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SHAMA MUSTAFA HAYDER
SALMAN HUSSAIN
WASIM AHMAD
MIRZA JAHANZAIB
ABAID ULLAH

University of Engineering and Technology, Taxila, Punjab, Pakistan

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OPTIMIZATION OF LOW-COST COW DUNG BASED ACTIVATED CARBON FOR THE REMOVAL OF CARBOFURAN FROM AQUEOUS SOLUTION

Article Highlights

- Cow dung can be utilized to produce low-cost activated carbon by waste-to-wealth concept
- Cow dung-based activated carbon can be employed for removing pesticides from aqueous solution
- Maximum activated carbon yield and pesticide removal were 16 and 94%, respectively
- The optimized activated carbon yield and pesticide removal were 14.78 and 89.187%, respectively
- Most significant factors include activation temperature and impregnation ratio

Abstract

Water pollution has become a serious issue of this century due to increased industrialization. Several methods have been adopted to tackle this issue, including adsorption by activated carbon (AC). Conventional sources of AC preparation are costly and non-renewable as well. Several fruit and agricultural wastes have characteristics to become sustainable feedstock for AC preparation. This study aims to prepare cost effective AC from sustainable raw material, cow dung. The preparation has been analyzed and optimized by utilizing central composite design (CCD). The effect of activation temperature, time, and impregnation ratio (IR) on responses of percent yield (R_1) and percent pesticide removal (R_2) has been analyzed. Quadratic models have been suggested with R^2, adjusted R^2, and predicted R^2 values of 0.98, 0.96, 0.89 for R_1, and 0.97, 0.94, 0.87 for R_2, respectively. Activation temperature and KOH/Feedstock ratio significantly influence the yield and pesticide removal. Optimized conditions of activation temperature, KOH/Feedstock ratio, and activation time are 708.07 °C, 1.22 and 0.66 h, respectively. These conditions produced 14.78% yield and 89.18% pesticide removal. SEM and BET analysis of optimized AC also confirmed porosity development and large surface area availability due to activation process. Findings of this study suggest that cow dung can be used to prepare low-cost AC for pesticide removal from aqueous solution.

Keywords: adsorbent, activated carbon, biowaste, cow dung, pesticides, wastewater treatment.

Pesticides are synthetic substances used to mitigate the attacks of pests to avail the maximum yield of crops. However, along with the benefits of pesticides, there exist some hazards associated with their use. Most of the pesticides are toxic for living organisms and some of these are persistent in the environment posing a great hazard. Their persistence in environmental bodies like food, soil and water have potential to bio-accumulate and ultimately bio-magnify in living organisms causing detrimental effects [1]. Moreover, inappropriate and excessive use of pes-

Correspondence: S.M. Hayder, University of Engineering and Technology, Taxila, Taxila, Punjab, Pakistan
E-mail: shamamustafahayder@gmail.com
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ticide pollutes the water bodies endangering the aquatic life and rendering the water bodies unsuitable for routine operations [2].

The global amount of sprayed pesticide has reached above 4.6 million tons per annum. The effective amount accounts for only 1% and the rest 99% ends up in different environmental bodies. A report of United States' EPA says that out of 127 pesticides at least one is present in many rural wells. A study reported the presence of pesticides in 90 different sites, from the equator to cold regions. Considerable amounts have also been found in Greenland ice sheets and Antarctic penguins [3].

In Pakistan, 245 metric tons of pesticides were consumed in 1954 and by 2011 it has reached up to 70,000 tons. The extra amount applied, the careless handling and storage, improper transportation and use of outdated and banned pesticides have led to a number of environmental problems [4]. Some studies have indicated the presence of pesticides in water bodies of different agricultural areas of Pakistan [5-11].

Carbofuran is a carbamate pesticide, widely used for a variety of fruits and vegetables. It is highly toxic to humans, birds and aquatic life, having acute and chronic effects. It causes cholinesterase inhibition in humans and animals and has been found to be responsible for escalated risks of diabetes [12]. The World Health Organization (WHO) has recommended the drinking water standard of 3 μg/L for carbofuran [5]. However, in Pakistan it has been found in some water samples above permissible limits [5,7]. So, there is dire need to regulate its exposure into the environment and to eliminate the existing quantities from environmental bodies.

Various processes have been proposed for the treatment of contaminated water to make it potable and safe for other applications. These processes include adsorption, membrane filtration and advanced electrochemical oxidation methods. Adsorption is extensively studied and applied due to lower cost, easy operation and higher efficiency than the other methods [13]. Activated carbon has been used as adsorbent material and it provides exceptional results. A recent study employed an activated carbon fixed bed setup for adsorption of Ni ions from aqueous solution. The effects of different parameters were studies and the adsorption mechanism was determined by CFD analysis. The study concluded that activated carbon is capable of 90% removal of metal ions from solution [14]. Activated carbons available on the market are expensive owing to their reliance on conventional non-sustainable and non-renewable raw materials and hence the high cost of production cannot be justified for use in wastewater treatment. So, in search of inexpensive and renewable raw materials, researchers have successfully prepared activated carbons for water treatment from fruit and agricultural bio-wastes like orange tree leaves [15], hemp fibers [16], and corncobs [17] following the waste-to--wealth concept [18]. However, due to a large spectrum of pollutants it is highly desirable to produce very specific activated carbon for specific application.

The major factors controlling the qualities of carbon are its preparation conditions which can be manipulated to get suitable properties. The effect of various factors can easily be analyzed through an appropriate experimental design. Response surface methodology (RSM) is an opposite tool to analyze the interaction of different factors. RSM can also be used to optimize the experimental conditions and it has been used for many processes and preparation of activated carbons as well [19].

Cow dung is an abundantly available waste material due to a huge livestock industry. The composition of cow dung (35.97% holocellulose and 19.02% lignin) implies that it can be a worthy feedstock for activated carbon preparation [20].

Bhattacharjya *et al.* prepared cow dung-based activated carbon for electrodes of capacitors. Surface area of 1500-2000 m^2/g with different KOH ratios and maximum capacitance of 124 F/g was obtained [21]. Demiral *et al.* studied the surface properties of cow dung-based activated carbon and reported that surface area as high as 1916 m^2/g can be achieved with KOH activation [22]. Elaigwu prepared activated carbon from cow dung to remove metallic ions from simulated water solution and described that cost effective adsorbent can be prepared by cow dung having good capability to remove lead(II) ions [23]. Li *et al.* carried out activation of cow dung using various activating agents and stated that $ZnCl_2$, KOH and K_2CO_3 produced good activated carbons. Moreover, sewage from cow farm was treated to remove chemical and biological oxygen demand effectively and it was showed that after treatment the sewage met the discharge standards [20].

Limited studies were found utilizing the cow dung-based activated carbon for water treatment, especially using RSM. Thus, the novelty of the current work is to produce a low-cost, highly selective and sustainable cow dung-based KOH-activated AC for carbofuran removal from simulated water solution using RSM. Moreover, the effect of different variables and optimal conditions for maximum pesticide removal and yield are also a point of interest. Potassium hydroxide (KOH) is used for activation of cow dung as

it is an environment-friendly activating agent and it keeps tar formation at minimum. It reacts with carbon in the feedstock to make K_2CO_3 which upon reaction with more carbon produces potassium, potassium oxide, carbon monoxide and carbon dioxide. All these reactions produce porosity and large volumes of activated carbon [24,25].

EXPERIMENTAL

Materials and instruments

Analytical grade 99% pure carbofuran ($C_{12}H_{15}NO_3$) and ≥85% pure potassium hydroxide (KOH) were utilized, purchased from a local dealer of Sigma Aldrich. Distilled water and hydrochloric acid (37%, Sigma Aldrich) were used for washing of samples. All solutions were made in distilled water. Cow dung was fetched from a local dairy farm in dried form. Scanning electron microscope (Tescan Vega LMU) was used for surface morphology of AC. Surface area and porosity measures were taken by using BET surface area and porosity analyzer (Tristar II 3020).

Preparation of activated carbon

Dry cow dung fetched from a local dairy farm has been used as feedstock for AC preparation following the steps given in Figure 1. The feedstock was pulverized using mortar and pestle and sieved to get uniformity of particles. The powdered feedstock was dried in oven at 100 °C to eliminate the moisture content until constant weight. The dried feedstock was mixed with KOH in different ratios (KOH: Feedstock) and activated at different conditions according to experimental design in a furnace at constant heating rate. The obtained material was allowed to cool down to room temperature and rinsed with water to eliminate the activating agent. Washing with 0.5 M HCl was also carried out to remove the ash contents. Washing with water was continued till the pH of washed solution reached about 6-7. Washed carbon was dried in an oven at 1000 °C until it attained constant weight.

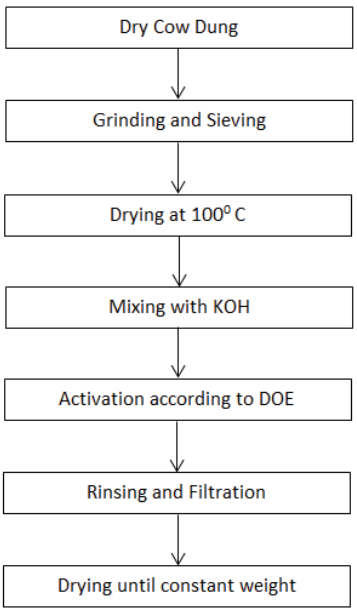

Figure 1. Steps of cow dung-based activated carbon preparation.

Performance measurements

Percentage yield

Yield of cow dung-based AC was computed on dry basis. Eq. (1) [26, 27] was used to calculate the percentage yield of prepared samples:

$$Yield = 100\frac{w_o}{w_i} \quad (1)$$

where w_o and w_i are final weights of dry AC and dry feedstock, respectively.

Percentage pesticide removal

Batch tests were conducted to evaluate the adsorption capacity of prepared activated carbons. Carbofuran solution having 100 mg/L concentration was taken in an Erlenmeyer flask and 0.30 g of cow dung-based AC (pH around 7.8) was mixed with it. The flask was kept in an isothermal shaker at 250 °C and 100 rpm and was occasionally checked for normal operation until the attainment of equilibrium which was around 6 h. The solution was then filtered to separate the AC and the remaining concentration of solution was measured by UV-1800 Perkin Elmer 750 nm spectrophotometer. The wavelength of carbofuran for maximum absorption was determined by taking 100 µg/mL in a cuvette and measuring its absorption at different wavelengths. It was found near 275 nm for carbofuran as evident from spectrum given in Figure 2. The calibration curve for carbofuran was found by measuring the absorbance of standard solutions of

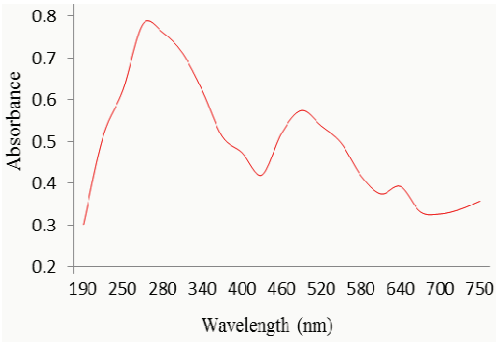

Figure 2. Maximum absorption spectrum for carbofuran.

carbofuran and the regression coefficient (R^2) for the calibration curve was 0.998. The calibration curve was used to measure the unknown concentration of solutions. The removal of carbofuran was determined by using Eq. (2) [27,28]:

$$\text{Percentage removal} = 100\frac{C_0 - C_f}{C_f} \quad (2)$$

where C_0 and C_f (mg/l) refer to initial and final concentrations of carbofuran in solution, respectively.

Design of experiments

Central Composite Design (CCD) was employed to study the effect of selected factors on activated carbon preparation. CCD is an efficient design able to employ appropriate mathematical models to study and optimize the effect of different factors on preparation of a product with a minimum number of experiments. It is a vital tool for experimentation as it allows modeling the data points with minimum number of experiments in a limited time and cost. Besides data fitting in an appropriate model, RSM is capable of optimization of results for desired outcome or to produce a highly specific product. Usually, it involves three types of points; (1) "2^k" Factorial/Cube (2) "$2k$" Axial/Star and (3) "C" Center points. The minimum number of experimental runs required for given number of factors (k) can be calculated by Eq. (3) [27]:

$$n = 2^k + 2k + C \quad (3)$$

Three important factors with their ranges were selected from literature. These factors included activation temperature, impregnation ratio (IR) and activation time. The total numbers of experiments for three factors based on Eq. (3) were 20, with 6 center points. These factors are important in deciding the characteristics of AC [29]. Cow dung-based AC yield and carbofuran removal were two responses measured and used to develop polynomial mathematical equations showing the relationship between the response and selected factors. Second order polynomial equation (Eq. (4)) was used to model the data points and to estimate the regression equation for both responses [28]:

$$R_i = \alpha_0 + \sum \alpha_i X_i + \sum \alpha_{ii} X_i^2 + \sum_{i<j} \sum \alpha_{ij} X_i X_j + \varepsilon \quad (4)$$

where R_i, α_0, α_{ii}, α_{ij}, X_i, X_j and ε are the i-th response, constant, linear coefficient, square coefficient, interaction coefficient, i-th variable, j-th variable and random error, respectively. ANOVA along with other model adequacy checks were performed to check the significance of variables. Design Expert 7.0.0 was employed for data analysis. Selected factors for AC preparation and responses are given in the Table 1. The α values refer to the axial points of design.

ANALYSIS OF RESULTS

The design matrix of cow dung-based AC along with two responses is given in the Table 2, and the

Table 2. Design matrix with responses of yield and pesticide removal

Run	Variable factor			R_1	R_2 / %
	(A)	(B)	(C)		
1	500	1	1	16.33	62.90
2	700	1	1	13.33	87.00
3	500	3	1	13.40	85.00
4	700	3	1	10.53	94.60
5	500	1	2	14.80	70.00
6	700	1	2	11.73	81.60
7	500	3	2	13.20	84.30
8	700	3	2	10.20	91.00
9	432	2	1.5	13.80	69.80
10	768	2	1.5	9.00	93.60
11	600	0.32	1.5	15.20	61.00
12	600	3.68	1.5	10.33	89.10
13	600	2	0.66	14.10	88.30
14	600	2	2.34	12.33	88.70
15	600	2	1.5	11.40	93.60
16	600	2	1.5	11.13	88.40
17	600	2	1.5	10.86	88.20
18	600	2	1.5	10.66	88.00
19	600	2	1.5	10.80	88.10
20	600	2	1.5	11.10	91.00

Table 1. Selected factors and responses

Factor	$-\alpha$	Lower level	Center point	Upper level	$+\alpha$
Activation temperature (°C) (A)	432	500	600	700	768
Impregnation ratio (B)	0.32	1	2	3	3.68
Activation time (h) (C)	0.66	1	1.5	2	2.34
Responses					
1	Yield of AC, %			(R_1)	
2	Removal of pesticide, %			(R_2)	

coded factor-based models for responses are given by Eqs. (5) and (6). The magnitude of coefficients of the equation indicates the relative effect of factors on response. These equations can be used to predict the response at given levels of factors. The usefullness and quality of models can be assessed through the value of R^2. Usually the value of R^2 ranges from 0 to 1 and indicates good or bad fit of expermental data in the suggested model. A value closer to 1 suggests a good fit of experimental data in the model. However, adjusted and predicted R^2 is a better indicator of good fit as contrary to simple R^2, as simple R^2 always increases with the addition of the independent factor. Adjusted R^2 improves only when the new term in the model improves it. The predicted R^2 is calculated by deleting response points one by one and then re-estimating them using the developed model and hence it represents how accurately the developed model estimates the data point. With an increased number of factors the value of simple R^2 may increase due to random noise, providing the likelihood of overfitting of model with a high R^2 value but with a poor ability of making predictions. So, reporting the other two R^2 values for the validation of model becomes of great significance in such scenarios. For Eq. (5) the values of R^2, adjusted and predicted R^2 are 0.98, 0.96 and 0.89, respectively. The high value of R^2 suggests a good fit of the data in the suggested model. The adequately high values of adjusted R^2 and predicted R^2 suggests that the model is accurate and can be used to estimate the response. For Eq. (6) the values are 0.97, 0.94 and 0.87, respectively. The adequacy of the model is confirmed by these appropriate values and hence it is suggested that the model can used to predict the response accurately.

$$R_1 = 10.98 - 1.47A - 1.25B - 0.49C + 0.025AB - \\ -0.025AC + 0.33BC + 0.23A^2 + 0.71B^2 + 0.87C^2 \quad (5)$$

$$R_2 = 89.53 + 6.74A + 7.37B - 0.14C - 2.42AB - \\ -1.92AC - 0.75BC - 2.61A^2 - 4.96B^2 - 0.21C^2 \quad (6)$$

Eq. (4) can be used to predict the impact on R_1 by putting the levels of each factor and then changing the level of one factor to estimate its impact on R_1. The code for upper level is 1 and -1 for lower level. Below is given the calculation for R_1 for lower level (-1) of factor '*A*' and upper level (1) of factor '*B*' and '*C*':

R_1 = 10.979 - 1.4654*(-1) -1.2485*(1) - 0.486*(1) +
+ 0.025*(-1)*(1) - 0.025*(-1)*(1) +0.325*(1)*(1) +
+ 0.22686*(-1)^2+0.70946*(1)^2+0.86856*(1)^2

Hence, the value of R_1 comes out to be 12.8398.

By taking upper level (1) of factor '*A*' with higher levels (1) of factor '*B*' and '*C*', the R_1 becomes 9.9089:

R_1 = 10.979 - 1.4654*(1) -1.2485*(1) - 0.486*(1) +
+ 0.025*(1)*(1) - 0.025*(1)*(1) + 0.325*(1)*(1) +
+ 0.22686*(1)^2 + 0.70946*(1)^2 + 0.86856*(1)^2

It can be seen that by switching the factor '*A*' from lower to upper level, the value of response decreases. Hence it can be predicted that yield (R_1) decreases by increasing the activation temperature (*A*).

Similarly, the effect of factor level can be estimated for R_2 by taking lower level (-1) of factor '*A*' and upper level (1) of factor '*B*' and '*C*'. By putting the level values in Eq. (5):

R_2 = 89.53 + 6.74*(-1) + 7.37*(1) - 0.14*(1) -
- 2.42*(-1)*(1) - 1.92*(-1)*(1) - 0.75*(1)*(1) -
- 2.61*(-1)^2 - 4.96*(1)^2 - 0.21*(1)^2

R_2 = 85.83

Now Eq. (5) can be solved for upper level (1) of all factors to analyze the effect of factor level:

R_2 = 89.53 + 6.74*(1) + 7.37*(1) - 0.14*(1) -
- 2.42*(1)*(1) - 1.92*(1)*(1) - 0.75*(1)*(1) -
- 2.61*(1)^2 - 4.96*(1)^2 - 0.21*(1)^2

R_2 = 90.63

It is evident from the above calculation that carbofuran removal (R_2) is lower for lower level (-1) of activation temperature (*A*) and it becomes higher for upper level (1) of activation temperature (*A*) keeping the other two factor levels constant. It can be inferred that more activation is achieved at higher temperature due to which more removal is observed.

Analysis of variance (ANOVA)

ANOVA is another check of the model and it also provides information about significant terms. The significant terms have considerable effect on responses and play an important role in predicting the overall response. Ignoring any significant term renders the model less precise to estimate the response. The ANOVA results of R_1 and R_2 are provided in the Tables 3 and 4, respectively. *F*-value is defined as the ratio of source variability to residual variability. A high *F*-value suggests that residual variability is lower and the selected model can better explain the behavior of response. The *P*-value, smaller than 0.05, suggests that the specific term is significant. *P*-value is the probability of null hypothesis to be true for the observed *F*-value. Hence *P*-value lower than 0.05 suggests the rejection of the null hypothesis which states that an additional term would not render the model better. Rejection of the null hypothesis means that

Table 3. ANOVA for percent yield

Source	Sum of squares	Degrees of freedom	Mean square	*F*-Value	*P*-value
Model	71.323	9	7.924	62.698	< 0.0001
A	29.326	1	29.326	232.021	< 0.0001
B	21.287	1	21.287	168.417	< 0.0001
C	3.225	1	3.225	25.517	0.0005
AB	0.005	1	0.005	0.039	0.8463
AC	0.005	1	0.005	0.039	0.8463
BC	0.845	1	0.845	6.685	0.0272
A^2	0.742	1	0.741	5.868	0.0359
B^2	7.254	1	7.253	57.389	< 0.0001
C^2	10.872	1	10.871	86.015	< 0.0001

Table 4. ANOVA for percent carbofuran removal

Source	Sum of squares	Degrees of freedom	Mean square	*F*-Value	*P*-value
Model	1867.22	9	207.47	40.94	< 0.0001
A	620.12	1	620.12	122.36	< 0.0001
B	741.91	1	741.91	146.39	< 0.0001
C	0.27	1	0.27	0.05	0.8215
AB	47.04	1	47.04	9.28	0.0123
AC	29.64	1	29.64	5.85	0.0361
BC	4.50	1	4.50	0.89	0.3682
A^2	98.34	1	98.34	19.40	0.0013
B^2	355.02	1	355.02	70.05	< 0.0001
C^2	0.62	1	0.62	0.12	0.7330

additional terms have effect on the response and are called significant terms.

From Table 3, the *F*-value for R_1 is 62.698 suggesting that the model is significant. The terms "*A*, *B*, *C*, *BC*, A^2, B^2, C^2" are significant for R_1.

The *F*-value of 40.94 for R_2 presented in Table 4 specifies significance of the suggested model. Other significant terms of the model include "*A*, *B*, *AB*, *AC*, A^2, B^2".

The root mean square error (*RMSE*), mean absolute percentage error (*MAPE*), coefficient of variance (C.V) and variance accounted for (*VAF*) values are 0.25, 1.819, 2.91 and 98.26 for R_1, and 1.59, 1.59, 2.67 and 97.34 for R_2, respectively. The coefficient of variance *C.V* measures the dispersion of data around the mean and a lower values of *C.V* for R_1 and R_2 indicate a precise estimate of data and less dispersion around the mean. Lower *RMSE* and *MAPE* value are desirable for model adequacy. The obtained values of *RMSE* and *MAPE* are considerably low and hence suggest an accurate reproducibilty of data. The higher values of *VAF* for both models implies the closeness of experimental and predicted data [30].

Model diagnostics

Normal probability plots are employed to examine that if the data is normally distributed or not. The data is assumed to be normally distributed if all the residuals are adequately near to the straight line [31]. It can be seen from Figures 3 and 4 that for both responses the residual points are sufficiently close to the standard line suggesting the normality of data. Figure 5 presents the actual *vs*. predicted values of yield and pesticide removal data. The closeness of the points with the straight line discloses that actual and predicted values differ slightly. It also confirms the model adequacy.

Factor effects on cow dung AC yield (R_1)

Temperature of activation has the highest effect as indicated by a highest F-value of 232.02 from Table 3. Impregnation ratio and activation time also have an effect on yield but to a lesser extent than the temperature. It is observed that all three factors have a negative effect on the yield as evident from Table 2. The effect of activation time and impregnation ratio on R_1 with constant activation temperature at center point (T=600 °C) is shown in Figure 6(a). It is evident that higher yield is obtained at lower activation time and impregnation ratio. However, IR seems to have more effect than activation time on yield. Figure 6(b) depicts the response graph of activation time and temperature with constant IR at center point (IR=2). A higher value of these factors produces lower yield.

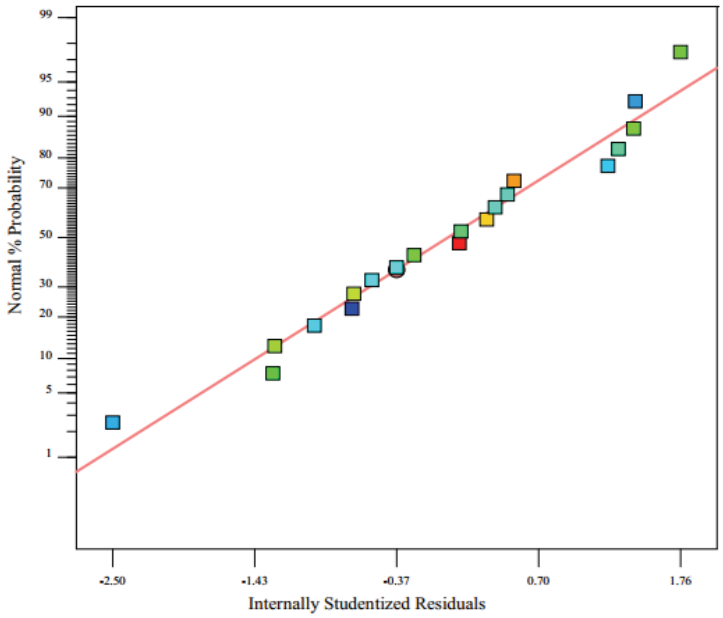

Figure 3. Normal probability plot for % yield.

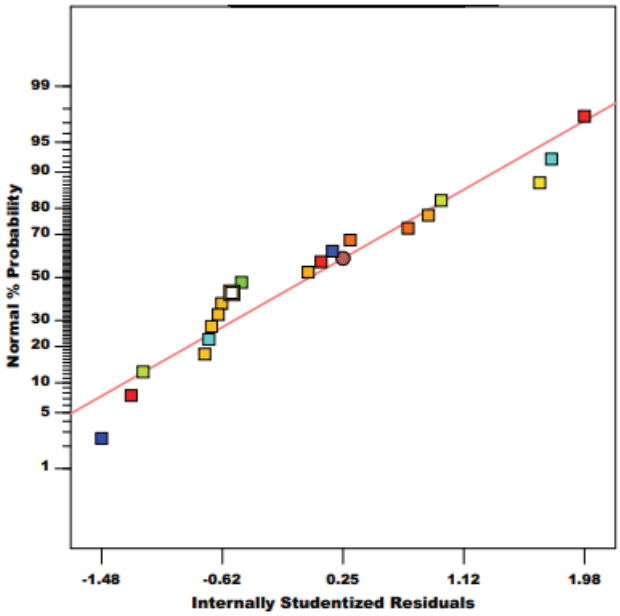

Figure 4. Normal probability plot for % carbofuran removal.

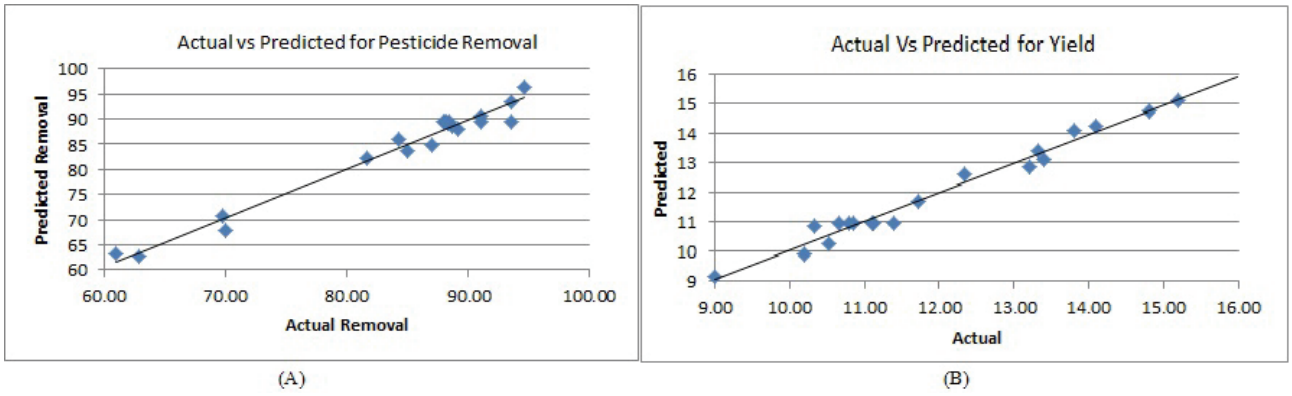

Figure 5. Parity chart (A) pesticide removal (B) yield.

Activation temperature seems to have more significant effect than time. Figure 6c presents the response graph of activation temperature and *IR* with constant activation time at center point (t = 1.5 h). A higher value of both factors lowers the yield considerably. Both have almost same effect on yield but relatively higher than activation time.

The increase in temperature increases the discharge of volatile matter owing to enhanced elimination reactions along with increased C-KOH and C-CO_2 reaction, thus causing a lower yield [32]. Higher *IR* also produces a lower yield due to excessive burn-off of surface carbon atoms and emission of volatile matter. At higher amounts of KOH, the gasification of surface carbon atoms is increased resulting in a lower carbon yield [33].

In the present study, the percentage yield obtained varies from 9 to 16.33%. In another study a yield of (12.58±1.2)% was obtained using KOH as activating agent at 800 °C [19]. Percentage yield of the present study is comparable with the stated work and the difference can be attributed to small differences in preparation techniques.

Factor effects on pesticide removal (R_2)

Activation temperature and *IR* seem to have higher effect on R_2 as it can be noticed in Table 4. Activation time has been found insignificant in this case. Interaction effect of *IR*, activation temperature, and activation time is moderate while that of *IR* and activation time is not significant. The quadratic effect of *IR* is higher than the quadratic effect of activation temperature, while for activation time it is insignificant.

Figure 7a depicts the response graph of activation temperature and *IR* for R_2 with constant activation time at center point (t = 1.5 h). It reveals that at the lower end of these factors, a lesser amount of removed carbofuran is obtained while the reverse is true when both factors are at the higher end. Individually, these factors affect the response in same fashion. Figure 7b describes the response graph of activation temperature and time with constant IR at center point (*IR* = 2). It is clearly visible that activation time has constant response at all values while activation temperature has a positive effect. A higher removal is obtained at higher temperature. From Figure 7c it is apparent that activation time has a constant response at all values while *IR* has significant positive effect on the response as higher removal is obtained at higher IR.

Sudaryanto *et al.* [34] also stated the insignificance of activation time towards pore development and structure and hence it had no effect on adsorption

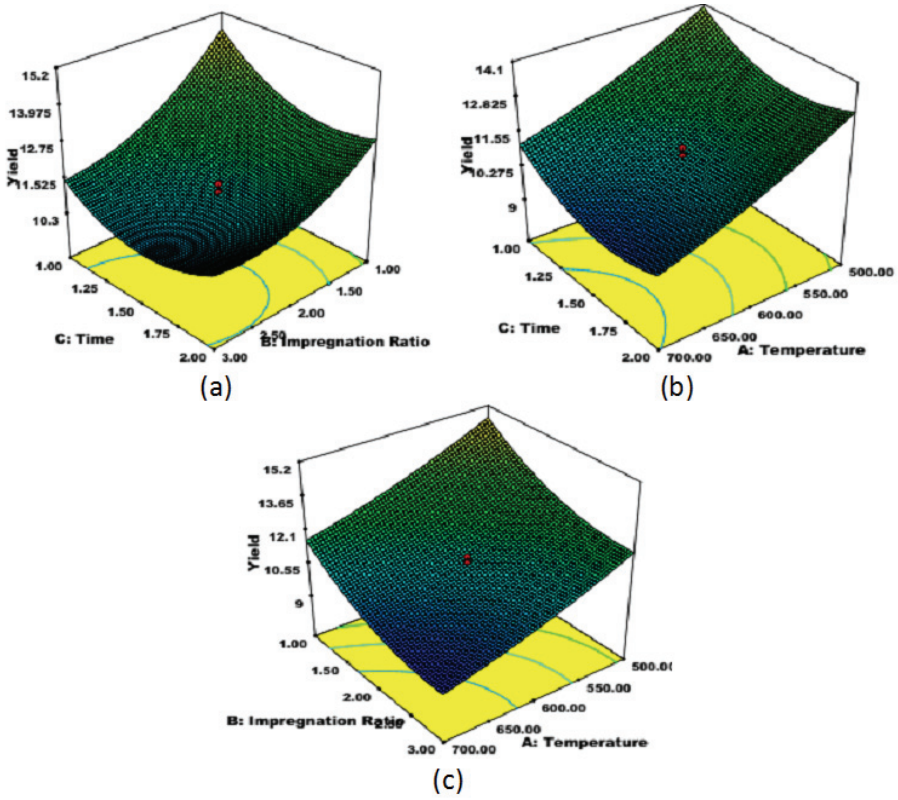

Figure 6. Three-dimensional graph of AC yield with: a) activation time and IR; b) activation temperature and time; c) activation temperature and IR.

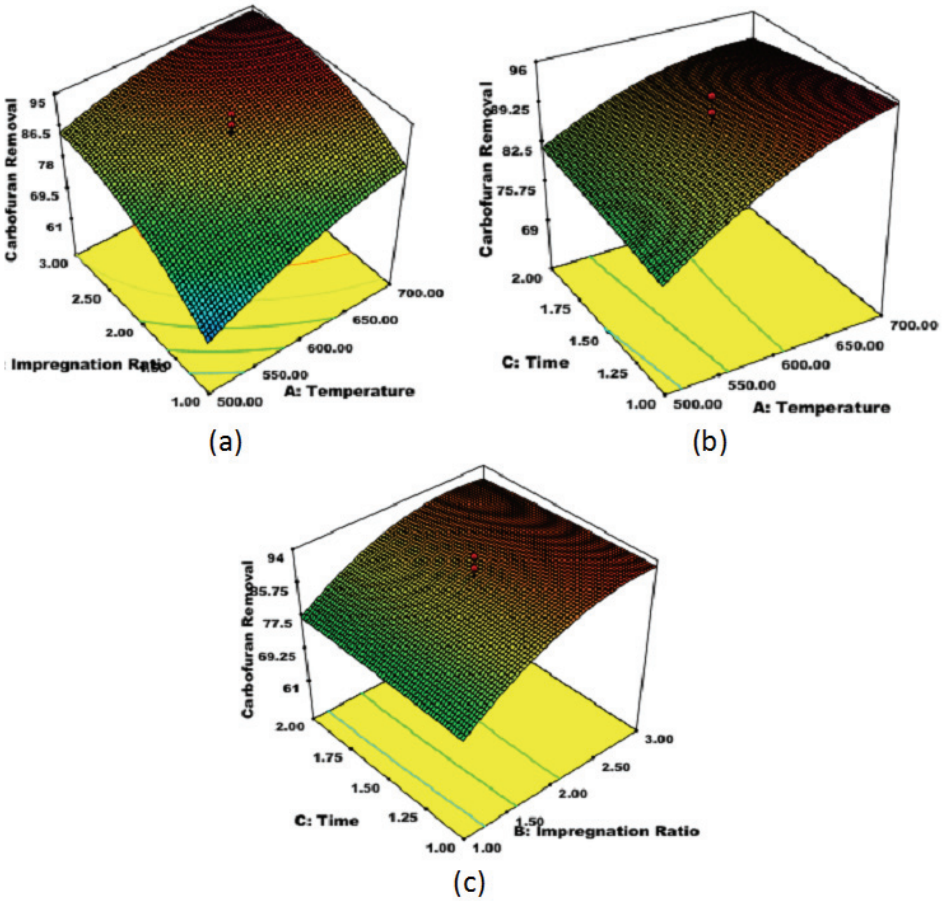

Figure 7. Three-dimensional graph of pesticide removal with: a) activation temperature and IR; b) activation temperature and time; c) IR and activation time.

capability of AC. The higher pesticide removal at higher *IR* and activation temperature is credited to higher activation of AC and porosity development. Shoaib *et al.* [35] also reported that activation at higher temperature increases the porosity and hence the uptake capacity of the product. Porosity development at higher temperature is due to the increased C-KOH, gasification and de-volatilization reactions. The higher *IR* favors oxidation reaction due to which porosity is developed [36].

Optimization of responses

It has been seen that the activated carbon yield and pesticide removal results have a conflicting situation. The conditions favoring higher activated carbon yield produce lower pesticide removal capacity and *vice versa*. To overcome this conflict, a tradeoff is necessary to get acceptable results. The desirability function of Design Expert 7.0.0 is used to get optimal results in this situation. The result with maximum desirability value is selected as optimal among all feasible solutions. Table 5 presents the optimized results for the preparation of cow-dung based activated carbon to have optimal responses.

Characterization of activated carbon

Figure 8 represents the SEM image (x1000) of cow dung-based AC prepared under obtained optimized conditions. Well-developed porosity can be observed from the image and it can be attributed to the activation process. These pores are responsible for adsorption of carbofuran molecules on AC surface. BET and Langmuir surface area were found to be 1123.37 and 1563.28 m^2/g, respectively. The prepared AC had total pore volume of 0.631 cm^3/g and average pore diameter of 2.53 nm. The prepared AC was classified as mesoporous as its pore diameter was found to be 2.53 nm. The high surface area and

Table 5. Optimized preparation conditions

Activation temperature (°C)	Impregnation ratio	Activation time (h)	Yield (%)	Carbofuran removal (%)
708.07	1.22	0.660	14.785	89.187

pore volume are achieved due to chemical activation process and these are directly related to enhanced adsorption of carbofuran onto the surface of AC. Porosity also adds to the available surface area and can be improved by using higher amounts of activating agent.

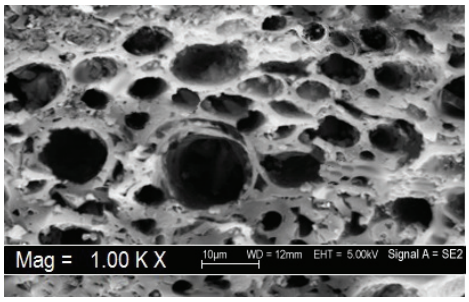

Figure 8. SEM Image of cow dung-based activated carbon under optimum conditions.

Validation of developed models

Some additional experimental runs were performed to validate the proposed models after data analysis. The selected data points for experimentation were different than the design points previously employed for experimentation and analysis. Percentage error was measured between the predicted and actual values. An absolute percent error of below 5% was observed for all validation runs, thus validating the adequacy of proposed models. Table 6 shows the validation data points along with percent error. Percent error was calculated by using Eq. (7):

$$\text{Percent Error} = = 100\frac{|\text{Actual value - Predicted value}|}{\text{Predicted value}} \quad (7)$$

Table 6. Validation runs

Factor	Run		
	1	2	3
A	550	650	708
B	1.50	1.50	1.22
C	1.25	1.8	0.66
Actual yield	13.55	10.72	14.4
Predicted yield	13.11	11.01	14.784
Error, %	3.35	2.67	2.60
Actual removal	77.600	89.110	87.2
Predicted removal	79.318	87.407	89.187
Error, %	2.166	1.949	2.25

CONCLUSION

Cow dung was utilized to make AC and tested to remove pesticide from simulated contaminated water. CCD was employed to model and optimize the experimental results. *IR* and activation temperature had a significant effect on AC yield and uptake capacity. Higher values of both factors favor the removal of pesticide at the cost of AC yield. The optimized conditions of 708.07 °C activation temperature, 1.22 *IR*, and 0.66 h of activation time produced 14.78% yield and 89.18% pesticide removal. SEM image of optimized AC revealed that it has numerous pores on its surface which aid in adsorption. BET analysis confirmed the availability of large surface area and pore volume for better adsorption. These optimized conditions not only produce best results but are also economical from a cost point of view. Hence a low-cost and highly selective AC can be obtained from cow dung and the problem of water contamination by carbofuran can be addressed by exploiting an apparent waste following the waste-to-wealth concept.

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SHAMA MUSTAFA HAYDER
SALMAN HUSSAIN
WASIM AHMAD
MIRZA JAHANZAIB
ABAID ULLAH

University of Engineering and Technology, Taxila, Punjab, Pakistan

NAUČNI RAD

OPTIMIZACIJA JEFTINOG AKTIVNOG UGLJA OD KRAVLJE BALEGE ZA UKLANJANJE KARBOFURANA IZ VODENOG RASTVORA

Zagađenje vode postalo je ozbiljno pitanje ovog veka zbog povećane industrijalizacije. Usvojeno je nekoliko metoda za rešavanje ovog problema, uključujući adsorpciju aktivnim ugljem. Konvencionalni izvori dobijanja aktivnog uglja su, takođe, skupi i neobnovljivi. Nekoliko voćnih i poljoprivrednih otpadaka ima karakteristike održivih sirovina za dobijanje aktivnog uglja. Cilj ovog istraživanja je dobijanje isplativog aktivnog uglja iz održive sirovina - kravlje ibalege. Postupak dobijanja je analiziran i optimizovan primenom centralnog kompozitnog dizajna. Analiziran je uticaj temperature aktivacije, vremena i odnosa impregnacije na odgovore prinos (R_1) i stepen uklanjanja pesticida (R_2). Predloženi su kvadratni modeli sa koeficijentima determinacija R^2, R_{adj}^2 i R_{pred}^2 od 0,98, 0,96, 0,89 za prinos pesticida i 0,97, 0,94 i 0,87 za stepen uklanjanja pesticida, redom. Temperatura aktivacije i odnos KOH/sirovina značajno utiču na prinos i stepen uklanjanje pesticida. Optimizovani uslovi temperature aktivacije, odnosa KOH/sirovina i vremena aktivacije su 708 °C, 1,22 i 0,66 h, redom. Pri ovim uslovima, ostvern us prinos 14,78% i stepen uklanjanje pesticida 89,18%. SEM i BET analize optimizovanog aktivnog uglja su, takođe, potvrdile njegovu poroznost i veliku površinu. Rezultati ovog istraživanja sugerišu da se kravlja balega može koristiti za dobijanje jeftinog aktivnog uglja za uklanjanje pesticida iz vodenog rastvora.

Ključne reči: adsorbent, aktivni ugalj, biootpad, kravlja balega, pesticidi, prečišćavanje otpadnih voda.