitrogenation, etc. Biodegradation is also used for the degradation of these compounds. Among various heterocyclic compounds removal techniques, adsorption is known to be more useful and economical. The adsorbents used in adsorption must be cheap, easily available, and regenerable with large surface area and high adsorption affinity for the adsorabtes. The adsorption of indole with other components from diesel fuels, light cycle oils and aqueous solution on activated carbons[6-11] and other adsorbents with few metal organic frame work[12-20] have been investigated by various researchers (Table 1). Few studies have been reported on adsorption of pyrrole along with other components onto metal and other surfaces.[21-29]

A few studies are reported in literature on simultaneous adsorption of simple aromatic nitrogenous compounds such as aniline, nitrophenol, nitrobenzene, etc. Suresh *et al.*[30] reported adsorptive removal of phenol, aniline and nitrophenol from aqueous solution using GAC. They applied Taguchi's method of design to study the effect of various parameters. Lataye *et al.*[31] reported pyridine and 2,4 picoline removal by adsorption from aqueous solution using bagasse fly ash. However, in both these studies, multicomponent isotherm modelling was not done and only optimization of parameters was studied. Jadhav *et al.*[32] studied the simultaneous adsorption of nitrobenzene, aniline and phenol onto activated carbon where isotherm modelling of the adsorption data was done by ideal and real adsorbed solution theories. However, Jadhav *et al.*[32] didn't study the optimization of parameters. Koubaissy *et al.*[33] investigated the removal of various nitrophilic compounds from aqueous solution using zeolites. In this investigation, adsorption equilibrium data was well described by using Fowler-Guggenheim equation. Adsorption capacity of zeolite for ortho-nitrophenol adsorption was found to be higher than that of other nitrophilic compounds. The Langmuir and Freundlich models did not perform well for adsorption equilibrium data. Koyuncu *et al.*[34] conducted experiments to study adsorption characteristics of o- , m-, and p- nitrophenols by doing organic modification on bentonites at different temperature.

Studies on simultaneous adsorption of heterocyclic nitrogenous compounds like pyrrole, indole, etc. from aqueous solutions are scarcely reported. However, few studies are reported on their adsorption from liquid fuels (Table 1). Ahmed *et al.*[14-16] investigated adsorptive denitrogenation of model fuel by metal organic frame works (MOFs). Langmuir, Freundlich and Temkin isotherms were applied to interpret the adsorption data for the removal of compounds like indole and quinoline. Voorde *et al.*[17] studied the influence of metal ions in MOFs on adsorptive removal of these heterocyclic compounds by combining isotherms with microcalorimetric and IR spectroscopic characterizations. Zhang *et al.*[19, 20] studied adsorption of pyrrole and indole along with other nitrogenous compounds from diesel fuel by molecular sieve Ti- HMS and MCM-41. It was observed that MCM-41 found to be most suitable for maximum uptake of indole and Ti- HMS for pyrrole adsorption.

Pyrrole is a five-membered nitrogen-containing heterocyclic aromatic organic compound whereas indole structure consists of a six-membered benzene ring fused to a pyrrole ring. Thus, molecular size of indole is more than twice of that of pyrrole. Pyrrole is weakly basic with a pK_a of -3.8, however, indole is not basic. Pyrroles generally react with electrophiles at the α position (C2 or C4) whereas indole undergoes electrophilic substitution, mainly at position 3. The bonding situation of pyrrole and indole are completely analogous. Owing to the fact that pyrrole and indole are both nitrogen-containing heterocyclic aromatic organic compound, however, they have different molecular size and bascity and are likely to affect the adsorption of each other from aqueous solution. Therefore, study on simultaneous adsorption of pyrrole and indole from aqueous solution is very necessary for understanding their interference on the adsorption of each other. However, no study is reported on simultaneous adsorptive removal of pyrrole and indole from binary aqueous mixture.[6,19-20]

In the present study, first the parameters for simultaneous adsorptive removal of pyrrole and indole from aqueous solution have been optimized by usage of Taguchi's methodology which is a statistical technique for optimization of multi-component adsorption. Thereafter, single and binary adsorption isotherm data at 30°C were obtained using the optimized condition obtained in the first step. These binary isotherm data have been further used for determination of binary isotherm parameters for pyrrole and indole which can be used in future for design of adsorption beds. Taguchi's methodology was first used in multi-component adsorption by our research group and now has received greater application.[35] The methodology adopted in the present study can be further extended to ternary adsorption also and it helps in performing the optimization and modeling studies in lesser number of experiments as compared to traditional 'one parameter at a time' optimization approach.

2. Materials and methods

2.1. Adsorbent and adsorbate

GAC was procured from NICE chemicals private limited, Kochi, India. Indole was obtained from Himedia Laboratories private limited, Mumbai, India. Pyrrole was purchased from Sigma Aldrich, Bangalore, India. All analytical reagent (AR) grade chemicals were used in this study. To prepare stock solutions, indole was dissolved with hot double distilled water whereas pyrrole was dissolved with normal double distilled water. The working solutions were prepared by appropriate dilutions of stock solution with distilled water as per requirement.

2.2. Instrumentation

Moisture content was calculated by determining loss of mass after keeping known mass of GAC in oven at 108 ±2 ^{o}C. For determining the volatile matter, preweighed quantity of air dried sample of GAC was taken in cylindrical silica crucible with well fitted lid and was heated at 900 ±10 ^{o}C in muffle furnace for 7 min. The difference in weight before and after heating gave volatile matter present in GAC. For determining the ash content, known weight of GAC was taken in silica crucible and heated at 500 ^{o}C for 30 minutes in muffle furnace. This temperature was raised to 815±10^{o}C in further 30 min and maintained at this temperature up to run-up period.[36] The separation module was used for analysis of binary mixture was done using Waters Acquity ultra performance liquid chromatograph (UPLC) H Class at 205 nm using a C18 column (2.1 x 50 mm, 1.7 m particle size). Chromatographic separation was achieved by gradient elution at flow rate of 0.5 mL min^{-1} by maintaining column and sample temperature at 35 ^{o}C and 20 ^{o}C respectively. Mobile phases applied during analysis were 60% millipore water and 40% acetonitrile.

X-ray diffraction (XRD) unit (Phillips (Holland), Model PW1140/90) was used for structural analysis using copper and nickel as target and filter media, respectively. Brunauer-Emmett-Teller (BET) surface area analysis was performed using surface area and porosity analyzer (ASAP 2020, Micromeritics). Virgin and loaded GAC samples were degassed at temperature 200 °C for three hours which will not cause a structure change to the sample.[11] The field emission scanning electron microscope (FE-SEM)/energy-dispersed X-ray (EDX) spectra of GAC were obtained using scanning electron microscope (LEO 435 VP). Nicolet Avatar 370 CsI spectrometer (Thermo Electron Corporation, USA) was used to obtain Fourier Transform Infrared (FTIR) spectra over a range of 4000-400 cm^{-1} by using KBr pellet in order to determine the chemical nature and type of functional groups present on the adsorbent. MAC bulk density meter was used for determining the bulk density of GAC. Thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out in presence of air in a temperature range from room temperature up to 1000 °C. The heating rate was kept 10°C/min.

2.3. Experimentation

Synthetic stock solution of pyrrole and indole were prepared with double distilled water to 500 mg L^{-1} and 1000 mg L^{-1}. Mixing were done in equal proportion to get binary mixture each having concentrations 250 mg L^{-1} or 500 mg L^{-1}. Similarly, binary mixtures of different concentrations of each solute were prepared. In each experimental run, 100 ml of a solution containing desired concentration of indole and pyrrole with desired adsorbent dose of GAC was taken in a 250 ml conical flask with glass stopper. This flask was kept in an orbital shaker under controlled temperature at shaking rate of 150 rpm. Most of the experiments were performed at three temperatures (i.e. at 15, 30 and 45 °C) while isotherm study was done at 30 °C only. After the desired contact time, Samples were withdrawn at appropriate time, centrifuged at 10,000 rpm for 5 min using research centrifuge (Remi Instruments, Mumbai) and analyzed for residual pyrrole and indole concentration with the help of UPLC.

3. Results and discussions

3.1. Adsorbent characterization

Moisture content, volatile matter, ash and fixed carbon for blank GAC were found to be 9.1%, 27.33%, 2.1% and 61.47%, respectively. Bulk density for GAC was measured to be 628 kg/m^3. XRD spectra showed absence of any crystalline peak except for the presence of a broad peak in GAC indicating presence of silica in amorphous form. EDX analysis showed the presence of 95.54% C and 4.46% O in blank GAC.

Sorption properties of any adsorbent for adsorption of any adsorbate are highly dependent on its textural properties particularly surface area and pore size.[37] Textural characteristics of GAC before and after simultaneous pyrrole and indole adsorption are shown in Fig. 1. In accordance with the International Union of Pure and Applied Chemistry (IUPAC) classification, pore size are classified as micro pores ($d < 20$ Å), meso pores (20 Å $< d < 500$ Å) and macro pores ($d > 500$ Å).[38] Single point total pore volume for GAC before and after simultaneous pyrrole and indole adsorption was found to be 0.188 cm³ g^{-1} and 0.101 cm³ g^{-1}. BJH adsorption/desorption pore area and pore volume (17 Å $< d < 3000$ Å) for blank GAC were 47.99/36.65 m^2 g^{-1} and 0.029/0.022 cm³ g^{-1}, respectively.[39] BET surface area of GAC before and after simultaneous pyrrole and indole adsorption was found to be 354.76 m^2 g^{-1} and 190.93 m^2 g^{-1} indicating adsorption of nitrogenous heterocyclic compounds on GAC. The analytical summary indicate that micro-pore (pore diameter (d) < 20 Å) have total pore area of 42.88 % and meso-pores (20 Å$< d < 500$ Å) total pore area of 57.11 % in GAC. For GAC, the fractal dimension (D) value of 2.98 indicates rough irregular surface.

TGA and DTA analysis of blank and simultaneous pyrrole and indole loaded GAC were done at 10 K min^{-1} heating rate (Fig. 2). It was found that weight loss due to loss of light volatile molecules and moisture for blank GAC and loaded GAC were 28.6% at 381°C and 15.9% at 408

^{o}C, respectively, without any endothermic transition indicating no phase changes during the heating process up to these temperatures.[40] Blank GAC showed 69.8% weight loss between 381°C and 578 °C whereas loaded GAC showed 71.5% weight loss between 408 ^{o}C and 530 ^{o}C. This study shows that GAC is fully stable up to 381^{o}C and that the loaded GAC can be nearly fully oxidized in oxidative environment with sufficient recovery of energy.

FTIR spectrum (Fig. 3) of GAC shows a broad band with peak at ≈3400 cm^{-1} indicating free and hydrogen -bonded OH groups. It also shows a peak at ≈1634 cm^{-1} indicating C=C stretch. The band at 1375 cm^{-1} is ascribed to be C-H bending in plane. The peak in the region of 1748 cm^{-1} indicates the presence of a CO group stretching from anhydride and esters. The sharp band at 3464.82 cm^{-1} is attributed to N–H stretching.[41] Bands at 2850 and 2917 cm^{-1} indicate C-H Stretching on GAC. Band at 1590 cm^{-1} shows stretching and deformation of N–H bond and vibration modes of C2 and C3 aromatic bonds.The band at 1375 cm^{-1} is related to modes involving the C8–N–C2–C3 group. Band at 1235 cm^{-1} signifies the heterocyclic ring stretching modes.

3.2 Optimization of parameters for binary adsorption of pyrrole and indole

3.2.1. Multi-component study using Taguchi's method

Taguchi's orthogonal array (OA) method was used to show the effects of parameters. In the optimization of a process by Taguchi's method, certain steps should be followed.[35] First step is the identification of performance characteristics and selection of process parameters. Second step is to decide the number of process parameters and their interaction. Based on the previous study for individual compound adsorption, factors that affected the simultaneous removal of pyrrole and indole from waste water onto GAC were identified. In the present study, five process parameters were selected for experimental design. The process parameters and their level are given in Table 2. In simultaneous adsorption, two parameter interactions between initial concentrations of adsorbates ($C_{o,Py}$ X $C_{o,,Ind}$) is very important as removal efficiency is sometimes highly dependent on characteristics of each other. Third step is to select orthogonal array (OA) and assign parameters to it. The selected OA must satisfy the inequality that the total degree of freedom required for the experiment should be less than or equal to total degree of freedom (DOF) of the OA.[35, 42] The total required degree of freedom for the experiment is 14 (5 x (3-1) + 1 x 4 = 14). This is due to the fact that three level parameter has DOF=2 (number of levels – 1) and for each two parameter interaction DOF value is 4 (2x2).[43] Based upon the number of parameters and their levels, L_{27} OA (Table 3) was used for carrying out experiments for simultaneous pyrrole and indole adsorption onto GAC. The individual adsorption capacities of pyrrole and indole (q_{Py} and q_{Ind}) and the total adsorption capacity (q_{tot}) were estimated using following relationships:

$$q_{tot} = q_{Py} + q_{Ind} = [(C_{0,Py} - C_{e,Py}) + (C_{0,Ind} - C_{e,Ind})] / m \qquad (3)$$

The calculated average value of q_{Py}, q_{Ind} and q_{tot} for each parameter at different levels are given in Fig. 4. It is seen that adsorption of both pyrrole and indole is highly dependent on the parametric conditions.

3.2.2. Process parameters effects

The effects of parameters on q_{tot}, q_{Py} and q_{Ind} for adsorption of pyrrole and indole onto GAC are given in the Fig. 4. The values of $q_{tot,}$ q_{Py} and q_{Ind} are found to be highly dependent on various parameters (C_{oi} T, m and t). It can be seen from the graph that an increase in $C_{o,i,}$ and t from 1 to 2 and 2 to 3 resulted in an increase in q_{tot} value.

Temperature (T) is found to affect the q_{Py} and q_{Ind} values differently. When T increases from 15 °C to 45 °C, q_{Py} decreases indicating exothermic nature of the adsorption process, however, q_{Ind} increases with an increase in T from 15 ^{o}C to 30 ^{o}C and decreases from 30 ^{o}C to 45 ^{o}C. When adsorption of pyrrole decreases, q_{Ind} increases and when adsorption of indole decreases q_{Py} increases. This is because both pyrrole and indole compete for the same active sites. But effective q_{tot} increases with increase in all other parameters for particular designed adsorption process. Results may vary from those that were obtained for individual adsorption as there was a lot of interaction between pyrrole and indole for same adsorption sites.

It is seen that q_{tot} value increased with an increase in time from level 1 to 3 (i.e. from 1 h to 11 h). Adsorption of pyrrole and indole increases with an increase in contact time until equilibrium is achieved between the adsorbates and the adsorbent. It is observed that indole achieved equilibrium earlier as compared to pyrrole. During the initial stages numbers of vacant sites are available for adsorption but after sometime sites get occupied due to which repulsive forces come into play between the solute molecules. Adsorption slows down in the later stages because of pyrrole and indole molecule travel deeper into the pores of adsorbent creating resistance to transport molecules. q_{tot} decreases with increase in dose (m) from level 1 to 2 and then from 2 to 3 , however, percent removal (analysed separately) increased with an increase in adsorbent dose due to presence of more sites at higher adsorbent dose for adsorption.

Relative influence of various parameters can also be studied from Fig. 4. It can be seen that adsorbent dose has the greatest effect at level 1 on q_{tot} whereas temperature and time greatly affect at level 2 and $C_{o,Py}$ has highest effect at level 3. It can also be seen that overall $C_{o,i}$ and time have strongest influence on q_{tot} than other parameters. q_{Py} increased with $C_{o,i}$ because of the increase in mass transfer driving force which resulted in the decrease of resistance to the adsorbate uptake. $C_{o,Ind}$ has significant effect at level 1 on q_{Py} whereas $C_{o,Py}$ significantly affect at level 2 and 3. Highest difference between level 1 and level 2 for $C_{o,Py}$ indicates stronger influence on q_{Py} as compared to other parameters. Similarly, $C_{o,Py}$ and adsorbent dose significantly affect q_{Ind} at level 1. Again largest difference between level 1 and level 2 for $C_{o,Ind}$ indicates stronger influence on q_{Ind} as compared to other parameters.

The effect of concentration of one component with respect to other component i.e. the interaction between the components has a significant effect on q_{tot} values (Fig. 5). Parallel lines indicate no interaction whereas non–parallel lines indicate existence of an interaction between $C_{o,i}$ as seen in the interaction graph. Large difference in values of slopes of lines of $C_{o,Py}$ and $C_{o,Ind}$ results in significant interaction in the tested range.[44,45]

ANOVA results for responses q_{tot}, q_{Py} and q_{Ind} during binary adsorption of pyrrole and indole onto GAC are given in Table 4. The level of factors can be controlled in a manner that higher or lower values produce the preferred results. Thus the level of factor which produces preferred result can easily be predicted.

3.2.3. Optimum level selection and optimum response characteristics estimation

Optimum levels of parameters for maximum adsorption were obtained by examining the q_{tot} values. Higher value of q_{tot} were found to be at first level parameter for D (m), at second level parameter for C (temperature) and at third level parameter for A, B ($C_{o,i}$), and E (time). The optimal value of the response curve was measured by following relationship:[35,46]

$$q_{tot,predicted} = \overline{T} + (\overline{A_3} - \overline{T}) + (\overline{B_3} - \overline{T}) + (\overline{C_2} - \overline{T}) + (\overline{D_1} - \overline{T}) + (\overline{E_3} - \overline{T}) \quad (4)$$

Where, $\overline{C_2}$ and $\overline{D_1}$ is the average value of response at second level of parameter C and first level of parameter D, respectively. For parameters A and B, third level was chosen so as to check the adsorption efficiency for maximum concentration. The predicted maximum value of q_{tot}, q_{Py} and q_{Ind} for GAC were 0.35, 0.15 and 0.20 mmol g^{-1}, respectively. Three confirmation experiments were conducted at selected optimal levels for the simultaneous removal of pyrrole and indole from binary solution by GAC. The calculated value of q_{tot}, q_{Py} and q_{Ind} for GAC were 0.34, 0.16 and 0.18 mmol g^{-1}, respectively. These values are within 95% confidence interval.

3.3. Multi-component isotherm study

For binary isotherm study, binary mixture of pyrrole and indole were taken and simultaneous adsorption was studied at 30°C. For each initial concentration of indole: 50, 100, 250, 500 and 750 mg L^{-1}, initial concentration of pyrrole was varied from 50 to 750 mg L^{-1}. From Table 5, it is observed that equilibrium uptake of indole increased as its concentration was increased for fixed concentration of pyrrole. But individual percent removal decreased for the same component as pyrrole concentration increased. Similar trend was observed for pyrrole with increasing concentration of indole.

Binary isotherm study results (Table 6) show that for 4.27 mmol L^{-1} (500 mg L^{-1}) concentration of indole with presence of 7.45 mmol L^{-1} (500 mg L^{-1}) of pyrrole, q_{Ind} was 0.18 mmol g^{-1}. Similarly for 6.402 mmol L^{-1} (750 mg L^{-1}) concentration of indole with presence of 11.17 mmol L^{-1} (750 mg L^{-1}) of pyrrole, q_{Ind} was 0.19 mmol g^{-1}. Reduction in capacity for competitive adsorption is dependent on the molecular structure of the competing adsorbates, the initial concentration of the pollutants, and the surface structure of the adsorbent.[47] Binary equilibrium adsorption data indicate that adsorption capacity of GAC is higher for indole than that of pyrrole. There are interactions between the species in the solution as well as on the surface. Solute–surface interactions complicate adsorptions in multicomponent systems. Multi-ion systems have received less attention than single-ion systems.[48] Basic Langmuir model for single adsorbate adsorption is extended as in the form of non-competitive Langmuir model for multi-component systems. Langmuir model is applicable for monolayer coverage whereas Freundlich model is applicable for multilayer adsorption.[49] These isotherms are applied by various researchers for single component adsorption process.[50,51] Adsorption of individual component constant may not define the exact behaviour in the multicomponent system. Therefore for better accuracy modified isotherms may be applied by using individual isotherm parameters obtained with correction factor.

Various multi-component isotherms like non-modified, modified and extended-Langmuir, R-P models, extended-Freundlich, etc.[46,52] have been used to fit the data obtained from simultaneous adsorption of pyrrole and indole onto GAC using SSE. SSE for multi-component adsorption is given by:

$$SSE = \sum_{i=1}^{n} ((q_{e,meas} - q_{e,calc})_{Ind} + (q_{e,meas} - q_{e,calc})_{Py})_i^2 \tag{5}$$

Table 6 shows SSE values between calculated and experimental q_e values for pyrrole and indole data with various parameters of single and multi-component isotherms. Non-modified models show poor fit for adsorption data for binary system as SSE values are very large for these models. For non- modified Langmuir model, SSE value is found to be 1.36 which is much higher than extended-Langmuir and modified-Langmuir model. It is also found that extended-Langmuir with SSE value 0.037 has better fit as compared to modified-Langmuir with SSE value 0.103. In extended-Langmuir model, K_i value reflects the affinity between adsorbate and adsorbent in a binary mixture which is 4.70 for indole and 0.66 for pyrrole while overall adsorbate uptake q_{max} is 0.32 mmol g^{-1}. Extended-Langmuir model and Extended-Freundlich model gives SSE value 0.037 and 0.038 respectively. The parity plots (Fig. 6) presents comparison between actual and theoretical q_e values of pyrrole and indole.

Non-modified Langmuir and non-modified Redlich-Peterson models use the parameters calculated from individual compound adsorption only for modeling binary adsorption isotherm and have large SSE values. Modified Langmuir model and modified Redlich-Peterson models use only one interaction parameter (η_i) for each compound for modeling binary adsorption isotherm in addition to individual compound isotherm parameters, and thus, show lower SSE values and better representation of experimental data as compared to non-modified models. However, still their predictions are not satisfactory. It is known that the extended Freundlich model takes into account the interactive effects of individual adsorbates between and among themselves and the adsorbent reasonably well (SSE=0.038).[53] GAC has generally heterogeneous surface, although less heterogeneous as compared to other low cost adsorbents reported in the literature; and also the adsorption of the individual adsorbates have also been well represented by the Langmuir isotherm equation. Therefore, the lowest SSE value (SSE=0.037) was observed for the fitting of the extended-Langmuir model. Thus, any of extended-Langmuir or extended-Freundlich isotherm model can be used for representing the binary adsorption data.

4. Conclusions

Taguchi's method was found to be very useful and economical for optimizing the operating parameters for simultaneous adsorptive removal of pyrrole and indole from binary aqueous solution onto GAC. Adsorbent dose and interaction between $C_{o,i}$'s were found to be the most significant factors for particular adsorption process along with time and temperature optimized at three different level. q_{tot} increased with $C_{o,i}$ because of the increase in mass transfer driving force which resulted in the decrease of resistance to the adsorbate uptake. Results may vary from those for individual adsorption as there was a lot of interaction between pyrrole and indole for binary adsorption system. In the binary system, adsorption was found to be antagonistic in nature, and the adsorption capacity for indole was found to be higher than that of pyrrole. Overall extended-Langmuir model best represents the binary adsorption data in the adsorptive removal of pyrrole and indole from binary aqueous solution.

Nomenclature

A, B, C, D, E - Interaction parameters

$\overline{A_3}$, $\overline{B_3}$, $\overline{C_3}$, $\overline{D_1}$, $\overline{E_3}$ -Average values of the response at the third levels of parameters *A, B, C and E respectively and* D_1 is the first level of parameter *D*

$C_{0,i}$	Initial concentration of each component in solution (mmol L^{-1})
$C_{0,Py}$	Initial concentration of pyrrole (mmol L^{-1})
$C_{0,Ind}$	Initial concentration of indole (mmol L^{-1})
$C_{e,i}$	Equilibrium concentration of adsorbate (mmol L^{-1})
m	Adsorbent dosage (g L^{-1})
$q_{e,Py}$	Amount of pyrrole adsorbed per unit mass of GA Cat equilibrium (mmol g^{-1})
$q_{e,Ind}$	Amount of indole adsorbed per unit mass of GAC at equilibrium (mmol g^{-1})
q_{tot}	Total amount of solute adsorbed per unit mass of GAC (mmol g^{-1})
$\overline{T}$	Overall mean of response
a_R	Constant of Redlich- Peterson isotherm (L $mmol^{-1}$)
$K_{EL,i}$	Individual extended Langmuir isotherm constant of each component (L $mmol^{-1}$)
k_L	Langmuir isotherm constant of each component (L $mmol^{-1}$)
$K_{L,i}$	Individual Langmuir isotherm constant of each component (L $mmol^{-1}$)
k_F	Mono component (non-competitive) constant of Freundlich isotherm of single component ((mmol g^{-1})/(L $mmol^{-1}$)$^{1/n}$)
$k_{F,i}$	Individual Freundlich isotherm constant of each component ((mmol g^{-1})/(L $mmol^{-1}$)$^{1/n}$)

k_R	Constant of Redlich- Peterson isotherm (L g^{-1})
n	Mono component (non-competitive) Freundlich heterogeneity factor of single component
n_i	Individual Freundlich heterogeneity factor of each component
$q_{\max}$	Constant in extended Langmuir isotherm
β	Constant of Redlich- Peterson isotherm ($0 < \beta < 1$)

SSE- Sum of square of errors

$\eta_{L,i}$	Multicomponent (competitive) Langmuir adsorption constant of each component, dimensionless
$\eta_{R,i}$	Multicomponent R-P adsorption constant of each component, dimensionless.
GAC	Granular activated carbon
t	Time
Py	Pyrrole
Ind	Indole

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Table 1 Literature on adsorption of pyrrole and indole by activated carbon and other few adsorbents.

Components	Model oil/ Solvent	Adsorbent	Type of Process	Process Conditions	Percent Removal/ adsorption capacity	Ref.
Indole and quinoline	Model Oil, decane	Activated carbon(AC1,AC3, AC4, AC6)	Batch Process	$C_o = 20$ µmol.g^{-1} m = 0.2 g each	q_{Ind} forAC1 = 15.9, AC3 = 23.2, AC4 = 19.3, AC6 = 9.4 mg (N) g^{-1}	6
Indole, carbazole dibenzothiophene etc.	Diesel fuels, light cycle oils	Activated carbon	Batch Process	Temperature (T) =298 K, 313 K and 328 K Molar conc.(Co) = 23.8 µmol g^{-1}	$q_{Ind} = 1.32$ mmol g^{-1} $q_{Qui} = 1.17$ mmol g^{-1}	7
Indole and phenol	Distilled water	Activated carbon	Batch Process	C_o= 2 mmol l^{-1}		8
Indole and phenol	Distilled water	Activated Carbon	Continuous process	C_o= 0.35mmol l^{-1}		9
Indole, Naphthalene, dibenzothiophene, etc.	Diesel fuel	Activated carbon, activated alumina and nickel-based adsorbent	Fixed-bed adsorption	$C_o = 10.7$ µmol.g^{-1}	activated carbon, $q_{Ind} = 0.705$ mmol g^{-1} activated alumina , $q_{Ind} = 0.195$ mmol g^{-1} Ni/SiO2-Al2O3, $q_{Ind} = 0.167$ mmol g^{-1}	10
Indole, carbazole, diabenzothiophene , etc	Model fuel, Ethyl acetate	Activated carbon	Batch Process	m = 1 g C_o=23.8 µmol g^{-1} each	$q_{Ind} = 0.31$ mmol g^{-1}	11
Indole and 2-methylindole	Distilled water	Cobalt II carboxylated diaminoethane sporopollenin	Fixed-bed column	T = 298 K, $C_o = 0.0125$ to 0.200 mmol l^{-1}	$q_{Ind} = 0.17$ mmol g^{-1}	12
Indole, pyridine, quinoline, carbazole, etc	Hexane	Zeolite	Batch Process	T = 293 K C_o= 0.68 mmol l^{-1} each compounds	20 wt %	13

Indole, quinoline and benzothiophene	Model fuel n-octane and p-xylene.	MIL-101 and MIL-101 (1.0% PWA) phosphotungstic acid	Batch Process	V= 5 ml m = 5 mg C_o=2.5- 10.3 mmol l^{-1}	For MIL-101 q_{Ind} = 1.38 mmol g^{-1} MIL-101 (1.0% PWA) q_{Ind} = 1.30 mmol g^{-1}	14
Indole, quinoline and benzothiophene	Model fuel n-octane and p-xylene	MIL-100(Cr) ,Ethylenediamine(ED)-MIL-100(Cr), aminomethanesulfonic acid (AMSA)-MIL-100(Cr)	Batch Process	V= 10 ml m = 10 mg C_o=1.3- 10.3 mmol l^{-1}	MIL-100(Cr), q_{Ind} = 0.88 mmol g^{-1} ED-MIL-100(Cr), q_{Ind} = 0.80 mmol g^{-1} AMSA- MIL-100(Cr) ,q_{Ind} = 0.83 mmol g^{-1}	15
Indole, quinoline and benzothiophene	Model fuel n-octane and p-xylene	MIL-101 and 0.25% Graphite Oxide (GO)/ MIL-101	Batch Process	V=5 ml m = 5 mg C_o=2.5- 10.3 mmol l^{-1}	MIL-101, q_{Ind} = 2.08 mmol g^{-1} 0.25% GO/ MIL-101 q_{Ind} = 2.72 mmol g^{-1}	16
Indole ,thiophene, 1,2dimethylindole	Model fuel, heptane	MIL-100(Fe, Cr, Al, V)	Batch Process	Volume(V)=1.8ml m = 0.025 g C_o= 0.004 M Temp.= 298 K	MIL-100(Al) q_{Ind} = 670 MIL-100(Cr) q_{Ind} = 560 MIL-100(Fe) q_{Ind} = 670 MIL-100(V) q_{Ind} = 370 mols per unit cell	17
Indole, carbazole etc.	Model fuel, isooctane	(Materials of Institute Lavoisier)MIL-101	Batch Process	m = 10 mg Co=78 ppmw	q_{Ind} = 18 mg (N) g^{-1}	18
Indole, pyridine, quinoline and pyrrole.	Model fuel, n- octane	Ti-HMS	Batch Process	C_{oInd}= 10.93 mmol l^{-1} C_{oPy}= 10.71 mmol l^{-1} Temp.= 293-333K, M = 0.1 g V =10 ml	q_{Ind} = 0.132 mol g^{-1} q_{Py} = 0.145 mmol g	19

Indole, pyridine, quinoline and pyrrole.	Model fuel, n- octane	Hexagonal molecular sieve(HMS),(Mobil Composition of Matter No. 41) MCM-41	Batch Process	C_{oInd}= 10.93 mmol l^{-1} C_{oPy}= 10.71 mmol l^{-1}	HMS, q_{Ind} = 0.128 mmol g^{-1} q_{Py} = 0.143 mmol g^{-1} and MCM-41q_{Ind} = 0.137 mmol g^{-1} q_{Py} = 0.14mmol g^{-1}	20
Indole and pyrrole	Double distilled water	Activated carbon	Batch Process	V= 100 ml $C_{o,Py=}$0–7.45 $C_{o,Ind=}$0-4.27 mmol L^{-1} Dose(m) = 4-20 g L^{-1}	q_{tot} = 0.34, $q_{Py\ =}$ 0.16 and $q_{Ind\ =}$ 0.18 mmol g^{-1}	Present Study

Table 2 Multi-component adsorption study parameters for the adsorption of pyrrole and indole onto GAC using Taguchi's OA.

Parameters			Units	Levels		
				0	1	2
A:	Initial concentration of pyrrole	**$C_{o,Py}$**	mmol L^{-1}	0	3.73	7.45
B:	Initial concentration of indole	**$C_{o,Ind}$**	mmol L^{-1}	0	2.13	4.27
C:	Temperature	**T**	(^{o}C)	15	30	45
D:	Adsorbent dose	**m**	(g L^{-1})	4	12	20
E:	Contact time	**t**	(min)	60	360	660

Table 3 Taguchi's L_{27} (3^{13}) orthogonal array for multi-component adsorption of pyrrole and indole system onto GAC.

Exp. No.	A	B	AxB	AxB	C	D	E	q_{Py}	q_{Ind}	q_{tot}
1	0	0	0	0	15	4	1	0.00	0.00	0.00
2	0	0	0	0	30	12	6	0.00	0.00	0.00
3	0	0	0	0	45	20	11	0.00	0.00	0.00
4	0	2.13	1	1	15	4	1	0.00	0.09	0.09
5	0	2.13	1	1	30	12	6	0.00	0.16	0.16
6	0	2.13	1	1	45	20	11	0.00	0.11	0.11
7	0	4.27	2	2	15	4	1	0.00	0.14	0.14
8	0	4.27	2	2	30	12	6	0.00	0.22	0.22
9	0	4.27	2	2	45	20	11	0.00	0.20	0.20
10	3.73	0	1	2	15	12	11	0.18	0.00	0.18
11	3.73	0	1	2	30	20	1	0.09	0.00	0.09
12	3.73	0	1	2	45	4	6	0.19	0.00	0.19
13	3.73	2.13	2	0	15	12	11	0.09	0.15	0.24
14	3.73	2.13	2	0	30	20	1	0.05	0.09	0.14
15	3.73	2.13	2	0	45	4	6	0.07	0.14	0.21
16	3.73	4.27	0	1	15	12	11	0.05	0.14	0.19
17	3.73	4.27	0	1	30	20	1	0.03	0.11	0.14
18	3.73	4.27	0	1	45	4	6	0.03	0.16	0.19
19	7.45	0	2	1	15	20	6	0.25	0.00	0.25
20	7.45	0	2	1	30	4	11	0.39	0.00	0.39
21	7.45	0	2	1	45	12	1	0.18	0.00	0.18
22	7.45	2.13	0	2	15	20	6	0.12	0.10	0.22
23	7.45	2.13	0	2	30	4	11	0.03	0.13	0.16
24	7.45	2.13	0	2	45	12	1	0.05	0.06	0.11
25	7.45	4.27	1	0	15	20	6	0.08	0.16	0.24
26	7.45	4.27	1	0	30	4	11	0.09	0.26	0.35
27	7.45	4.27	1	0	45	12	1	0.03	0.06	0.09
Total								2.00	2.47	4.47

Table 4 ANOVA of q_{tot} for multicomponent adsorption of pyrrole and indole onto GAC.

	Sum of squares	DOF	Mean square	% contribution	F-value
			q_{tot}		
A	0.06	2	0.03	29.44	18.85
B	0.01	2	0.01	4.81	3.08
C	0.01	2	0.00	3.82	2.45
D	0.01	2	0.00	3.88	2.48
E	0.04	2	0.02	19.20	12.30
$A \times B$	0.06	4	0.02	29.48	9.44
Residual	0.02	12	0.00	9.37	
Model	0.20	14	0.08	90.63	48.69
Cor. total	0.22	26	0.08	100.00	
			q_{Ind}		
A	0.00	2	0.00	0.86	0.61
B	0.12	2	0.06	78.06	55.38
C	0.00	2	0.00	2.27	1.61
D	0.00	2	0.00	3.88	0.70
E	0.01	2	0.01	7.39	5.24
$A \times B$	0.00	4	0.00	1.99	0.70
Residual	0.01	12	0.00	8.46	
Model	0.14	14	0.07	91.54	64.24
Cor. total	0.16	26	0.07	100.00	
			q_{Py}		
A	0.09	2	0.04	36.40	23.87
B	0.07	2	0.03	28.38	18.61
C	0.00	2	0.00	1.24	0.81
D	0.00	2	0.00	1.19	0.78
E	0.01	2	0.00	4.16	2.73
$A \times B$	0.05	4	0.01	19.48	6.39
Residual	0.02	12	0.00	9.15	
Model	0.21	14	0.09	90.85	53.18
Cor. total	0.23	26	0.10	100	

Table 5 Comparison of individual and total adsorption uptakes and yields found at different pyrrole concentrations with increasing concentration of indole onto GAC.

$C_{e,Ind}$	$C_{e,Py}$	$q_{e,Ind}$	$q_{e,Py}$	$Ad_{Ind}\%$	$Ad_{Py}\%$	$Ad_{tot}\%$
0.001	0.15	0.02	0.03	99.69	80.30	87.36
0.002	0.18	0.04	0.03	99.73	75.96	88.65
0.02	0.28	0.11	0.02	99.02	62.88	89.67
0.44	0.42	0.19	0.02	89.65	43.43	82.78
1.68	0.45	0.23	0.01	73.38	39.83	69.84
0.002	0.41	0.02	0.05	99.63	72.67	78.67
0.006	0.56	0.04	0.05	99.25	62.20	75.69
0.03	0.66	0.11	0.04	98.58	55.49	80.86
0.39	0.88	0.19	0.03	90.91	41.07	78.01
1.48	0.95	0.24	0.03	76.48	36.38	68.81
0.01	0.99	0.02	0.14	97.34	73.34	75.81
0.02	1.30	0.04	0.12	97.65	65.19	71.24
0.03	1.87	0.11	0.09	98.40	49.92	67.57
0.45	2.50	0.19	0.06	89.45	32.90	63.09
2.64	2.81	0.18	0.05	58.16	24.59	45.70
0.01	2.67	0.02	0.22	96.86	62.24	64.21
0.03	2.72	0.04	0.22	96.86	61.54	65.35
0.02	3.58	0.11	0.17	98.90	49.40	60.86
0.76	5.18	0.18	0.09	82.22	26.84	47.67
2.17	5.32	0.21	0.10	65.58	27.77	45.20
0.004	4.92	0.02	0.30	98.95	55.31	56.94
0.005	5.75	0.04	0.26	99.42	47.77	51.48
0.14	7.24	0.09	0.19	93.64	34.24	43.88
0.79	7.47	0.17	0.18	81.53	32.21	45.99
2.60	7.93	0.19	0.15	58.84	28.04	39.26

Table 6 Individual and multi-component isotherm parameter values for the pyrrole and indole adsorption onto GAC at 30^{o}C.

Individual isotherm models[46,49,50,51]		**Parameter**	**Pyrrole**	**Indole**
Langmuir	$q_e = \frac{q_m k_L c_e}{1 + k_L c_e}$	q_m	0.698	0.364
		k_L	1.044	4.573
		SSE	0.002	0.0004
Freundlich	$q_e = k_F c_e^{1/n}$	k_F	0.332	0.281
		$1/n$	0.426	0.312
		SSE	0.004	0.008
Redlich-Peterson	$q_e = \frac{k_R c_e}{1 + a_R c_e^{\beta}}$	k_R	1.410	1.401
		a_R	3.093	3.604
		β	0.742	1.119
		SSE	0.001	0.0002
Multicomponent isotherm models[46]				
Non-modified Langmuir model	$q_{e,i} = \frac{q_{m,i} K_{L,i} C_{e,i}}{1 + \sum_{j=1}^{N} K_{L,j} C_{e,j}}$	SSE	1.36	
Modified Langmuir model	$q_{e,i} = \frac{q_{m,i} K_{L,i} \left(\frac{C_{e,i}}{\eta_{L,i}} \right)}{1 + \sum_{j=1}^{N} K_{L,j} \left(\frac{C_{e,j}}{\eta_{L,j}} \right)}$	$\eta_{L,i}$	8.49	2.23
		SSE	0.10	
Extended Langmuir	$q_{e,i} = \frac{q_{\max} K_{EL,i} C_{e,i}}{1 + \sum_{j=1}^{N} K_{EL,j} C_{e,j}}$	K_i	0.66	4.70
		$q_{\max}$	0.32	
		SSE	0.037	
Extended Freundlich	$q_{e,1} = \frac{K_{F,1} C_{e,1}^{n_1 + x_1}}{C_{e,1}^{x_1} + y_1 C_{e,2}^{z_1}}$, $q_{e,2} = \frac{K_{F,2} C_{e,2}^{n_2 + x_2}}{C_{e,2}^{x_2} + y_2 C_{e,1}^{z_2}}$	X	0.30	0
		Y	7.67	0.35
		Z	0.24	0.42
		SSE	0.038	
Non-modified Redlich-Peterson	$q_{e,i} = \frac{K_{R,i} C_{e,i}}{1 + \sum_{j=1}^{N} a_{R,j} \left(C_{e,j} \right)^{\beta_j}}$	SSE	2.06	
Modified Redlich-Peterson	$q_{e,i} = \frac{K_{R,i} \left(\frac{C_{e,i}}{\eta_{R,i}} \right)}{1 + \sum_{j=1}^{N} a_{R,j} \left(\frac{C_{e,j}}{\eta_{R,j}} \right)^{\beta_j}}$	$\eta_{R,i}$	15.72	0.18
		SSE	0.14	

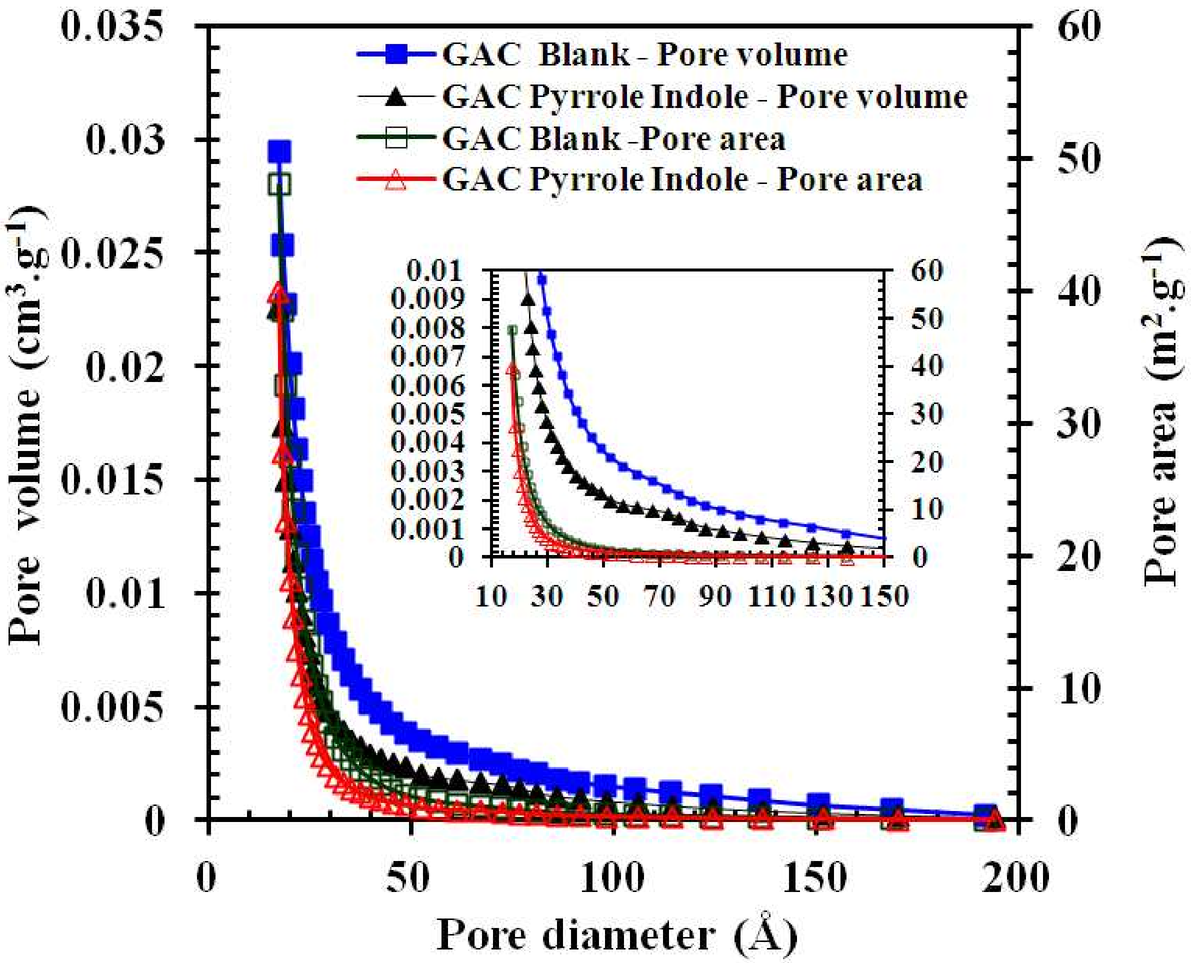
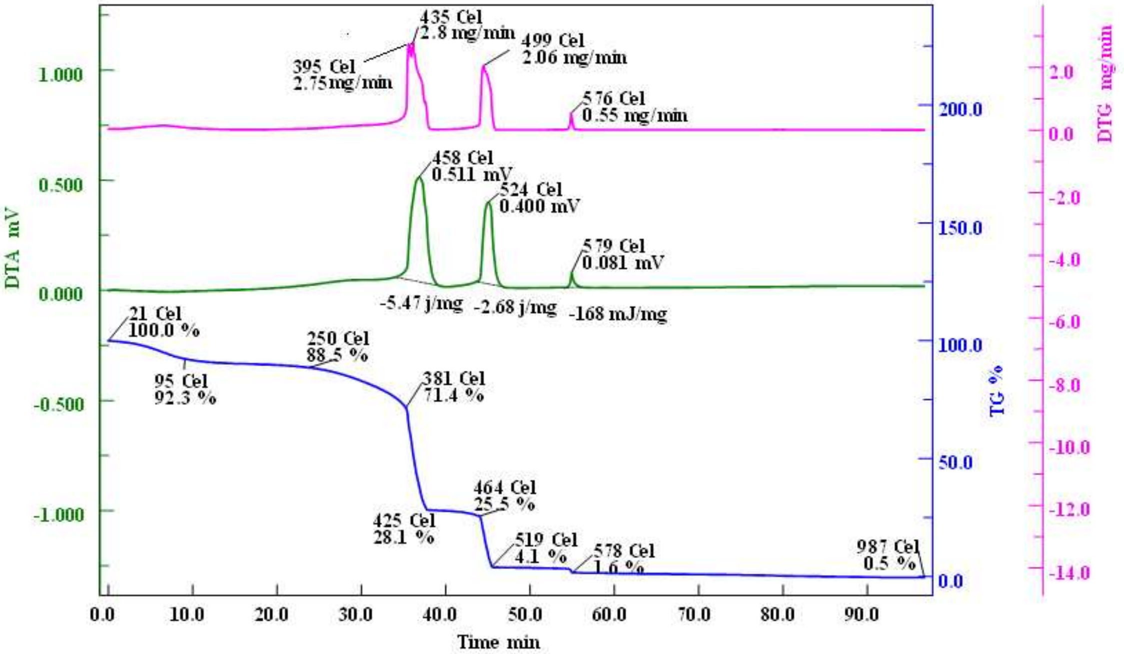
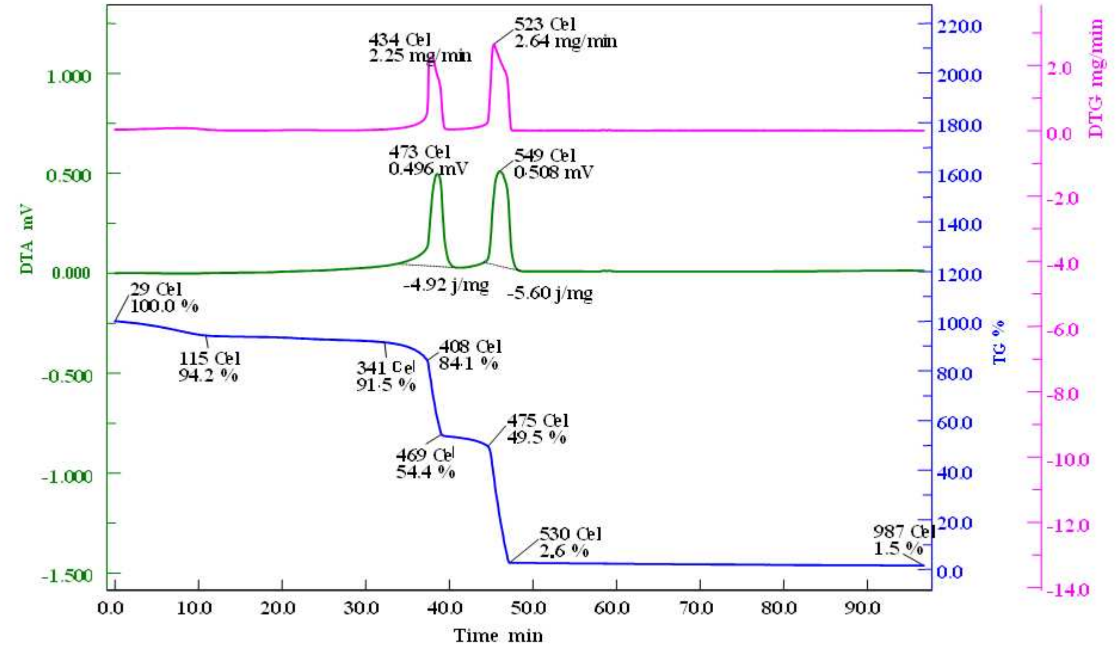


Fig. 1 Textural characteristics of GAC before and after simultaneous pyrrole and indole adsorption



(a)



(b)

Fig. 2 Thermogravimetric analysis under air atmosphere (a) GAC blank and (b) GAC loaded with pyrrole and indole.

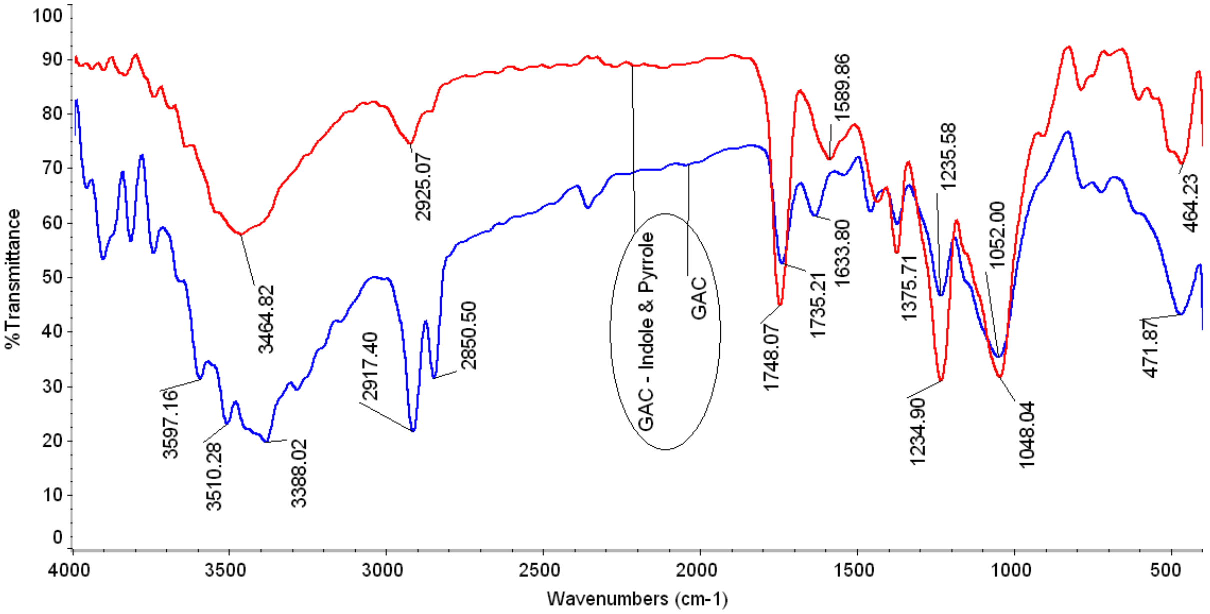


Fig. 3 FTIR of GAC before and after adsorption

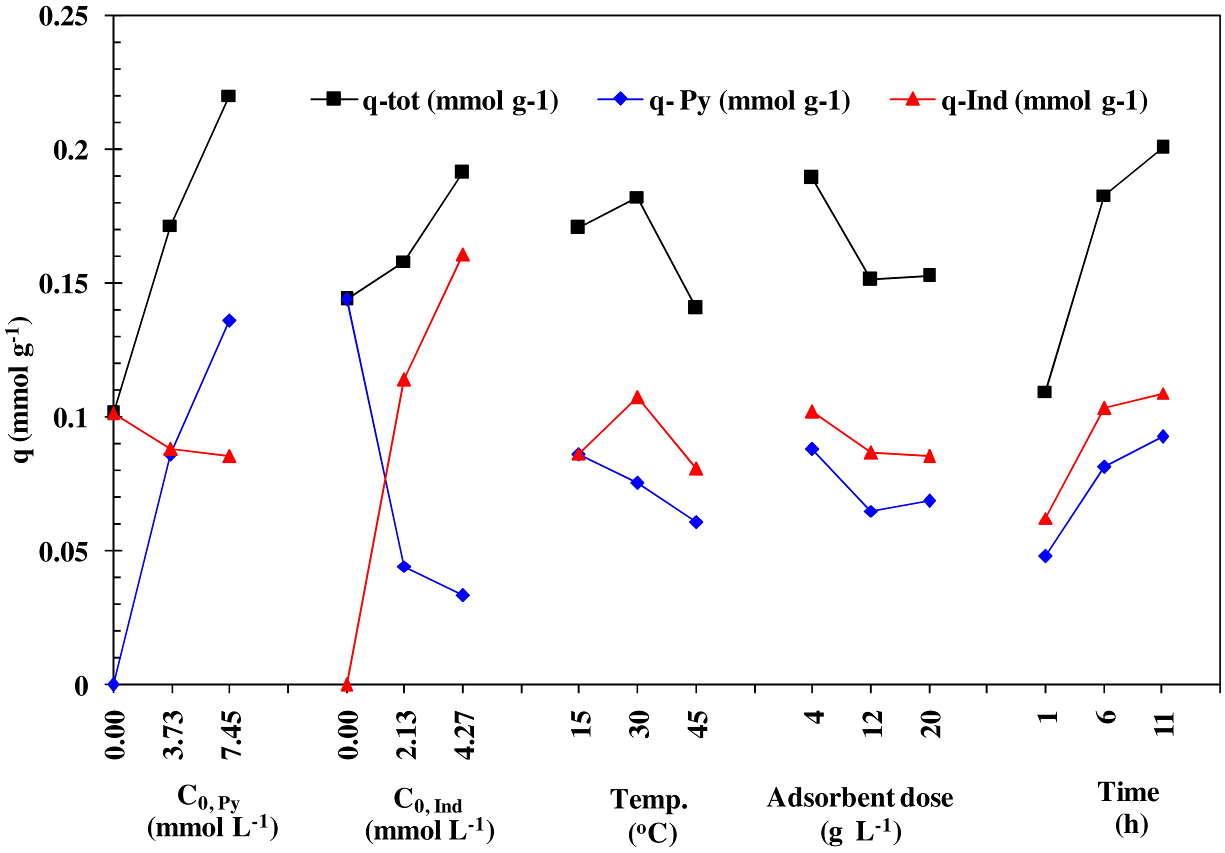
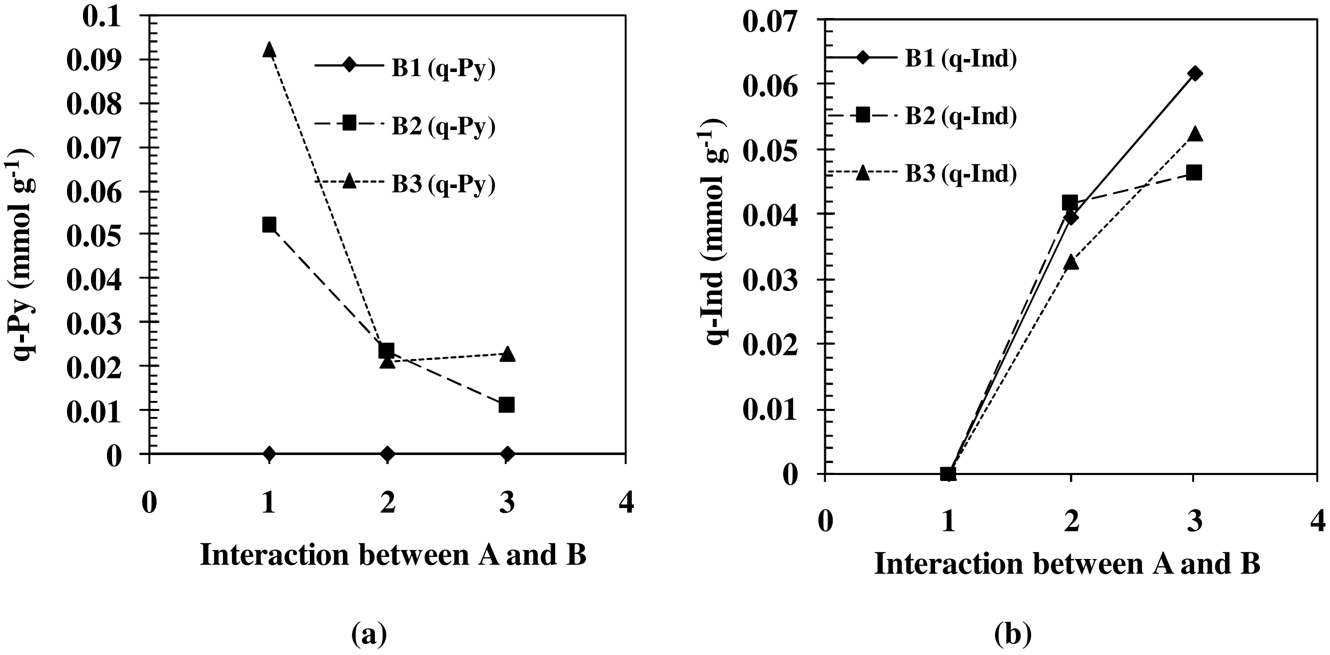
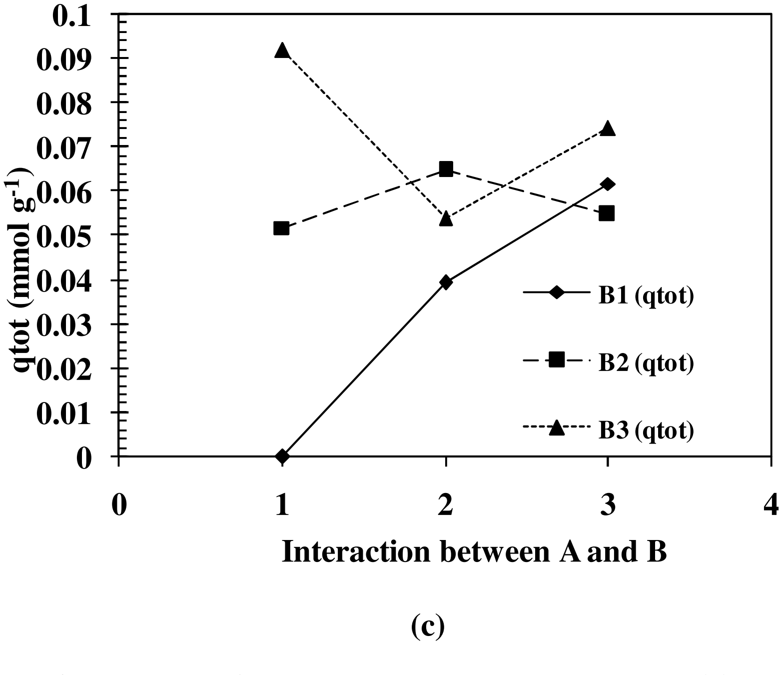


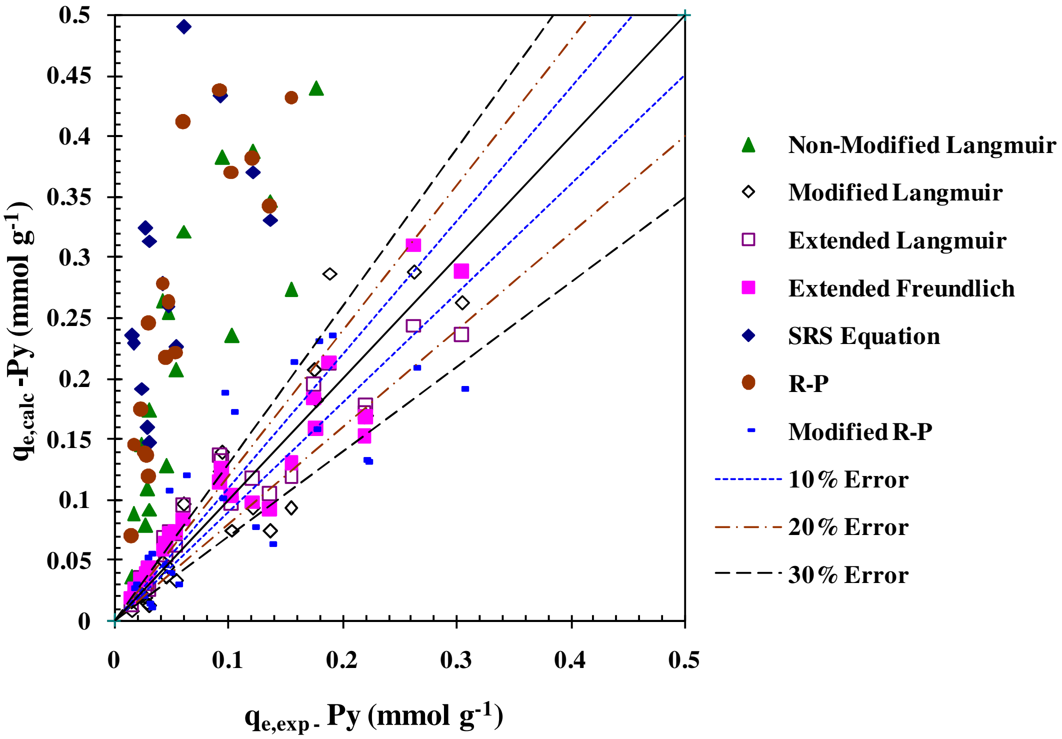
Fig. 4 Effect of process parameters on q_{tot} for multicomponent adsorption of pyrrole and indole onto GAC



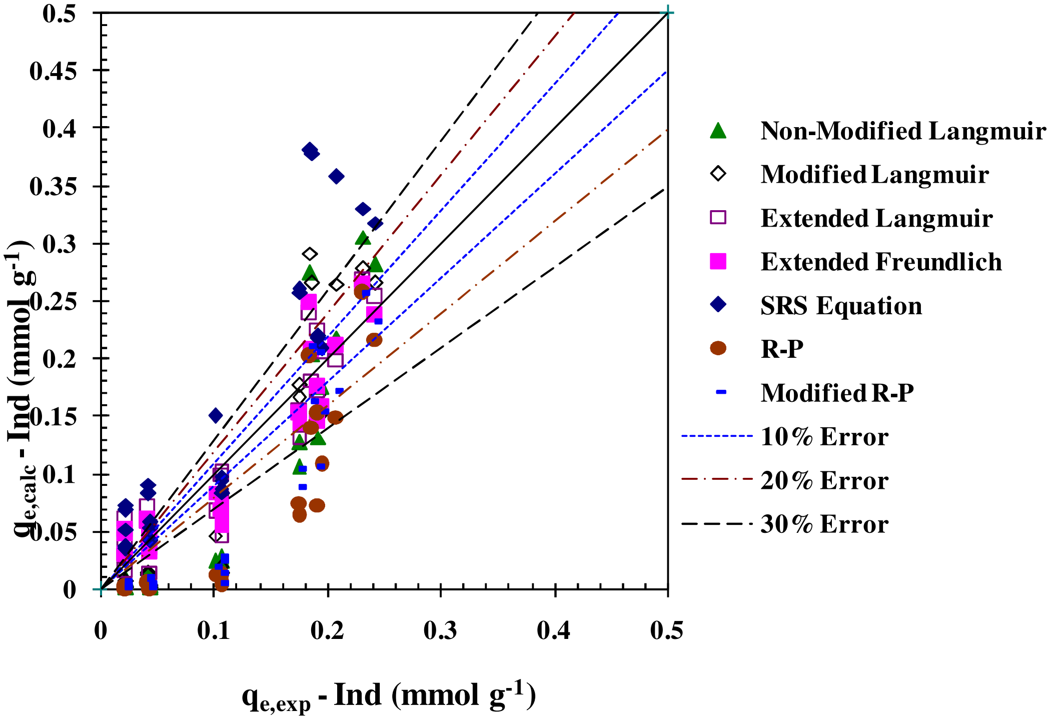


(c)

Fig. 5 The interaction between A and B parameters at 3 levels on (a) q_{Py}, (b) q_{Ind} and (c) q_{tot} for multicomponent adsorption of pyrrole and indole onto GAC



(a) Pyrrole



(b) Indole

Fig. 6 Comparison of actual and theoretical equilibrium adsorption values of pyrrole (Py) and indole (Ind) in a binary mixture

FIGURE CAPTIONS

Fig. 1 Textural characteristics of GAC before and after simultaneous pyrrole and indole adsorption

Fig. 2 Thermogravimetric analysis under air atmosphere (a) GAC blank and (b) GAC loaded with pyrrole and indole

Fig. 3 FTIR of GAC before and after adsorption.

Fig. 4 Effect of process parameters on q_{tot} for multicomponent adsorption of pyrrole and indole onto GAC

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