(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
11 February 2021 (11.02.2021)

WIPO | PCT

(10) International Publication Number
WO 2021/024272 A1

(51) International Patent Classification:
C02F 9/00 (2006.01) *C02F 1/44* (2006.01)
C02F 1/28 (2006.01)

(21) International Application Number:
PCT/IN2020/050687

(22) International Filing Date:
04 August 2020 (04.08.2020)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
201941031628 05 August 2019 (05.08.2019) IN

(71) Applicant: **INDIAN INSTITUTE OF TECHNOLOGY MADRAS (IIT MADRAS)** [IN/IN]; The Dean, Industrial Consultancy & Sponsored Research (IC & SR), Indian Institute of Technology Madras, IIT Post, Chennai, Tamil Nadu 600 036 (IN).

(72) Inventors: **ARAVAMUDAN, Kannan**; F12, First Floor, Mahalakshmi Flats, 137, 138 Pillayar Koil Street, Jafferkhanpet, Chennai, Tamil Nadu 600083 (IN). **RETNAM, Bharathi Ganesan**; 36E, Second Street, Tooveypuram, Thoothukudi, Tamil Nadu 628003 (IN).

(74) Agent: **KUMAR, G., Arun** et al.; K&S PARTNERS, Intellectual Property Attorneys, Door No. 15 (Old No. 3) Postal Colony 4th Street, West Mambalam, Chennai, Tamil Nadu 600 033 (IN).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, IT, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *of inventorship (Rule 4.17(iv))*

Published:
— *with international search report (Art. 21(3))*
— *in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE*

WO 2021/024272 A1

(54) Title: A METHOD FOR MAXIMIZING MULTICOMPONENT ADSORPTION OF THE SOLUTES FROM AN AQUEOUS STREAM DISCHARGE

(57) Abstract: The invention is for a method to maximize multicomponent adsorption of the solutes from an aqueous stream discharge by increasing the total solute loading (q_{Total}) of the adsorbent to the maximum loading capacity (global maximum). The method of the invention is for Mixture Process Variable (MPV) design, for determining the main and interaction effects of mixture variables, pH, adsorbent dose and adsorbent type on the total solute loading q_{Total}. Further the method is for arriving at loci of maximum adsorbent loadings en route to the globally optimum q_{Total} from any initial compositions and process conditions using ridge analysis and numerical constrained optimization techniques. The invention is also for experimental and statistical validation of the Mixture Process Variable (MPV) design for arriving at the global optimum.

A METHOD FOR MAXIMIZING MULTICOMPONENT ADSORPTION OF THE SOLUTES FROM AN AQUEOUS STREAM DISCHARGE

FIELD OF INVENTION

The invention pertains to the field of adsorption engineering with specific reference to the method to maximize multicomponent adsorption of the solutes from an aqueous stream discharge.

BACKGROUND

Aqueous stream discharges contain varied compounds which can be anything from a chemical compound such as paracetamol, or any washing machine ingredient, and even food and beverage constituents. In water stressed urban landscapes, there is always a scope of water reusage. Recycling of water is one such option and contaminants in a stream may be reduced by suitable treatment before reusage. Adsorption is one such simple treatment technique for recycling and is nothing but a preferential transport of solutes present in fluid phase onto a solid adsorbent owing to their higher affinity towards the latter. In practical applications involving adsorption, multicomponent, rather than single component solutions are frequently encountered. In such cases, the affinities of different solutes in the multicomponent mixture towards the adsorbent may be different from the affinities when these individual solutes are present alone in the solution. For example, during adsorption of fermentation broths containing ethanol-glucose-glycerol-acetic acid or ethanol-acetoin-acetic acid, presence of acetic acid or acetoin respectively affected the adsorption of ethanol.

Even though multi-solute adsorption studies are practically vital, they are relatively scarce in literature. Simultaneous and accurate estimation of the different species compositions in the mixture require sophisticated analytical methods. When large number of components (≥3) is involved, the experiments and analytical methods may become tedious, expensive and time consuming for investigating multicomponent adsorption. Adsorption further depends on various factors such as solutes' feed concentration, nature of the adsorbent and operating conditions viz. pH, temperature and adsorbent dose. One Variable (or factor) at a Time (OVAT) approach by Fritz and Schluender (1974) required a considerable number of multicomponent adsorption experiments to be performed even for a binary solute system at fixed process conditions of 2 g/L adsorbent dose, natural pH and 20°C. When effects of process variables such as pH, temperature and adsorbent dose on the multicomponent

adsorption equilibria are to be investigated in addition to the effect of feed compositions especially for systems with ≥3 components, a large number of experimental runs are necessitated using the OVAT method (Montgomery, 2010). Moreover, the feed compositions and process conditions identified for best performance by OVAT strategy may actually turn out to be only local optima (Leardi, 2009), rendering the overall strategy inefficient.

Different approaches have been attempted to predict multicomponent adsorption isotherms from single component isotherms, formulation of multicomponent isotherms through the development of Artificial Neural Network (ANN) models, empirical model development using design of experiments (DOE) and the like. However, interpreting the effect of process conditions as well as mixture compositions on adsorbent capacity (Lu et al., 2008; Zolgharnein et al., 2017) is not straightforward. Complications arise when different variables affect the overall adsorption either individually or through their interactions with one another in different possible combinations. These include not only interactions among the component concentrations but also those between component concentrations and process variables. Often these interactions may even exert more influence than the individual variables (Cornell, 2011; Montgomery, 2010). Thus, there is need for a model/method to identify the main and interaction effects involving mixture composition, pH, adsorbent dose and adsorbent type for maximum adsorption of the components.

OBJECT OF THE INVENTION:

An object of the invention is for a method to maximize multicomponent adsorption of the solutes from an aqueous stream discharge by increasing the total solute loading (q_{Total}) of the adsorbent to the maximum loading capacity (global maximum).

Another object is for a Mixture Process Variable (MPV) design, determining the main and interaction effects of mixture variable, pH, adsorbent dose and adsorbent type on the total solute loading q_{Total}.

Another object is arriving at a loci of maximum adsorbent loadings *en route* to the globally optimum q_{Total} from any initial composition and process conditions using enhanced ridge analysis and numerical constrained optimization techniques.

Another object is for experimental and statistical validation of the Mixture Process Variable (MPV) design for arriving at the global optimum.

DRAWINGS AND FIGURES

Figure 1 represents the different mixture and process variables and identification of their effects and interaction through a mixture process variable design.

Figure 2 represents the experimental responses of total solute loading (q_{Total} mg/g) for each process variable revealing the uniqueness of AC type and pH.

Figure 3 depicts the nineteen candidate solute compositions in the mixture process design.

Figure 4 depicts a) The circles originating from the focus located on the BTA-CAF edge illustrate the ridge analysis. The optimum eventually lie outside the triangular composition space with increasing distance from the focus. b) Truncated circles are only considered after imposing constraint that the search region should not lie outside the composition space.

Figure 5 Fisher's 95% confidence intervals to check if the individual factor levels are different from one another in affecting the total adsorption capacity

Figure 6 compares the coefficients of the coded q_{Total} model for the three carbons UN, AT and MAT and highlights the interaction effects

Figure 7 depicts the parity plot for validation of the q_{Total} model based on MPV design. The dashed line indicates ±10% deviation.

Figure 8 depicts (a) optimal responses (b) process and (c) mixture variables with increasing radial distance from the focus. (d) The loci of mixture compositions along the path of steepest change during optimization with MPV model, composition and circular constraints.

DEFINITIONS

Feed concentration: Mass of compound present per unit volume of the feed solution.

Mixture Variable: The feed composition and the feed concentrations of the different solutes of an aqueous stream discharge.

Process Variable: The process conditions of the adsorption such as pH, dose of the adsorbent, types of the adsorbents.

Multicomponent adsorption: Simultaneous adsorption of more than one species by the adsorbent.

Dose: The amount of the adsorbent present per unit volume of the solution.

q_{Total} = total solute mass loading on the adsorbent, also termed as total adsorption capacity and total adsorbent loading.

Global maximum: is the maximum possible total solute loading in the adsorbent within the bounds of the experimental variables chosen.

DETAILED DESCRIPTION:

The invention is described in detail in the description below are provided as an illustration and are not intended to restrict scope of invention in any manner. Any embodiments that may be apparent to a person skilled in the art are deemed to fall within the scope of the present invention.

Accordingly, the invention is for a method to maximize multicomponent adsorption of the solutes from an aqueous stream discharge by increasing the total solute loading (q_{Total}) of the adsorbent to its maximum loading capacity (global maximum).

In an aspect of the invention the method is for determining the optimum mixture variable and the optimum process variables of the adsorption.

The mixture variable is the feed concentration of one of the different solutes present in the aqueous stream and the process variable is one of pH, dose and type of the adsorbent.

In another aspect the method is for determining the main and interaction effects of mixture and process variables, on the total solute loading q_{Total}.

In an embodiment the method is for arriving at a global maximum for the solute loading (q_{Total}) from specified mixture variable, also called as the focus, by a mixture process variable design (MPV) using circular constraints and simultaneously optimizing the values of both the said mixture and said process variables, and identifying the path of steepest ascent towards the said global optimum, using enhanced ridge analysis.

In an aspect in the MPV design, the constraints of the mixture variable is a function of the feed concentration when tracking the path towards the said global optimum during the said enhanced ridge analysis.

In an aspect in the MPV design, the process variables is constrained between lower and upper limits when tracking the path towards the said global optimum during the said enhanced ridge analysis.

In an embodiment, in the MPV design the optimal settings of the mixture and process variables are identified to maximize q_{Total} through numerical optimization with above constraints. The procedure involves the search for optimal settings of process and mixture variables in separate loops. The optimum mixture variables identified in the first loop for a given set of process variables are fed to the second loop where the optimum process variables are next identified. The mutual passing of optimum variables between the two loops continues until the absolute value of the change in their values fell below the specified tolerance.

In an aspect of the invention the mixture process variable design is used for higher number of operating conditions and solutes. The utility of the mixture process variable design is demonstrated with three solutes but the number of solute components that can be handled by the MPV design can be scaled up for real systems depending on the number of solute components in the aqueous stream where the number of species in wastewater for example is in the order of tens.

In an aspect the MPV design is modelled for reaching the global optimum of the solute loading with three different types of adsorbents. Activated carbon is used as a representative example of the adsorbent and three types of the carbon, unmodified activated carbon (UN), acid treated (AT), and microwave and acid treated (MAT) activated carbon were taken as the absorbents, for removing a mixture of three different representative organic compounds. The representative organic compounds were acetaminophen (ACT), benzotriazole (BTA) and caffeine (CAF). This methodology is comprehensive in identifying the mixture proportions of the feed and process conditions that would lead to optimal removal of the species in solution by the adsorbent.

In an aspect in MPV design, both mixture and process variables are varied simultaneously. The distance based optimality criteria was preferred so as to disperse the points throughout the design space. In each cycle of this algorithm, a substitution experimental condition is

selected so that it provides the largest possible inter-distances between the experimental points. This provides finally a uniform distribution of the experiments selected from the set of allowed candidate experimental conditions specified *a priori*. Using this approach, design points that lead to unusual combination of the factors such as low non-zero concentrations could be avoided. For the mixture composition, all three possibilities, viz. single, binary and ternary mixture compositions were considered with a constant total concentration constraint of 700 mg/L (Eqn.(1)).

$$C_{0,ACT} + C_{0,BTA} + C_{0,CAF} = 700 \frac{mg}{L} \quad (1)$$

The interior design space was investigated thoroughly by considering more number of binary and ternary candidate points instead of considering only a few multicomponent blends. In addition, three process variables, namely a) pH as a numeric variable with three levels (3, 6.5 and 10), b) adsorbent dose as a numeric variable assigned between 0.6 and 1.2 g/L and c) carbon type as category variable with three levels (UN, AT and MAT), were chosen.

Further, the coefficients of an empirical model that relates the selected response with combination of the input variables was estimated by linear regression. The significant terms in the model were identified based on the contribution of each term to the model by means of analysis of variance (ANOVA). The empirical model with only significant and necessary terms was used in further analysis. Quadratic by Quadratic model (Eqn (2)) was chosen from which only the significant terms was chosen after the ANOVA exercise. The variables A, B, C indicate the feed concentrations of acetaminophen, benzotriazole and caffeine solutes (in mg/L) respectively while D, E and F indicate pH, dose (mg/100mL) and type of carbon respectively.

$$\begin{aligned} \text{Response} = {} & (a_1 A + a_2 B + a_3 C + a_4 AB + a_5 AC + a_6 BC) \\ & \times (b_1 + b_2 D + b_3 E + b_4 F + b_5 DE + b_6 DF + b_7 EF + b_8 D^2 + b_9 E^2) \end{aligned} \quad (2)$$

The final model for the q_{Total} response after parameter estimation through linear regression is given in Eqn. (3). This model is expressed in terms of coded variables with the coding indicated by the apostrophe symbol.

$$q_{Total} = 236.2 \times A' + 273.7 \times B' + 245.6 \times C' - 51.39 \times B'D'^2 + 61.05 \times A'B' + 73.84 \times A'C' + 153.0 \times B'C' - 37.17 \times A'D' - 54.38 \times B'D' - 37.85 \times A'F'[1] + 1.854 \times A'F'[2] - 11.24 \times B'E' - 8.938 \times C'D' - 25.61 \times B'F'[1] - 6.293 \times B'F'[2] + 2.405 \times C'E' - 45.89 \times C'F'[1] - 5.459 \times C'F'[2] + 83.86 \times A'B'D' + 43.57 \times B'C'D' + 7.906 \times A'D'F'[1] - 23.97 \times A'D'F'[2] + 3.294 \times B'D'F'[1] + 17.26 \times B'D'F'[2] + 10.01 \times C'D'E' + 2.821 \times C'E'F'[1] + 20.37 \times C'E'F'[2] \quad (3)$$

The numeric process variables were scaled between -1 and 1 using the high (pv_{high}) and low levels (pv_{low}) of each factor as shown in Eqn. (4).

$$PV_{coded} = \left(\frac{pv_{actual} - \frac{(pv_{high} + pv_{low})}{2}}{\frac{(pv_{high} - pv_{low})}{2}} \right) \quad (4)$$

The mixture variable is coded by scaling the actual feed concentration of a solute with the specified total feed concentration of all the solutes.

The adsorbent type was treated as a categoric variable and assigned codes [1 0], [0 1] and [-1, -1] for UN, AT and MAT respectively.

In an aspect the method of the invention is to maximize multicomponent adsorption of the solutes from an aqueous stream discharge by increasing the total solute loading (q_{Total}) of the adsorbent to the maximum loading capacity (global maximum), - the said method comprising the steps of:

determining the mixture and the process variables of the adsorption wherein the mixture variable is feed concentration of one of the different solutes present in the aqueous stream and the process variable is one of pH, dose and type of the adsorbent;

determining the main and interaction effects of mixture variable, pH, adsorbent dose and adsorbent type on the total solute loading q_{Total}; by a mixture process variable design;

arriving at a global maximum for the solute loading (q_{Total}) from specified mixture variables, also called as the focus, using circular constraints and simultaneously optimizing the values of both the said mixture and said process variables, and identifying the path of steepest ascent towards the said global optimum, using enhanced ridge analysis;

validation of the total solute loading (q_{Total}) arrived from the mixture process variable design;

wherein the maximum total solute loading (q_{Total}) of the adsorbent is a function of both mixture and process variables.

In the method of the MPV design, the pH is between 3 and 10, both inclusive; the dose of the adsorbent is between 0.6 and 1.2 g/L, both inclusive; the number of different types of adsorbent is 3; the number of solutes of the mixture variable is 3.

In addition, the feed concentration of individual mixture variable is between 0 and 700 mg/L; whereas the total feed concentration of the mixture variable is specified value of 700 mg/L.

In the MPV design, the constraints of the process variable are fixed as per the lower and the upper bounds of the specified process variables.

In an aspect the MPV design applied to determine the feed proportions of a multicomponent system and process conditions for maximum solute loading of the adsorbent is for an aqueous stream discharge from industries which may include but not restricted to is one of dairy industry, sugar industry, fermentation industry, decentralized household water treatment units, and wastewater treatment plants.

In another aspect the MPV design applied to determine mixture proportions and process conditions that are tuned flexibly towards either maximum possible removal of the multicomponent mixture or selective removal of particular component subsets in the mixture.

In an aspect, in the method according to the invention, the maximum solute loading (q_{Total}) arrived by the mixture process variable design is validated statistically in addition to the experimental measurements of the same.

In an aspect, in the method according to the invention, the maximum solute loading (q_{Total}) arrived by the mixture process variable design is validated with experimental measurements of the same. The q_{Total} of the experimental and the predicted value is within a difference of ±10%.

EXAMPLES:

The invention is described in detail in the description, and the following examples below are provided as an illustration and are not intended to restrict the scope of the invention in any manner. Any embodiments that may be apparent to a person skilled in the art are deemed to fall within the scope of the present invention.

Materials:

Commercial activated carbon procured from Active Char Products Pvt. Ltd. Edyar, Kerala was washed, dried in vacuum oven for 24 hr at 110°C, sieved to 0.425 – 0.5 mm and labelled as UN. The three model solutes used, acetaminophen (ACT), benzotriazole (BTA) and caffeine (CAF), were of analytical grade purity and were bought from SD Fine–Chem Ltd, LobaChemie Pvt Ltd and Himedia Lab respectively.

Concentrated sulphuric acid (98% w/w) procured from Sisco Research Laboratories Pvt Ltd, Mumbai was of analytical grade and was diluted to 1M using ultrapure water from Evoqua Water Technologies purifier, Pennsylvania US. Acetonitrile of HPLC grade purchased from Finar Pvt Ltd, Mumbai was used to prepare HPLC mobile phase. The adsorption solutions were prepared using ultrapure water.

Example 1:

1.1.Enhancement of the adsorbent

Sulphuric Acid and Microwave Modification of Activated Carbon

As per Li et al., (2011), 20 grams of corresponding activated carbon (UN) was stirred in 400 mL of 1M H_2SO_4 at 400-500 rpm for 3 hours in a constant water bath at 60°C. This treated carbon was washed in distilled water until pH increased to that of the washing media. The washed carbon was dried at 110°C for 24 hr in a vacuum oven. This carbon was labelled as Acid Treated (AT). For microwave treatment, a t–neck containing cylindrical quartz tube (ID 2.5 cm and 30 cm height) was inserted inside a microwave oven (MW73AD, Samsung) from the top. 10 grams of UN carbon was added to the cylindrical quartz tube that was purged continuously with N_2 and exposed to 450 W microwave power for 20 minutes. The optimal microwave power and exposure time were determined from preliminary studies as 450 W and 20 minutes respectively. This microwave treated carbon was further subjected to 3 hours of acid treatment as mentioned above and labelled as microwave then acid treated carbon (MAT).

1.2.Characterization of Activated Carbon

The activated carbons (UN, AT and MAT) were characterized using pH_{pzc} and BET studies. BET isotherm experiments were carried out using nitrogen as analysis gas by Sprint Testing Solutions, Mumbai using Quantachrome ASiQwin instrument after degassing the sample at 200°C for 10 hours.

To determine the pH of point of zero charge (pH_{pzc}), salt addition method used by Gil et al., (2018) was carried out.

Pore volume, surface area and point of zero charge for the three carbons are tabulated in Table 1. It is observed that acid and MW treatments have respectively increased and decreased the BET surface area with reference to the unmodified carbon. This opposite trend may suggest that the underlying mechanisms for pore structure modification are different for MW and acid treatments. The BET surface area of UN decreased upon only microwave treatment by 17% but increased upon only acid treatment by 19%. The surface area of the MW treated carbon increased by 25% upon subsequent acid treatment thereby resulting in net gain in surface area of 3% than that of the unmodified carbon.

The surface charge on the adsorbent may be positive or neutral or negative if the solution pH is lower or equal to or greater than the adsorbent's pH_{pzc} value. The solute's ionic charge depends upon the nature of its functional groups and its pK_a value(s). The surface and ionic charges on the carbon and solute respectively along with the consequent electrostatic interactions aid to explain the variation in the adsorption patterns with pH and adsorbent type.

Table 1. BET surface area and pore volume of unmodified, acid treated and microwave then acid treated activated carbons

Carbon	BJH		BET Surface Area (m^2/g)	pHpzc
	Pore Volume (cc/g)	Pore Diameter (nm)		
UN	0.281	1.3	837.2	7.2
AT	1.289	1.986	996.2	5.5
MAT	0.297	1.556	865.3	6.3
MW Only	0.528	3.663	691.1	6.8

Example 2:

Adsorption Procedure

The total initial concentration was fixed at 700 mg/L in the experimental design. Subject to this constraint, 100 mL solutions containing different proportions of the three solutes were prepared. The initial pH, measured using Eutech 700 meter, was adjusted using 0.1N HCl and 0.1N NaOH. Appropriate carbons (UN, AT and MAT) were added to the samples and shaken at 130 rpm and 27°C for 72 hours in an orbital shaker, after which the equilibrium concentration was detected using HPLC.

The concentration of the three solutes in liquid was measured simultaneously by an isocratic HPLC procedure using C18 column (KyaTech Japan) attached to Jasco 2010 equipment with photo diode array detector. The mobile phase was 0.01M KH_2PO_4 at pH 3 (80% v/v) mixed with acetonitrile (20% v/v) flowing at 0.8 mL per minute. The absorbance was observed only at 260 nm after confirming its efficacy by comparing the values at 243 nm, 260 nm and 273 nm during preliminary studies. The mobile phase was well mixed, vacuum filtered, ultra-sonicated and cooled to room temperature before being pumped across the C18 column.

Mixture-Process Variable Design and Model Equation

In MPV design, both mixture and process variables are varied simultaneously. Design Expert 11 (Stat-Ease, Inc. Minneapolis) software was used to carry out the experimental design, model development, subsequent statistical analysis and preliminary optimization. Rigorous optimization was carried out using MATLAB (The MathWorks, Inc. Natick, Massachusetts), once the process model was obtained. Vertices, centres and thirds of edges, axial check blends, interior check blends and overall centroid were chosen as the 19 candidate points (Figure 3). The distance based optimality criteria was preferred so as to disperse the points throughout the design space. In each cycle of this algorithm, a substitution experimental condition is selected so that it provides the largest possible inter-distances between the experimental points. This provides finally a uniform distribution of the experiments selected from the set of allowed candidate experimental conditions specified *a priori*. Using this approach, design points that lead to unusual combination of the factors such as low non-zero concentrations could be avoided. For the mixture composition, all three possibilities, viz. single, binary and ternary mixture compositions were considered with a constant total concentration constraint of 700 mg/L (Eqn. (1)).

$$C_{0,ACT} + C_{0,BTA} + C_{0,CAF} = 700 \frac{mg}{L} \quad (1)$$

The interior design space was investigated thoroughly by considering more number of binary and ternary candidate points instead of considering only a few multicomponent blends. In addition, three process variables, namely a) pH as a numeric variable with three levels (3, 6.5 and 10), b) adsorbent dose as a numeric variable assigned between 0.6 and 1.2 g/L and c) carbon type as category variable with three levels (UN, AT and MAT), were chosen. For the suggested 91 runs, solute concentrations in the liquid were measured after 72 hours of equilibration, using HPLC and were used to calculate the different responses.

The coefficients of an empirical model that relates the selected response with combination of the input variables was be estimated by linear regression. The significant terms in the model were identified based on the contribution of each term to the model by means of analysis of variance (ANOVA). The empirical model with only significant and necessary terms was used in further analysis. Quadratic by Quadratic model (Eqn. (2)) was chosen from which only the significant terms was chosen after the ANOVA exercise. The variables A, B, C indicate the

initial concentrations of acetaminophen, benzotriazole and caffeine solutes (in mg/L) respectively while D, E and F indicate pH, dose (mg/100mL) and type of carbon respectively.

$$\text{Response} = (a_1 A + a_2 B + a_3 C + a_4 AB + a_5 AC + a_6 BC) \times (b_1 + b_2 D + b_3 E + b_4 F + b_5 DE + b_6 DF + b_7 EF + b_8 D^2 + b_9 E^2) \quad (2)$$

From the 54 possible terms of the quadratic by quadratic model (Eqn. (2)), the significant terms were identified using the model selection option of Design Expert 11 (Stat Ease, Inc., Minneapolis) to obtain the best statistical parameters. This software uses various criteria such as p-values, corrected Akaike information criterion (AICc), Bayesian Information Criterion (BIC) and adjusted R^2 to suggest various model terms. The models suggested by the above criteria were scrutinized using their ANOVA table and the final model choice was based on adequacy criteria such as high adjusted R^2, high predicted R^2, insignificant lack of fit and linear normal probability plot of the residuals. Parameter R^2 indicates the fraction of overall variability in the results that could be explained by the model. Adjusted R^2 penalizes over-parametrization of the model while predicted R^2 checks model predictive capability. The lack of fit checks whether the number of model terms chosen are adequate, and if significant lack of fit is found, either more terms have to be added or additional experiments are to be performed (Cornell, 2011). It is critical that the final form of the model has insignificant lack of fit for it to have good predictive capabilities. The linear probability plot ensures that the differences between experimental data and model predictions, termed as residuals, are indeed random.

Stationary Points of Mixture Design

When the process conditions viz. pH (D), dose (E) and type of carbon (F) are specified, the model (Eqn. (2))reduces to a quadratic form with only the mixture variables as below.

$$\text{Response} = a_1 A + a_2 B + a_3 C + a_4 AB + a_5 AC + a_6 BC \quad (5)$$

Using the mixture constraint (Eqn. (1)), C is substituted in terms of A and B. After rearrangement, Eqn. (6) is obtained in terms of A and B.

$$y = b_0 + b_1 A + b_2 B + b_3 AB + b_4 A^2 + b_5 B^2 \quad (6)$$

The above equation in the quadratic form was expressed in matrix form as Eqn. (7) where, vector **x** denotes the composition of ACT and BTA.

$$y = b_0 + \mathbf{x}'\mathbf{b} + \mathbf{x}'\mathbf{B}\mathbf{x} = b_0 + \begin{pmatrix} A & B \end{pmatrix}\begin{pmatrix} b_1 \\ b_2 \end{pmatrix} + \begin{pmatrix} A & B \end{pmatrix}\begin{pmatrix} b_4 & \frac{b_3}{2} \\ \frac{b_3}{2} & b_5 \end{pmatrix}\begin{pmatrix} A \\ B \end{pmatrix} \quad (7)$$

For a set of specified process conditions, the stationary point was found using Eqn. (8).

$$\mathbf{x}_s = -\frac{1}{2}\mathbf{B}^{-1}\mathbf{b} \quad (8)$$

Identification of Global Optima for Different Adsorbents

Design Expert software combines the maximization goals into a single desirability function which is then maximized using hill climbing technique. While optimizing using Design Expert, the pH values were restricted to be at the three values of 3 or 6.5 or 10.

The global maximum q_{Total} for each carbon was also identified using MATLAB routines. The mixture compositions, pH and dose that lead to global maximum value of q_{Total} were identified using Particle Swarm Optimization (PSO) routine of MATLAB R2018b. Alternatively, an expanding domain technique was also used. Here, the pH and dose were initially fixed to their lower bound values (3 and 60 mg/100 mL respectively) and the domain size was kept very small by fixing the upper bounds close to the lower bounds of the process variables. The locally optimal feed concentrations and process variables were identified using constrained optimization routine *fmincon* in MATLAB R2019a. As the minimum is sought by this routine, the objective function is specified as the negative of the total adsorbent loading q_{Total}. These locally optimal concentrations and process variables were used as initial guesses and the process variables domain encompassing pH and dose was expanded slightly. New locally optimal values were then identified. The entire process was repeated until the domain reached the upper bound of process variables. The best optimal value of q_{Total} obtained was confirmed to be the global optimum and were also confirmed–by comparing

with Design Expert's optimization predictor. Further, the predictions from *fmincon* were also confirmed by comparing with the contour plots.

Conventional Ridge Analysis for Mixture Designs

Three-dimensional response surface plots and contour plots cannot portray the variation of the response as a function of all the input factors, considered simultaneously, when they exceed two in number. The evolution of the maximum response and the corresponding factors may be captured by ridge analysis in a single graphical plot (Box and Draper, 2007).

In ridge analysis applied for mixture design (Eqn. 5), a particular focus **f** is chosen in the ternary composition space as a starting point. Concentric circles of increasing radii R are constructed with the focus as the centre (Figure 4a). The ridge analysis procedure enables the identification of optimum response which is constrained to lie on each circle centred on the focus **f**. This focus is the centroid of the triangle or any arbitrary point on any one of the three binary edges or within the triangle (Figure 4). Also plotted qualitatively in this diagram is the locus of points where the response is the maximum on each circle. The limitation of this method is that the process variables have to be specified *a priori* and only the mixture variables are allowed to vary during the optimization exercise. The ridge analysis has to terminate once the optimal compositions are identified beyond the feasible composition space, the triangular domain including its boundaries (Figure 4a).

The theory for ridge analysis involving mixtures is summarized below (Box and Draper, 2007; Myers et al., 2016). This theory applies to quadratic models. The mixture design model (Eqn (5)) coupled with Lagrangian multipliers λ and θ respectively is given by Eqn. (9). The terms attached to the Lagrangian multipliers λ and θ represent the equation of the circle and the initial concentration constraint (Eqn. (1)) respectively.

$$G = b_0 + \mathbf{x}'\mathbf{b} + \mathbf{x}'\mathbf{B}\mathbf{x} - \lambda((\mathbf{x}-\mathbf{f})'(\mathbf{x}-\mathbf{f}) - R^2) - \theta(\mathbf{A}\mathbf{x} - c) \quad (9)$$

Here R is the radial distance from the focal point **f** in the triangular composition diagram. R and **f** are related as follows

$$R = \sqrt{(\mathbf{x}-\mathbf{f})'(\mathbf{x}-\mathbf{f})} \quad (10)$$

For mixture design at specified process conditions, the model is in terms of only A, B and C Eqn. (5)). The mixture constraint matrix **A** and parameter c are given by Eqn. (11). Here q is three and represents the number of solutes.

$$\mathbf{A} = \left[\frac{1}{\sqrt{q}} \quad \frac{1}{\sqrt{q}} \quad \frac{1}{\sqrt{q}}\right] \text{ and } c = \frac{1}{\sqrt{q}} \tag{11}$$

Equating the partial derivative of the quadratic model G to zero, results in Eqn. 12. This yields the stationary point $\mathbf{x_s}$.

$$\mathbf{x_s} = \frac{1}{2}(\mathbf{B} - \lambda\mathbf{I})^{-1}(\mathbf{A}'\theta - \mathbf{b} - 2\lambda\mathbf{f}) \tag{12}$$

From the mixture constraint $\mathbf{Ax_s} = c$, Eqn (13) is obtained and it enables the estimation of the Lagrangian multiplier θ.

$$\theta = \{\mathbf{A}(\mathbf{B} - \lambda\mathbf{I})^{-1}\mathbf{A}'\}^{-1}\{2c + \mathbf{A}(\mathbf{B} - \lambda\mathbf{I})^{-1}(\mathbf{b} + 2\lambda\mathbf{f})\} \tag{13}$$

The Lagrangian multiplier λ is infinite when the circle centred at the focus has zero radius. The value of λ asymptotically reduces to zero as the radius monotonically increases towards infinity. Hence, in order to trace the locus of maximum q_{Total}, λ value was gradually decreased from a high value (λ=1000) until the optimal coordinates calculated by Eqn.12 went beyond the composition domain. For specified process conditions, the optimal response on each circle and the three compositions may be plotted against increasing radii, using Eqn. (5) and Eqn. (10).

Example 3:

Validation of Mixture-Process Variable (MPV) Design

Effect of Variation of Each Factor Assuming Absence of Other Factors

The experimental total adsorbent loading by the three solutes, q_{Total} is plotted as box plot for each process variable, namely, AC type, pH and adsorbent dose in Figure 2. The results indicate that a) sequentially exposing UN to microwave and then acid improved the mean adsorbent loading by 32% b) pH 10 significantly inhibits adsorption while pH 3 and 6.5 have similar average adsorbent loading and c) the effect of adsorbent dose is not significant. Outliers and the vertical spread in each box plot of Figure 2 are indicators of the accompanying influence of the remaining factors in addition to the factor under consideration.

Fisher's 95% confidence intervals were determined for the difference in means of each process variable levels and the results are plotted as Figure 5. This procedure helps in checking if process response at each level (or setting) of a process factor is comparable or significantly different from that at another level of the same factor. If the upper and lower bounds of a confidence interval drawn for the difference in mean total loadings of the adsorbent are of the same sign, then those two levels are statistically different from one another. If the upper and lower bounds encompass zero, then the difference in tested means is insignificant at the two levels tested. Figure 5a shows that the 95% confidence levels encompass zero for all the pairs tested. This implies that none of the means of dose levels are distinctive from one another in affecting the total loading on the adsorbent. Figure 5b indicates that pH 6.5 is not statistically different from pH 3 as the upper and lower bounds for the 95% confidence intervals have different signs. The mean total adsorbent loadings at both these pH conditions are however considerably different from pH 10, indicating that effect at pH 10 is unique. All three adsorbents viz. UN, AT and MAT are significantly different from one another in terms of their mean adsorbent loadings as their respective 95% confidence intervals do not have bounds of opposite signs (Figure 5c). The mean total adsorption capacity of UN, AT and MAT were 221, 248 and 296 mg solute/g carbon respectively.

Model Terms and Analysis of Variance Table

In the present study, the total adsorbent loading on the adsorbent (q_{Total}) was obtained by summing the individual adsorbent loading which in turn was found using the following equation,

$$q_{e,i} = \frac{V_L\left(C_{0,i} - C_{e,i}\right)}{m_a} \tag{14}$$

Here m_a is mass of the adsorbent and V_L is the liquid volume. The ratio $\frac{m_a}{V_L}$ is termed here as Dose. The individual factor analysis of the previous section reveals the significant main factors but failed to identify the interactions as it does not consider the effect of all factors simultaneously. Hence an empirical model (Eqn.(2)) that relates the response in terms of main factors taken alone and also in various combinations with one another was considered. The analysis of variance (ANOVA) table for the model allows us to find the statistical significance of each term by comparing their sum of square contributions with that of pure experimental error.

In an ANOVA table the significance of the contribution from each term to the process variability is evaluated on the basis of the p-value. Terms with low p-values (typically <0.05) contribute to the variation in the response in a statistically significant manner and those with higher p-values (> 0.1) do not affect the response significantly. The p-value indicates the probability of wrongly concluding a factor or an interaction to be significant. Thus, low p-values are preferred when stating a factor or interaction to be significant. The unequal effects of the interactions are denoted by the differences in their associated p-values. The opposing nature of the interactions is pointed to by the positive and negative sign on the coefficients in Eqn. (3). This respectively leads to synergetic and antagonistic effects of the interacting factors on the adsorption process.

When building the model, not all insignificant terms are removed. Insignificant terms whose higher order combinations are significant are still retained in order to maintain the model hierarchy. For instance, in Table 2, it is observed that CE and CD terms are insignificant, and yet their combination, CDE is significant (p-value = 0.0206). Removing these three terms led to lower adjusted R^2 and hence the model was not trimmed down further. Since the lack of fit is insignificant, it is not necessary to add more terms.

Analysing the p-values in Table 2, it was observed that the linear mixture effects representing contributions from individual solute concentrations are significant (p-value < 0.01). However, these contributions are relatively weaker when compared to the binary interaction terms i.e. combinations of two factors as the latter have p-values smaller than 0.0001. The interactions of different solutes with type of carbon (for e.g. AF or BF or CF) and pH (for e.g. BD), populate the highly significant binary terms (p-values < 10^{-4}). In other words, these interactions contribute considerably to the variability in the process response. A strong conclusion that may be made is that the type of carbon shows significant interaction with all three solutes, suggesting that the modification procedures affect the adsorption of individual solutes in a unique manner. The pH (D) strongly interacts with BTA concentration and the quadratic dependence on pH (BD^2) manifests only when BTA is present. The solutes interact significantly among themselves as well during the adsorption process, as the terms AB, BC and AC are significant. However, their nature of interaction is subject to pH changes since terms ABD and BCD are also present. Significant ternary interaction effects such as ADF, BDF, CEF and CDE in the ANOVA table, indicate that two process variables may also get

involved with the mixture variable. However, the model has to be scrutinized for its predictive ability before being analysed.

Table 2. Analysis of variance of q_{Total} where A (ACT), B (BTA) and C (CAF) are mixture concentrations, D is pH, E is adsorbent dose and F is type of carbon. The bold faced terms are statistically significant (p-value<0.01)

Source	Sum of Squares	DF	Mean Square	F-value	p-value	
Model	1.621×10^5	26	6236.41	71.31	**< 0.0001**	
BD	24486.42	1	24486.42	280.01	**< 0.0001**	
CF	18277.57	2	9138.78	104.50	**< 0.0001**	
AF	11137.46	2	5568.73	63.68	**< 0.0001**	
BF	10566.43	2	5283.21	60.41	**< 0.0001**	
BC	8348.38	1	8348.38	95.46	**< 0.0001**	
BD^2	7775.53	1	7775.53	88.91	**< 0.0001**	
ABD	1694.66	1	1694.66	19.38	**< 0.0001**	
AC	1634.76	1	1634.76	18.69	**< 0.0001**	**Significant**
BDF	1823.21	2	911.60	10.42	**0.0001**	
CEF	1546.80	2	773.40	8.84	**0.0004**	
BE	1051.66	1	1051.66	12.03	**0.0009**	
ADF	1349.50	2	674.75	7.72	**0.0010**	
AB	720.29	1	720.29	8.24	**0.0056**	
AD	678.57	1	678.57	7.76	**0.0070**	
(1) Linear Mixture	873.96	2	436.98	5.00	**0.0096**	
CDE	492.75	1	492.75	5.63	0.0206	
BCD	424.74	1	424.74	4.86	0.0311	
CD	165.47	1	165.47	1.89	0.1737	Insignificant
Lack of Fit	4594.28	53	86.68	0.9511	0.5830	Insignificant
CE	9.12	1	9.12	0.1043	0.7478	Insignificant
Residual	5596.78	64	87.45			
Pure Error	1002.50	11	91.14			
Total	1.677×10^5	90				

*DF is Degrees of Freedom

Testing the Adequacy of Model Equations

The coefficients of the terms chosen from the ANOVA table were estimated by linear regression and the response values were estimated from the resulting model equation. Once the model was found to be adequate i.e. with insignificant lack of fit (p value > 0.05), the model coefficients for different activated carbons could be compared and contrasted. Further, the model is used in optimization studies.

The adequacy of the models for different responses is quantified in terms of adjusted R^2, predicted residual error sum of squares (PRESS), predicted R^2 and lack of fit p-value. For the current model, these parameters were 0.9531, 10662.31, 0.9364 and 0.5830 respectively. Low PRESS values and high predicted R^2 values indicate that the models developed may be reliably used for making predictions within the problem domain. It is critical for the model to have insignificant lack of fit. It is imperative that model has adequate terms to fit the experimental data well and exhibits good predictive capabilities. This ensures that the model may be used to make reliable conclusions regarding the design, operation and optimization of the adsorption process. High adjusted R^2 and insignificant lack of fit imply that the number of parameters used in developing the final model is neither unduly in surplus nor in deficit.

The final model for the q_{Total} response after parameter estimation through linear regression is given in Eqn. (15). This model is expressed in terms of coded variables with the coding indicated by the apostrophe symbol.

$$\begin{aligned} q_{Total} = {} & 236.2 \times A' + 273.7 \times B' + 245.6 \times C' - 51.39 \times B'D'^2 + 61.05 \times A'B' \\ & + 73.84 \times A'C' + 153.0 \times B'C' - 37.17 \times A'D' - 54.38 \times B'D' - 37.85 \times A'F'[1] \\ & + 1.854 \times A'F'[2] - 11.24 \times B'E' - 8.938 \times C'D' - 25.61 \times B'F'[1] \\ & - 6.293 \times B'F'[2] + 2.405 \times C'E' - 45.89 \times C'F'[1] - 5.459 \times C'F'[2] \\ & + 83.86 \times A'B'D' + 43.57 \times B'C'D' + 7.906 \times A'D'F'[1] - 23.97 \times A'D'F'[2] \\ & + 3.294 \times B'D'F'[1] + 17.26 \times B'D'F'[2] + 10.01 \times C'D'E' + 2.821 \times C'E'F'[1] \\ & + 20.37 \times C'E'F'[2] \end{aligned} \quad (15)$$

The numeric process variables were scaled between -1 and 1 using the high (pv_{high}) and low levels (pv_{low}) of each factor as shown in Eqn. (4).

$$PV_{coded} = \left(\frac{pv_{actual} - \frac{(pv_{high} + pv_{low})}{2}}{\frac{(pv_{high} - pv_{low})}{2}} \right) \quad (4)$$

Concentrations of the different mixtures were scaled between 0 and 1 by dividing with the total initial concentration viz. 700mg/L. The categoric variable F was treated in terms of a two-dimensional vector to denote the three different carbons as recommended by the Design Expert software. The ranges, coding equation and various levels for each factor has been summarized in Table 3. The coded model (Eqn.15) is converted to the actual un-coded form (Eqn.16) by substituting the coding relations provided in Table 3. The scaled variables (A´-E´) ensure that they are all bounded within the same ranges. In general, the coded form of the model equation enables to evaluate and compare the relative impact of each coefficient on the process response by inspecting the magnitudes and signs of the coefficients attached to each term. The same may not be said of the un-coded form of the equation as the factors have different magnitudes which correspondingly affect the model coefficients as well.

Table 3. Coding relations for mixture and process variables

No.	Variable	Coding Equation	Actual & Coded Levels						
			Mixture Composition (Numeric)						
1	ACT	$A' = \frac{C_{ACT}}{700}$							
2	BTA	$B' = \frac{C_{BTA}}{700}$	mg/L	0	116.7	233.3	291.7	350	466.7	700
			Code	0	$\frac{1}{6}$	$\frac{1}{3}$	$\frac{5}{12}$	$\frac{1}{2}$	$\frac{2}{3}$	1
3	CAF	$C' = \frac{C_{CAF}}{700}$							
			Process Variables (Numeric)						
4	pH	$D' = \frac{pH - 6.5}{3.5}$	**pH**	3	6.5	10			
			Code	-1	0	+1			
5	Dose	$E' = \frac{Dose - 90}{30}$	mg/ 100mL	60	75	85	90	100	105	120
			Code	-1	$\frac{-1}{2}$	$\frac{-1}{6}$	0	$\frac{1}{3}$	$\frac{1}{2}$	1
			Process Variables (Categoric)							
					UN		**AT**		**MAT**	
6	Carbon Type	{ F′[1], F′[2] }	F′[1]		1		0		-1	
			F′[2]		0		1		-1	

However, though Eqn. 15 is in coded form, it does not allow any meaningful comparison of the coefficients as the vector of the categoric variable, F′ has to be specified. For example, replacing F′[1] with 0 and F′[2] with 1 results in the equation for acid treated carbon (Table 3). Specifying the F′ vector provides the coefficients in coded form for each type of carbon, which have been compared in Figure 6.

These coded coefficients (A′-E′) presented in Figure 6 may be compared across the carbons as well as within a carbon. The coefficients of some binary and ternary interaction terms remain constant for all three carbons. For example, AB, AC and BC coefficients are constant across carbons, owing to the absence of interaction with the adsorbent. The terms A′B′F′,

A′C′F′ and B′C′F′ terms are absent in the model equation (Eqn. 15). Hence these binary interactions of the solutes are unaffected by adsorbent modification. However, other terms highlight the effect of AC modification. For instance, interaction of BTA with pH (B′D′) and ACT with pH (A′D′) depend on the type of carbon. The improvement due to modification is reflected in the increasing positive linear coefficients (A′- C′) in the order UN < AT < MAT for all three solutes (Figure 6).

Also, coded equation provides insights on the adsorption performance as we increase or decrease a process variable from the design centre. At the design centre, the coded values are zero. Hence, at neutral pH and mid dose i.e. D′=0 and E′=0, the first three sets of bar columns of Figure 6 indicates the single solute preference of all three carbons are as ACT (A) ≈ CAF (B) < BTA (C). However, changing the process conditions disrupts this preference, implying that the single solute preference may be manipulated by altering the process conditions. For example, at pH 3, model predictions revealed that ACT ≈ BTA ≈ CAF while at pH 10 there is no pattern in the preference order as it depends on the carbon and its dose. The quadratic effect of pH (D^2) is exhibited only when BTA is present and the terms B′D′ and B′D'^2 have negative coefficients, indicating that increasing pH beyond the centre point reduces BTA loading. Grouping the terms that have two mixture components, we observe multiple interactions among the solutes as well as with the process conditions. For instance, the binary interaction between ACT and BTA as well as BTA and CAF are affected by pH giving rise to differences in the ternary interactions ABD and BCD. However, since the coefficient of B′C′ is higher than B′C′D′, even though pH affects their overall combination, the B′C′ interaction will be positive in magnitude. This indicates that BTA and CAF interact synergistically at any process. On the other hand, we observe that A′B′ has lower coefficient value than A′B′D′ (Figure 6). Thus the overall value of A′B′ is positive and negative when D′ is 1 and -1 respectively. Hence it is possible that for some pH values lower than the centre, i.e. when D′ takes negative values, the overall coefficient may take negative values. Hence, ACT – BTA interactions may be synergetic or antagonistic depending on the pH values. For instance, between pH 3 and pH 3.95 (D′= -1 to -0.7), the coefficient of A′B′ is negative beyond which it is positive indicating antagonistic and synergetic interactions respectively for all three carbons. The adsorbent dose (E′) affects mainly CAF adsorption, while it has a slight influence on BTA, it does not influence ACT adsorption at all.

Moreover, replacing and regrouping the coded variables A′-E′ with actual variables A-E respectively using the forms provided in Table 3 results in the coefficient values of uncoded form of variables A-E and their combinations (Eqn. 16)

$$q_{T,UN}=0.361\times A + 0.285\times B + 0.366\times C - 5.99\times10^{-3}\times BD^2 - 1.93\times10^{-4}\times AB + 1.51\times10^{-4} \times AC + 1.47\times10^{-4}\times BC - 0.0119\times AD + 0.0571\times BD - 5.35\times10^{-4}\times BE - 0.0159\times CD - 6.37\times10^{-4}\times CE + 4.89\times10^{-5}\times ABD + 2.54\times10^{-5}\times BCD + 1.36\times10^{-4}\times CDE$$

$$q_{T,AT}=0.502\times A + 0.275\times B + 0.349\times C - 5.99\times10^{-3}\times BD^2 - 1.93\times10^{-4}\times AB + 1.51\times10^{-4} \times AC + 1.47\times10^{-4}\times BC - 0.025\times AD + 0.0628\times BD - 5.35\times10^{-4}\times BE - 0.0159\times CD + 1.99\times10^{-4}\times CE + 4.89\times10^{-5}\times ABD + 2.54\times10^{-5}\times BCD + 1.36\times10^{-4}\times CDE \quad (16)$$

$$q_{T,MAT}=0.445\times A + 0.43\times B + 0.617\times C - 5.99\times10^{-3}\times BD^2 - 1.93\times10^{-4}\times AB + 1.51\times10^{-4} \times AC + 1.47\times10^{-4}\times BC-8.62\times10^{-3}\times AD + 0.0473\times BD - 5.35\times10^{-4}\times BE - 0.0159\times CD - 18.8\times10^{-4}\times CE + 4.89\times10^{-5}\times ABD + 2.54\times10^{-5}\times BCD + 1.36\times10^{-4}\times CDE$$

The coefficient values of the actual model equation (A-E Eqn.16)) should neither be compared for a given carbon nor across the carbons since the different factors have different orders of magnitudes. For example, pH varies between 3 and 10 only whereas adsorbent dose may take values between 60 and 120 mg/100mL, while the input concentration may vary between 0 and 700 mg/L. However, in coded form the numeric variables are scaled and the effects on the response are compared for a given adsorbent or across adsorbents quite easily, as illustrated in Figure 6.

Validation of q_{Total} Model at Randomly Chosen Conditions

The models chosen after ANOVA analyses were validated with a set of twenty experiments which were independent of the original design but were within the same experimental bounds. The parity plot in Figure 7 compares the model predictions against experimental values for the validation data set. The results indicate acceptable prediction capability of

within ±10%. The main advantage of the validated model is that it is comprehensive as it may not only be used for ternary mixtures but for binary and single component systems as well. For the latter two, the respective component concentration(s) are set to zero in the model equations. This represents a significant benefit as single, binary and ternary system adsorptions may be investigated holistically in an economical manner through this MPV approach.

Validation of q_{Total} Models at Optimal Conditions

The MPV model equations was used for optimization of user defined goal such as maximizing the adsorbent loading. In the present study, the optimal conditions suggested by Design Expert software to maximize q_{Total} for UN, AT and MAT are presented in Table 4. Also shown are experimental results at the suggested optimum conditions. As shown in this table, there is a reasonable match between predicted values and experimental values. The confirmations at the optimal points further strengthen the validations at the randomly chosen points, reaffirming the reliability of q_{Total} model.

Table 4. Comparison of confirmatory experimental results with model predictions at the suggested optimal conditions

C_{0ACT} mg/L	C_{0BTA} mg/L	C_{0CAF} mg/L	pH	Dose (mg / 100mL)	AC Type	Experimental q_{Total} values (mg/g)	MPV q_{Total} predictions (mg/g)
70	330	300	3	80	MAT	335±2	346
160	150	390	3	63	MAT	335±6	347
155	260	285	3	120	AT	276±3	284
0	500	200	6.5	60	UN	278±8	272

The optimal compositions and q_{Total} are tabulated in Table 5 for different pH conditions at a nominal adsorbent dose of 90 mg/100 ml.

Table 5. Validation of *fmincon* optimization at different pH conditions at nominal dose (90 mg/100mL)

pH	AC Type	$C_{0,ACT\ pred}$ mg/L	$C_{0,BTA\ pred}$ mg/L	$C_{0,CAF\ pred}$ mg/L	$q_{Total\ Pred}$ mg/g
3	UN	0	475.1	224.9	259.06
3	AT	587.6	0	112.4	301.12
3	MAT	0	424.3	275.7	346.10
6.5	UN	0	460.6	239.4	265.96
6.5	AT	0	412..3	287.7	293.23
6.5	MAT	0	369.7	330.3	339.64
10	UN	25.0	261.6	413.4	219.99
10	AT	0	256.8	443.2	257.67
10	MAT	57.9	137.9	504.2	298.20

It may be seen that MAT scores over the remaining carbons at different pH values. Further, optimum performance is noted in several cases for binary than ternary mixtures. Only for UN and MAT at pH 10, does the optimum lie within the domain boundaries.

The global maxima conditions and corresponding q_{Total} values are tabulated in Table 6.

Table 6. Globally optimum conditions for maximum possible q_{Total}

	$C_{0,ACT}$ mg/L	$C_{0,BTA}$ mg/L	$C_{0,CAF}$ mg/L	pH	Dose mg/100mL	q_{Total} mg/g
UN	0	530.77	169.23	4.91	60	279.69
AT	527.15	0	172.85	3	120	303.72
MAT	0	387.73	312.27	4.09	60	368.53

Optimization of MPV Design Considering Both Process and Mixture Variables

The conventional ridge analysis a) does not restrict the variables to be within the experimental range and b) it applies to either mixture or process variables separately but not simultaneously when MPV design needs to be analyzed. Hence the conventional ridge analysis is enhanced to handle the MPV design as explained below.

If process and mixture variables were allowed to change *simultaneously* using the cyclic and circular constrained optimization method, the entire mixture-process variables design space is comprehensively and simultaneously investigated because pH and dose in addition to composition are getting adjusted during the search for optimum. The cyclic and constrained optimization method is briefly mentioned below.

During the optimization of the MPV design where both process and mixture variables were handled simultaneously, it was found in some cases that the response trajectory did not pass through or terminate at the global optimum. To avoid local optima, the optimization strategy was changed. Rather than optimizing both process and mixture variables simultaneously, they were optimized separately in two loops. For process variables at lower bound, the mixture variables were optimized in the first loop. At these identified mixture variables, the process variables were optimized in the second loop. These optimized process variables in turn were fed back to the feed mixture composition i.e. first optimization loop. These passing of solutions between the two loops continued until the absolute difference between solutions in the loops fell below the specified tolerance level. Then the radius of the circle was incremented by a small step and the entire sequence of optimization steps was repeated. For each adsorbent, this strategy reduces the optimization variable space from one set of 5 to two sets of 2 process variables and 3 composition variables. This considerably eases the optimization search, facilitates the identification of true optimum on each circle and enables the finding of the global optimum as well in the feasible domain.

In this analysis, the choices of the foci were based on two criteria i) the focal points should not be close to the global optimum for the chosen carbon ii) subject to criterion i), the foci may be the centroid, or an arbitrarily chosen point lying on/ within the mixture composition space.

The optimum responses for the q_{Total} along the expanding circular arcs centred at the chosen focus and constrained within the composition domain are shown in Figure 8a. The radial distance of the optimal composition from the focus in the triangular domain was determined by Eqn.10. The constraint to lie within the composition domain was also schematically illustrated in Figure 8c. In Figure 8(b-d), plots for loci of pH, individual component concentrations and the steepest ascent path in the ternary composition space when tracing the maxima in q_{Total} are presented. In Figure 8b, the globally optimum pH is also shown for comparison.

For UN, at initial stages, a pH of 3 is found more suitable than the globally identified pH value of 4.91 as a higher q_{Total} may be achieved. This is shown in Figure 8a. However, in the case of MAT, the locus of maximum q_{Total} from mixture composition optimization nearly overlaps with that of MPV optimization. The optimal pH over the entire path varies between 4 and 4.5 and this range differs negligibly from the global optimum pH of 4.09. Due to the circular domain constraint, the variables are forced to lie on the circle rather than inside the circle. Hence, the evolving response as well as process variables need not be constant or change monotonically with radius as there may be a higher or lower local optimum relative to the previously identified one along the trajectory originating from the focus. These non-monotonic optima will be revealed as humps in the plot of q_{Total} vs radial distance (Figure 8a). However, among the carbons considered, only AT was the exception as it did not indicate non-monotonic behaviour towards the global optima. As depicted in Figure 8a, when the focus is at the BTA – CAF edge, a hump indicating local optima is observed at an intermediate location for AT carbon (red coloured lines) with pH nearing 6.5. Here, q_{Total} is about 298 mg/g. With further increase in the radial distance, a slightly better optimum (q_{Total} of 303.72 mg/g) involving ACT and CAF could be identified at pH 3.

ADVANTAGES:

In a wastewater treatment plant (WWTP), the inlet feed composition is expected to vary. Under such conditions, the proposed MPV optimization approach with circular constraint may be implemented to predict the optimal pH and dose for different initial feed concentrations, thereby enabling maximum utilization of the carbon's adsorption capacity. If wastes from different sources are stored in a WWTP, they may be mixed in such a manner to reach the best possible ideal mixture composition and suitable process variables may be then

set. This may lead to accumulation and depletion of certain wastes in the treatment plant and a new combination may be formulated based on the remaining quantities as the present treatment may be applied to single, binary or ternary mixtures. Hence the optimization analyses discussed in this work may aid in economical treatment and efficient waste management.

In a decentralised treatment plant of a housing complex, a map of treatment conditions versus waste composition be it single component, binary or ternary, may be helpful for optimum adsorption and water recycle.

REFERENCES

Box, G.E., Draper, N.R., 2007. Response surfaces, mixtures, and ridge analyses. John Wiley & Sons.

Cornell, J.A., 2011. Experiments with Mixtures: Designs, Models, and the Analysis of Mixture Data, Wiley Series in Probability and Statistics. Wiley.

Design-Expert (2018) version 11.1.2. Minneapolis: State-Ease, Inc.

Fritz, W., Schluender, E.-U., 1974. Simultaneous Adsorption Equilibria of Organic Solute in Dilute Aqueous Solution on Activated Carbon. Chem. Eng. Sci. 29, 1279–1282.

Gil, A., Taoufik, N., García, A., Korili, S., 2018. Comparative removal of emerging contaminants from aqueous solution by adsorption on an activated carbon. Environmental technology 1–14.

Leardi, R., 2009. Experimental design in chemistry: A tutorial. Analytica chimica acta 652, 161–172.

Li, N., Ma, X., Zha, Q., Kim, K., Chen, Y., Song, C., 2011. Maximizing the number of oxygen-containing functional groups on activated carbon by using ammonium persulfate and improving the temperature-programmed desorption characterization of carbon surface chemistry. Carbon 49, 5002–5013.

Lu, W.-B., Kao, W.-C., Shi, J.-J., Chang, J.-S., 2008. Exploring multi-metal biosorption by indigenous metal-hyperresistant Enterobacter sp. J1 using experimental design methodologies. Journal of hazardous materials 153, 372–381.

MATLAB. (2019). version 9.6 (R2019a). Natick, Massachusetts: The MathWorks Inc.

Montgomery, D.C., 2010. Design and Analysis of Experiments, 5th ed, Design and Analysis of Experiments. Wiley.

Myers, R.H., Montgomery, D.C., Anderson-Cook, C.M., 2016. Response surface methodology: process and product optimization using designed experiments, 3rd ed. John Wiley & Sons.

Zolgharnein, J., Bagtash, M., Feshki, S., Zolgharnein, P., Hammond, D., 2017. Crossed mixture process design optimization and adsorption characterization of multi-metal (Cu(II), Zn(II) and Ni(II)) removal by modified Buxus sempervirens tree leaves. Journal of the Taiwan Institute of Chemical Engineers 78, 104–117.

The Claim:

1. A method to maximise multicomponent adsorption of the solutes from an aqueous stream discharge by increasing the total solute loading (q_{Total}) of the adsorbent to the maximum loading capacity (global maximum) - the said method comprising the steps of:

   determining the mixture and the process variables of the adsorption wherein the mixture variable is feed concentration of one of the different solutes present in the aqueous stream and the process variable is one of pH, dose and type of the adsorbent;

   determining the main and interaction effects of mixture variables, pH, adsorbent dose and adsorbent type on the total solute loading q_{Total} using a mixture process variable design;

   arriving at a global maximum for the solute loading (q_{Total}) from specified mixture variables, also called as the focus, using circular constraints and simultaneously optimising the values of both the said mixture and said process variables, and identifying the path of steepest ascent towards the said global optimum, using enhanced ridge analysis;

   validation of the total solute loading (q_{Total}) arrived from the mixture process variable design;

   wherein the maximum total solute loading (q_{Total}) of the adsorbent is a function of both mixture and process variables.

2. The method as claimed in claim 1, wherein the pH is between 3 and 10, both inclusive.

3. The method as claimed in claim 1, wherein the dose of the adsorbent is between 0.6 and 1.2 g/L, both inclusive.

4. The method as claimed in claim 1, wherein the number of different types of adsorbent in the mixture process variable design is 3.

5. The method as claimed in claim 1, wherein number of solutes in the mixture process variable design is 3.

6. The method as claimed in claim 1, wherein mixture process variable design using optimization with constraints in the variables of both the mixture and the process are optimized separately in two loops, wherein mixture variables are optimized in a different loop and in turn are fed back to the process variables optimization loop.

7. The method as claimed in claim 6, wherein the constraints of the mixture variable is a function of the feed concentration when tracking the path towards the said global optimum during the said enhanced ridge analysis.

8. The method as claimed in claim 6, wherein the feed concentration of individual mixture variable is between 0 and 700 mg/L

9. The method as claimed in claim 6, wherein the total feed concentration of the mixture variable is specified value of 700 mg/L.

10. The method as claimed in claim 6, wherein the constraints of the process variable is fixed as per the lower and the upper bounds as claimed in claims 2 to 4.

11. The method as claimed in claim 1, wherein the (q_{Total}) of the experimental and the predicted value is a difference of ±10%.

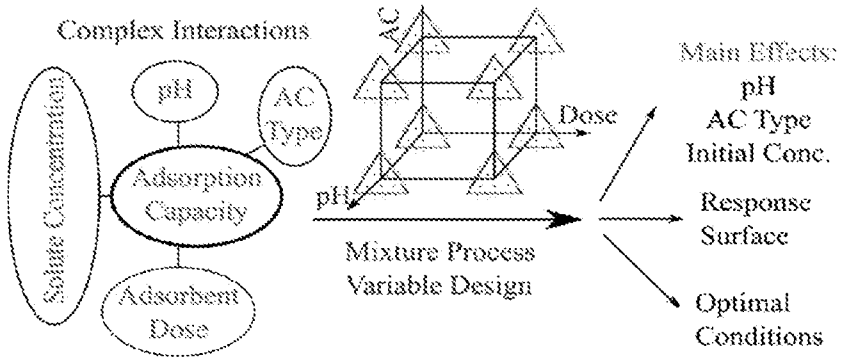

Complex Interactions
pH
AC Type
Solute Concentration
Adsorption Capacity
Adsorbent Dose
AC
Dose
pH
Mixture Process Variable Design
Main Effects:
pH
AC Type
Initial Conc.
Response Surface
Optimal Conditions

FIGURE 1

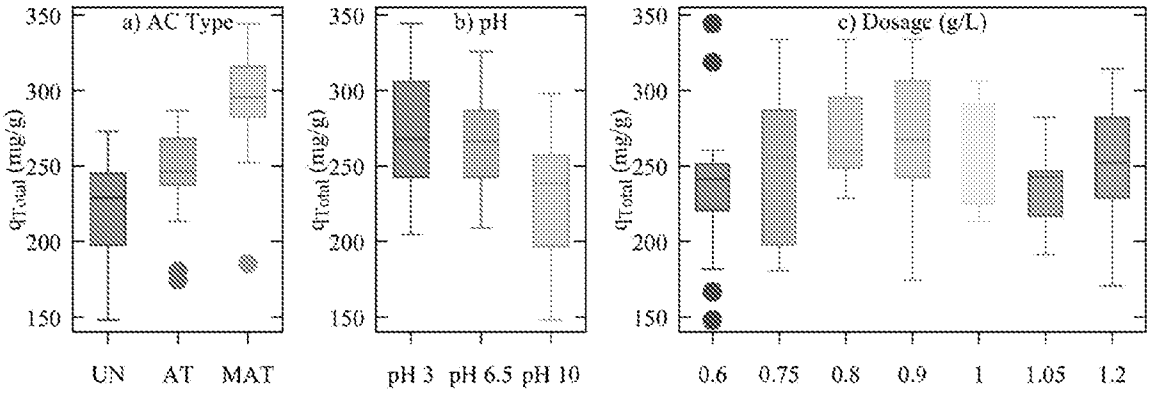

a) AC Type
b) pH
c) Dosage (g/L)
q_{Total} (mg/g)
350
300
250
200
150
UN
AT
MAT
pH 3
pH 6.5
pH 10
0.6
0.75
0.8
0.9
1
1.05
1.2

FIGURE 2

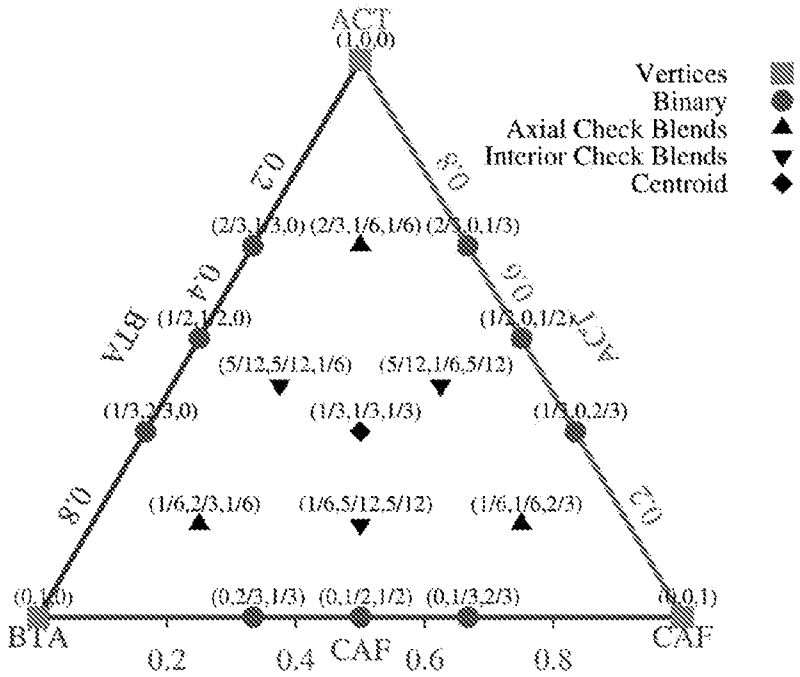

ACT
(1,0,0)
Vertices
Binary
Axial Check Blends
Interior Check Blends
Centroid
0.2
0.4
0.6
0.8
BTA
CAF
(2/3,1/3,0)
(2/3,1/6,1/6)
(2/3,0,1/3)
(1/2,1/2,0)
(1/2,0,1/2)
(5/12,5/12,1/6)
(5/12,1/6,5/12)
(1/3,2/3,0)
(1/3,1/3,1/3)
(1/3,0,2/3)
(1/6,2/3,1/6)
(1/6,5/12,5/12)
(1/6,1/6,2/3)
(0,1,0)
(0,2/3,1/3)
(0,1/2,1/2)
(0,1/3,2/3)
(0,0,1)
BTA
0.2
0.4
CAF
0.6
0.8
CAF

FIGURE 3

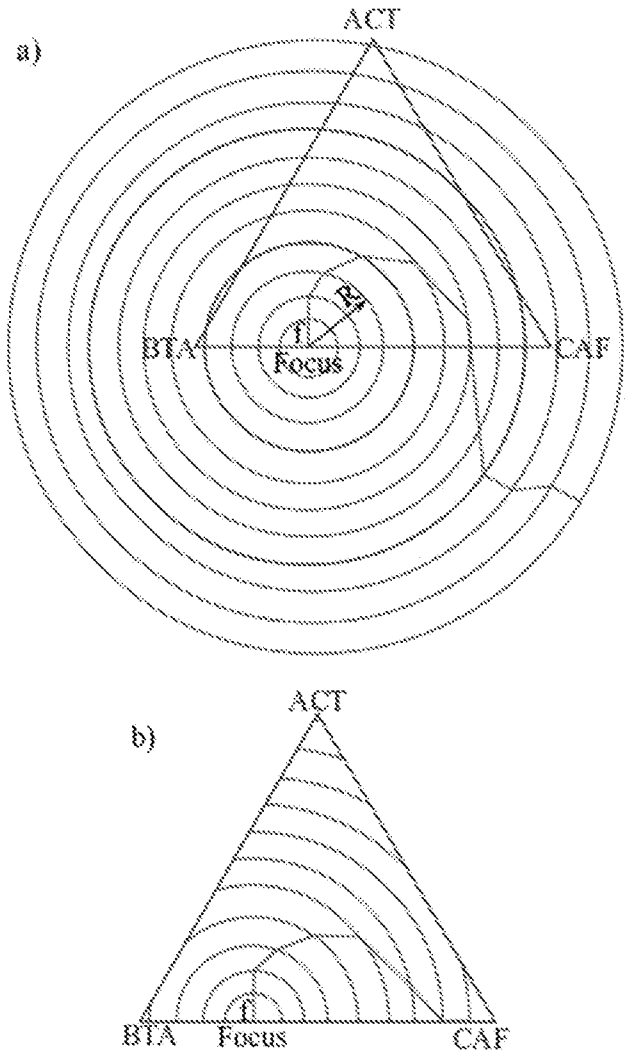


FIGURE 4

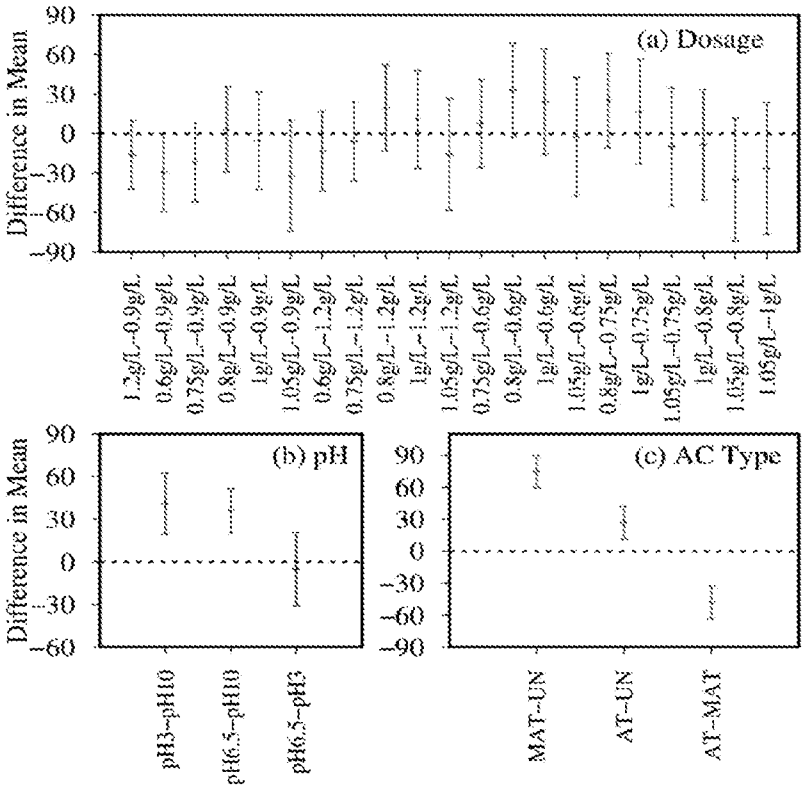

(a) Dosage
Difference in Mean
90
60
30
0
−30
−60
−90
1.2g/L–0.9g/L
0.6g/L–0.9g/L
0.75g/L–0.9g/L
0.8g/L–0.9g/L
1g/L–0.9g/L
1.05g/L–0.9g/L
0.6g/L–1.2g/L
0.75g/L–1.2g/L
0.8g/L–1.2g/L
1g/L–1.2g/L
1.05g/L–1.2g/L
0.75g/L–0.6g/L
0.8g/L–0.6g/L
1g/L–0.6g/L
1.05g/L–0.6g/L
0.8g/L–0.75g/L
1g/L–0.75g/L
1.05g/L–0.75g/L
1g/L–0.8g/L
1.05g/L–0.8g/L
1.05g/L–1g/L
(b) pH
pH3–pH10
pH6.5–pH10
pH6.5–pH3
(c) AC Type
MAT–UN
AT–UN
AT–MAT

FIGURE 5

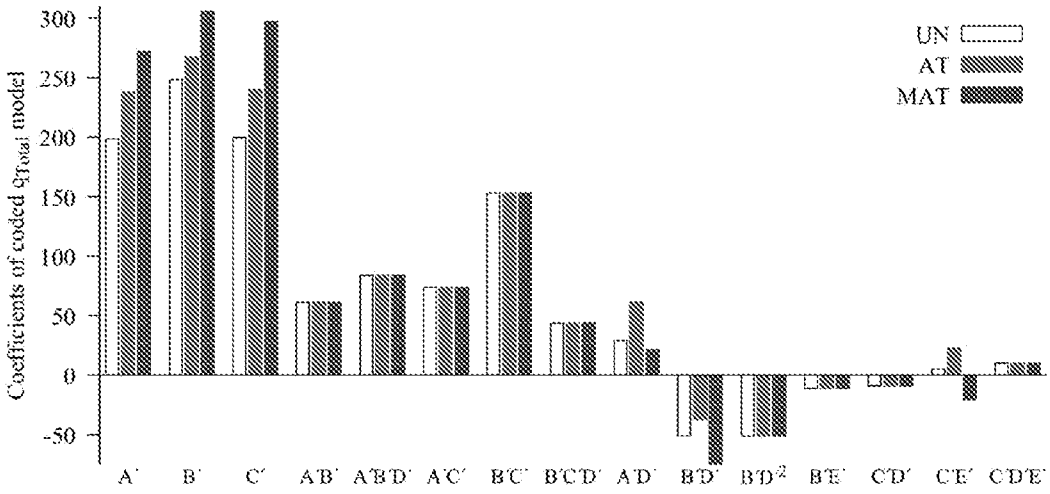

Coefficients of coded q_{Total} model
300
250
200
150
100
50
0
-50
UN
AT
MAT
A'
B'
C'
A'B'
A'B'D'
A'C'
B'C'
B'C'D'
A'D'
B'D'
B'D'^{2}
B'E'
C'D'
C'E'
C'D'E'

FIGURE 6

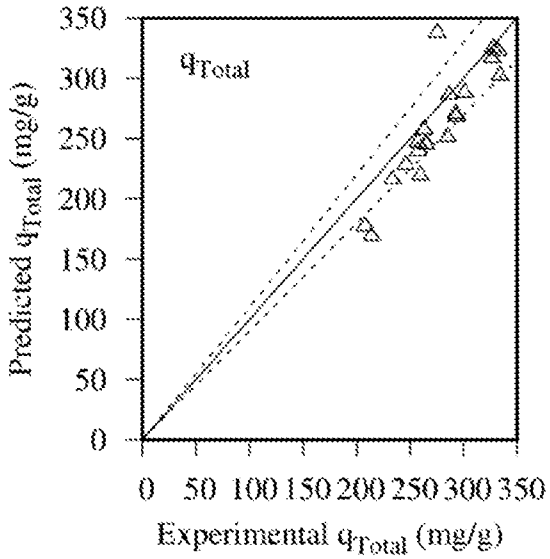

q_{Total}
Predicted q_{Total} (mg/g)
Experimental q_{Total} (mg/g)
0
50
100
150
200
250
300
350

FIGURE 7

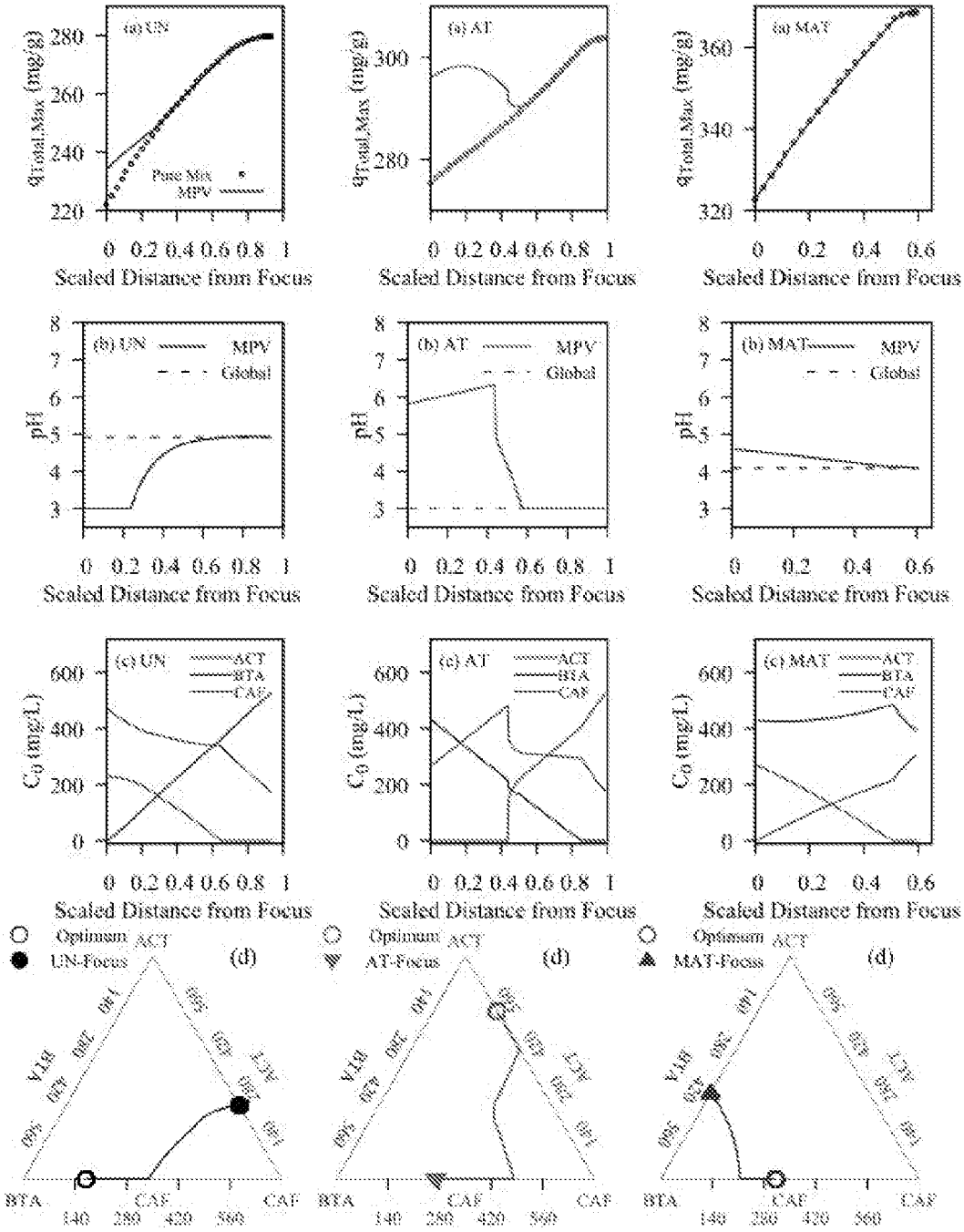

(a) UN
(a) AT
(a) MAT
$q_{Total,Max}$ (mg/g)
Pure Mix
MPV
Scaled Distance from Focus
(b) UN
(b) AT
(b) MAT
MPV
Global
pH
(c) UN
(c) AT
(c) MAT
ACT
BTA
CAF
C_0 (mg/L)
Optimum
UN-Focus
AT-Focus
MAT-Focus
(d)

FIGURE 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/IN2020/050687

A. CLASSIFICATION OF SUBJECT MATTER
C02F9/00,C02F1/28,C02F1/44 Version=2020.01

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C02F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

TotalPatent One, IPO Internal Database

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	"Kinetic evaluation of phenol/aniline mixtures adsorption from aqueous solutions onto activated carbon and hypercrosslinked polymeric resin (MN200)" by César Valderrama et. al.; Reactive & Functional Polymers, 70 (2010) 142-150; DOI:10.1016/j.reactfunctpolym.2009.11.003 pages 142-150	1-11
Y	"Competitive adsorption and desorption of a bi-solute mixture: effect of activated carbon type" by Özgür Akta¸s · Ferhan Çeçen, Adsorption (2007) 13: 159-169; DOI 10.1007/s10450-007-9017-5 pages 159-169	1-11

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"D" document cited by the applicant in the international application
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
05-11-2020	05-11-2020
Name and mailing address of the ISA/ Indian Patent Office Plot No.32, Sector 14,Dwarka,New Delhi-110075 Facsimile No.	Authorized officer Rewa Bhardwaj Telephone No. +91-1125300200