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Novel air agitated tapered adsorber for crystal violet removal on biomass combustion residue with process optimization using response surface modeling

Sandip Kumar Ghosh[a,b], Amitava Bandyopadhyay[a,*]

[a] University of Calcutta, 92, A.P.C. Road, Kolkata 700 009, India
[b] Indian Institute of Chemical Engineers. Kolkata 700 032, India

1. Introduction

Dyes are used in various process operations such as manufacture of dyes, textile, tannery, dyeing and bleaching that generate effluent containing colors. The effluent containing color requires adequate treatment before being discharged outside the process plant. There are various methods for the treatment of colored effluent [1], such as chemical oxidation, coagulation, photochemical oxidation, biological treatment, membrane separation and adsorption. In brief, the descriptions of these methods [2] are as follows. Colored waste water generally comprises high concentrations of BOD, COD, color, pH, and heavy metals. In order to treat such complex waste water stream chemical oxidation method using chemicals has been reported in the literature. In this method, generally the oxidation leads to the precipitation of the pollutant after oxidation that needs separation from the waste water stream before final discharge. In coagulation, colloidal materials are destabilized with the help of polymeric coagulating agents followed by flocculation after formation of the flocs. Inorganic coagulants for instance, aluminum sulfate, aluminum chloride and ferric sulfate are also reported to be used. The enhanced particle size due to formation of flocs enables removal from the stream easily. The photochemical oxidation process being an advanced oxidation process has also been reported to be used in the treatment of colored waste water. In this process, highly reactive hydroxyl radical formed is mainly responsible for degrading organics present in colored waste water. Sometimes solar radiation is used for enhancing the formation of the reactive hydroxyl radicals towards degrading the organics at a relatively reduced cost. Biological treatment can be used to treat colored waste water for degrading the biodegradable organics. The refractory organics however, require relatively longer time to degrade in the biological process than the simpler organic molecules. Different types of biological methods are in application such as aerobic, anaerobic and anoxic systems as well as suspended- and attached- growth according to microorganism growth. The membrane separation has also been applied for treating colored waste water. In this process, the feed is passed through the membrane (polymeric or ceramic) to produce clear liquid in the permeate while enriching the pollutant in the retentate. Though the process does not utilize any chemicals for the treatment, generation of the concentrate in the permeate limits it application due to further treatment of its discharge. Fouling and concentration polarization further complicate the process operation. Adsorption has been remaining as one of the most efficient processes among all other processes in the treatment of colored waste water. Its unique ability to remove pollutants from the waste water is reported. In this process the pollutants are adsorbed onto the surface of the adsorbent, owing to large surface area. The process is a surface driven phenomena. The generation of larger surface area at a relatively lower cost has been a challenge to the researchers for achieving the desired effluent quality. All water and waste water treatment methods are based only on the five mechanisms such as adsorption, co-precipitation, precipitation, size-exclusion, and volatilization [3]. Therefore, principally adsorption is one of the methods used in most of the waste water treatment scheme as a final or polishing stage. Moreover, it has the advantages of achieving higher removal efficiency, producing high quality water economically and not requiring skilled personnel in contrast to other methods. In waste water treatment, the adsorption seems an important step in treating colored effluent like other pollutants.

Legion of investigations have so far been carried out on the removal of Crystal Violet (CV) using various adsorbents under conventional batch operating mode using Erlenmeyer flasks in mechanical (orbital) shaker, such as biomass combustion residue [4], Peat of Brunei Darussalam III [5], Ricinus communis Pericarp Carbon [6], Jute Fiber Carbon [7], Lignocellulosic Waste from Bidi Industry [8], Novel hydrogel composite [9], zeolites from coal fly- and bottom- ashes [10], magnetically modified activated carbon and nanomagnetic iron oxide [11] so on and forth. The adsorptive removal of dyes onto different novel metal oxides either alone or in combination have also been reported in the literature, for example, adsorption of acid red 27 dye from aqueous solutions onto Fe_2O_3 nanoadsorbents [12], organic dyes from its aqueous solutions by magnetic Fe_3O_4 core–shell nanoparticles [13], reactive blue 21 onto TiO_2 [14], reactive yellow 15 onto Zn-Mn-Fe mixed nano oxide [15], methyl blue on amorphous transi-

* Corresponding author.
E-mail addresses: amitava.bandy@gmail.com, amitava.cuche@gmail.com (A. Bandyopadhyay).

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Nomenclature

A	Pre-exponential factor in arrhenius equation, dimensionless
AP	Adequate precision
a_R	Redlich–Peterson isotherm constant, (L/mg)
b_T	Temkin constant related to the heat of sorption indicating $1/b_T$ as the adsorption potential of the adsorbent, J/mol
C_e	Equilibrium concentration of CV, mg/L
C_f	Final concentration, mg/L
C_i	Ionic concentration of ith species, mol/L
C_0	Initial concentration of CV, mg/L
C_t	Concentration of CV at any time t, mg/L
CV%	Coefficient of variation
df	Degrees of freedom
D_f	Liquid film diffusion constant, min^{-1}
E	Sorption energy, kJ/mol
F	Faraday constant, 96500C/mol
F-value	Test for comparing term variance with residual (error) variance
$F_{(t)}$	Fractional attainment of adsorption equilibrium $\left[=\frac{q_t}{q_e}\right]$, dimensionless
g	Redlich–Peterson isotherm exponent
I	Intercept in Weber-Morris intra-particle diffusion model, mg/g
I_S	Ionic strength, mol/L
k_1	Pseudo-first order adsorption kinetic rate constant, min^{-1}
k_2	Pseudo-second order adsorption kinetic rate constant, g/mg.L.min
k_f	Freundlich isotherm constant, (mol/g). $(mol/L)^{-1/n}$
k_{id}	Rate constant [intra-particle diffusion], mg/g. $(min)^{0.5}$
K_H	Halsey constant, dimensionless
k_L	Langmuir constant, L/mg
k_R	Redlich–Peterson isotherm constant (L/g)
k_S	Sips isotherm model constant (L/g)
K_T	Temkin isotherm constant, L/gm
m	Mass of the adsorbent per unit volume, W/V, g/mL
MS	Mean squares, sum of squares divided by df
n	Number of data points
n_F	Freundlich constant, dimensionless
n_H	Halsey constant, dimensionless
n_s	Sips isotherm model exponent
p	Number of parameters
Q_a	Air flow rate, L/min
q_{DR}	Theoretical monolayer sorption capacity, mg/g
q_e or $q_{e,meas}$	Amount of CV adsorbed measured at equilibrium, mg/g
$q_{e,cal}$	Amount of CV adsorbed calculated at equilibrium, mg/g
q_m	Maximum amount of CV adsorbed, mg/g
q_t	Amount of CV adsorbed at time t, mg/g
r	Correlation coefficient, dimensionless
r^2	Coefficient of determination, dimensionless
r^2-Adj	Adjusted R-squared, dimensionless
r^2-Pred	Predicted R-squared, dimensionless
R	Universal gas constant, 8.314 J/mol K, 1.987 cal/mol.K
SD	Standard deviation
SS	Sums of squares, sum of the squared differences between the average values and the overall mean
t	Contact time, min
T	Absolute temperature, K
V	Volume of dye solution, l
W	Amount of adsorbent, g
x_i	Factor (independent variable)
x_j	Factor (independent variable)
Y	Response (dependent) variable
Z_i	Ionic charge upon ith species

Greek letters

β_0	Constant coefficient,
β_i	Coefficient for the linear effect
β_{ii}	Coefficient for the quadratic effect
β_{ij}	Coefficient for the interaction effect
β	Mean energy of sorption per molecule of sorbate related to the average energy of sorption as the dye molecule is transferred from the bulk of the system to the surface of the solid adsorbent, mol^2/J^2
γ	Error
χ^2	Chi-square, dimensionless
ε	Dubinin–Radushkevich isotherm constant
ε_w	Dielectric constant of water, 78.5
ε_o	Vacuum permeability, 8.854×10^{-12}, C/V-m
$\frac{1}{\kappa}$	Electrical double layer thickness (EDL), 1/m

tional metal oxide (Fe, Co and Ni oxides) nanoparticles [16] so on and forth.

The method of adsorption requires optimization of process variables alike any wastewater treatment method, and their influence to optimize the pollutant removal efficiency by the adsorbent. In adsorption, the solid-fluid interface plays the pivotal role in adsorbing the pollutant from the liquid stream. The process is intrinsically governed by various factors such as the contact time, initial adsorbate concentration, adsorbent dose, adsorbent surface area, functionalities over the adsorbent surface, operating solution pH, operating temperature and frequency of agitation of the solid-fluid slurry. Sometimes, the ionic strength of the solution also influences the adsorption process. Amongst these parameters, the influence of the contact time is necessarily investigated by rigorous experimentation for estimating the equilibrium time which classically constitutes the intrinsic design parameter for adsorption. The operating solution pH is necessarily dependent on the pH_{PZC} of the adsorbent. Before, investigating or optimizing the solution pH, a sound knowledge of pH_{PZC} is required based on which the domain of the operating pH is selected. The effluent discharge limitation of pH of the treated wastewater will further augment to consolidate the domain of the operating pH. In the light of these observations, optimizing the remaining process variables by the traditional methods reflecting the influence of the interactions among these variables on the dependent variable such as the percentage removal would become tedious and time consuming considering the requirement of a large number of experimental runs [17].

In the recent past, investigations have also been carried out to optimize the variables by linear- and non-linear- modeling as well as by multivariable process optimization [17]. In recent years, Response Surface Methodology (RSM), a collection of mathematical and statistical techniques, is gaining considerable attention by the researchers as a useful tool for modeling and analysis for investigating into the response of interest influenced by several variables by simultaneously varying them [18]. The RSM further allows one to perform only the limited number of experiments and is often employed for multiple regression analyses. There are three forms of RSM designs such as the central composite design (CCD), Box-Behnken design (BBD) and D-optimal design [19]. Amongst these, the CCD is the most widely used form of RSM employed to evaluate the effects as well as to optimize the various process variables for achieving the desired output. The experimental design followed from the optimization employing CCD under RSM has also been reported in the literature for adsorption of dyes including CV onto various adsorbents from aqueous solutions [16,20]. However, these studies are all limited to conventional batch experi-