



Equilibrium Studies on Batch Adsorption of Alizarin red in Aqueous Solution using Activated Carbons derived from Orange Peels

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ABSTRACT: Adsorption has been one of the most preferred methods for the removal of dyes from aqueous solutions due to its simplicity and economic advantages. In this research, activated carbon prepared from orange peels has been characterized using Boehm titration which revealed the surface as having 7.70 mmol/g and 3.64 mmol/g total acidic and basic sites respectively. Scanning Electron Microscope (SEM) imaging showed that the adsorbent had heterogeneous surface morphology while the pH of zero point charge (pH_{zpc}) of the adsorbent was found to be 3.6. Furthermore, Sear's titration has shown that the activated carbon specific surface area was $791.1 \text{ m}^2 \text{ g}^{-1}$. The influence of various experimental parameters have been probed and optimized. The optimized conditions were set for the study of adsorption equilibrium and the experimental data were treated using Langmuir, Freundlich, Dubnin-Radushkevich (D-R) and Halsey isotherm models. However, all the four isotherm models were in good fit with the data obtained as indicated by the regression coefficients (R^2 value) of 0.944 for the Langmuir isotherm, 0.993 for both Freundlich and Halsey models, and 0.980 for D-R model. The maximum monolayer coverage capacity (q_m) was determined to be 11.5 mg/g at room temperature, which is higher than some presented in the previous literature.

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Environmental pollution is one of the major and most urgent problems of the modern world whereby industries are the greatest polluters, with the textile industry generating high amount of liquid effluent pollutants due to the large quantities of water used in fabric processing (Wang *et al.*, 2007). Dyes contamination in wastewater causes problems in several ways: the presence of dyes in water, even in very low quantities, is highly visible and undesirable; color interferes with penetration of sunlight into waters, retards photosynthesis, inhibits the growth of aquatic biota and interferes with gas solubility in water bodies (Garg *et al.*, 2004). Direct discharge of dyes containing effluents into municipal environment may cause the formation of toxic carcinogenic breakdown products. The highest rates of toxicity were found amongst basic and diazo direct dyes (Wang *et al.*, 2008). Therefore, it is highly necessary to reduce dye concentration in wastewater. The conventional methods for treating dye containing wastewaters are electrochemical treatment, coagulation and flocculation, chemical oxidation, liquid-liquid extraction and adsorption (Wang *et al.*, 2005). Even when some these techniques were reported to be successful in decolorizing a particular wastewater, adsorption has been proven to be very effective

separation technique and now it is often considered to be superior to other techniques for water treatment in terms of initial cost, simplicity of design, ease of operation and insensitiveness to toxic substances (Parimaladevi and Venkateswaran, 2011).

The objective of this paper is to investigate the equilibrium studies on batch adsorption of alizarin red in aqueous solution using activated carbons derived from orange peels

MATERIALS AND METHODS

Study Area and Sample collection: The study area was Katsina urban which is located at the extreme margin of northern Nigeria that lies on geographic coordinates of $11^{\circ}08'N$ and $13^{\circ}22'N$ and longitudes $6^{\circ}52'E$ and $9^{\circ}20'E$. The urban area of Katsina covers a total land of over $3,370 \text{ km}^2$ (Ruma and Sheikh, 2010). Being one of the oldest urban centers of Nigeria, Katsina is believed to have been established in 1100AD. It has its roots stretching back considerably before the advent of British colonizers and has served as entre port to the Saharan and trans-Saharan trade (Isah, 2011). Katsina is the center of an agricultural region that produces food and cash crops such as guinea corn, millet, groundnut, beans, cotton and hides (Ladan, 2014).

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Oranges are found in abundance anywhere in Katsina. Their peels can easily be obtained from sale point, since they do not have any significant use, so they are treated as waste materials and thus are available in plenty free of charge.

Materials and Reagents: A digital pH meter (JENWAY, 3510), a Scanning Electron Microscope (PHENOM SEM 800-07334), a UV-visible spectrophotometer (PG Instruments, T60), and Flask Shaker (SF1 flask shaker) were used. Glassware items used for the experiments were volumetric flask, pipette, weighing cylinder etc. and are all made up of SIMAX glass, Czech Republic obtained from the chemistry laboratory of Umaru Musa Yaradua University Katsina, Nigeria. All the glassware items were rinsed thoroughly with water several times (tap water), followed with distilled water and finally dried in hot air oven to remove any trace of moisture present. All reagents used during this research are of analytical grade and all solutions were prepared using distilled-water. All reagents used were of analytical grade purchased from Sigma Aldrich and were used as received without further purification. All solutions were prepared using laboratory-grade distilled water.

Preparation of Adsorbent from the Orange peels: The orange peels obtained from sale points were thoroughly washed to remove dirt and unwanted particles adhered to them. They were cut into small pieces making them easy to handle. The small pieces of peels were dried in hot air oven (GENLAB, MINO/100/F) at a temperature of 70°C for two hours and 25g of the well dried sample was then soaked into 1.0M aqueous hydrochloric acid solution at 1:5 ratio for chemical activation (Grigis and Ishak, 1999). The mixture was allowed for 24 hours before heating to form paste. The paste was placed in a furnace and carbonized at 350 °C for 1 hour in the absence of oxygen (or reduced to the lowest minimum). The sample was then withdrawn from the furnace at this point and the activated carbon formed was cooled, neutralized using sodium hydroxide and washed with distilled water to constant pH. The sample was then dried at 100 °C in an oven and later removed to cool down at room temperature. This was thus crushed with a pestle in a very clean mortar and the resultant powder was sieved through mesh sieve. Finally the activated carbon was stockpiled in air tight packets and labeled as OP.

Batch Adsorption Studies: A comprehensive aqueous batch adsorption studies for the Alizarin Red (AR) dye onto OP were conducted and the influence of different relevant parameters was investigated. To optimize the operational conditions, adsorptions of the AR onto the

surface of OP adsorbent were observed at predetermined initial conditions, whereby a fixed quantity of the OP was added to the AR solutions and the mixtures were agitated in a shaker at predetermined time intervals, the AR solution was separated from the adsorbent via centrifugation followed by filtration. The supernatant was taken and the amount of the dye adsorbed by the adsorbent was measured from the concentration change of AR in supernatant using UV/visible spectrophotometer at 430nm (Zhao *et al.*, 2010). The amount of AR adsorbed at equilibrium, q_e (mg g⁻¹) was calculated using the following equation:

$$q_e = \left(\frac{C_0 - C_e}{w} \right) V \quad (I)$$

Where C_0 (mg g⁻¹) is the initial concentration, C_e (mg g⁻¹) is the dye concentration at equilibrium, V (L) is the volume of the solution, and W (g) is the mass of the adsorbent (Namasivayam and Yamuna, 1995).

Adsorption Equilibrium Studies: Generally, the adsorption capacity of an adsorbent for a particular adsorbate in solution involves the interplay between three fundamental properties namely: the equilibrium concentration C_e , of the adsorbate in the liquid medium, the equilibrium concentration, q_e , of the adsorbate on the adsorbent surface and the temperature T , of the system. By keeping the temperature constant, then C_e and q_e can be plotted to represent the equilibrium. A plot of this nature is termed as an adsorption isotherm. An adsorption isotherm represents the equilibrium relationship between the concentration of the solute in the solution and the concentration adsorbed on the surface at constant temperature. This is particularly important in the design of effective adsorption systems. Furthermore, such adsorption isotherms may prove useful in scaling-up batch type processes with moderate success (Habib *et al.*, 2015).

In this work, Langmuir, Freundlich, Halsay, and Dubinin-Radushkevich isotherm models were employed to describe the relation between the amount of AR dye adsorbed on the OP and the residual amount that was left in the solution. For this, aqueous solutions of AR were prepared at the concentration range of 10 to 50 mgL⁻¹ and at room temperature. Each of the AR solution was individually agitated with 0.3g of OP at pH of 3.0 in a shaker for 110 min. The mixtures were then filtered, centrifuged and the amounts of AR were determined in the filtrates (Oliveira *et al.*, 2004).

RESULTS AND DISCUSSION

Characterizations of OP Adsorbent: The point of zero charge pH_{ZPC} , of an adsorbent is a very important

parameter that characterizes the pH at which the adsorbent surface has net electrical neutrality. The pH_{ZPC} for the OP was found to be 3.60, thus according to literature the adsorption of cations at neutral pK_a is favored at $pH > pH_{ZPC}$, while the adsorption of anions is favored at $pH < pH_{ZPC}$ (Janos *et al.*, 2003). Boehm titration method was used to calculate the number of oxygenated acid groups as well as that of the basic groups on the surface of the OP. The results of this titration showed that the number of acid groups (7.70) being larger than that of their basic counterparts (3.64), implying the surface as being predominantly acidic. Sear's analysis of the OP adsorbent gave the specific surface area value of $791.1\text{m}^2\text{g}^{-1}$ which is greater value than that reported by some researchers including Kamsonlian *et al* (2011). The low ash content (3.14%) found in the OP indicates that it has a significant fixed carbon and low inorganic contents whereas the scanning electron microgram of the OP as illustrated Plate 1 shows the adsorbent as having heterogeneous and irregular surface structure with significant number of cavities.

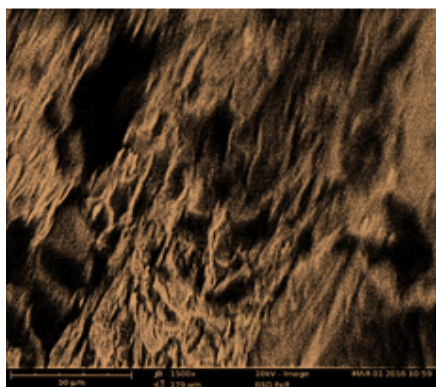


Plate 1: SEM Image of OP adsorbent (1500X)

ADSORPTION EQUILIBRIUM STUDIES

Langmuir Adsorption isotherm: The linear plot of $1/q_e$ versus $1/C_e$ was made as illustrated in Figure 1, and the values of q_m and K_L were obtained and presented in Table 1

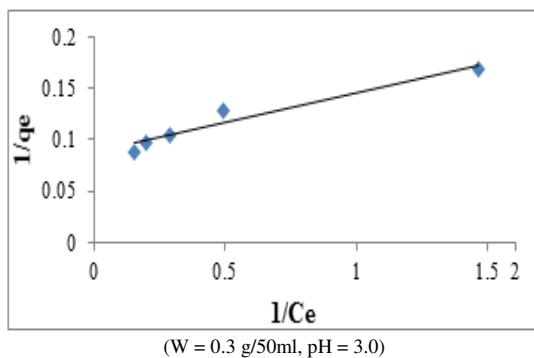
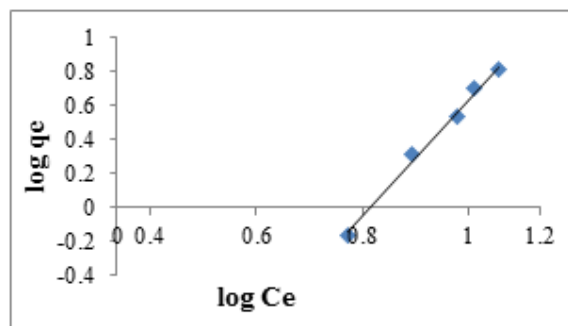


Fig. 1: Plot of Langmuir isotherm for AR adsorption on OP

The data presented in Table 1 shows the maximum monolayer coverage capacity (q_m) which was determined to be 11.5 mg/g while the Langmuir isotherm constant (K_L) is 1.526 L/mg . The linear regression coefficient R^2 of 0.944 indicates there is a good agreement between the experimental data and the linearized Langmuir isotherm model. The values of R_L (the dimensionless separation factor) were found to be 0.058, 0.003, 0.021, 0.016, and 0.013 for initial AR dye concentrations of 10, 20, 30, 40, and 50 mgL^{-1} , respectively indicating that the equilibrium adsorption of AR dye onto OP was favorable over all the concentrations range, since $0 < R_L < 1$ in each case (Vermeulan and Vermeulan, 1996).

Comparison shows that the q_m obtained is better than (8.97 mg g^{-1}) obtained by Khalid *et al.* for the adsorption of AR onto activated carbon (Khalid *et al.*, 2000).

Freundlich Adsorption isotherm: The Freundlich constants K_F and $1/n_F$ were calculated from the slope and intercept of the $\log q_e$ versus $\log C_e$ plot, as shown in Figure 2, and the model parameters are shown in Table 1. The magnitude of K_F showed that the OP had a good capacity for removing AR from the aqueous solution. A $1/n_F$ value being greater than unity indicates cooperative adsorption (Mohan and Karthikeyan, 1997). The values of R^2 for the Freundlich isotherm was found to be 0.993, which is even larger than that for Langmuir isotherm. This shows clearly that Freundlich model has well fitted the adsorption equilibrium data obtained for the adsorption of AR onto the OP adsorbent. This also an indication that adsorption AR onto OP follows heterogeneous coverage which has overlapping or multilayers (Qada *et al.*, 2008).

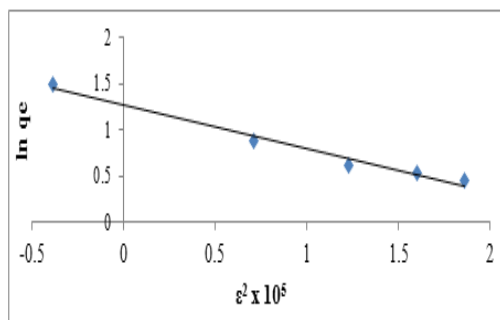


(W = 0.3 g/50ml, pH = 3.0)

Fig. 4: Plot of Freundlich isotherm for AR adsorption on OP

Dubinin-Radushkevich isotherm: The Dubinin – Radushkevich isotherm was used to estimate the characteristics porosity of the OP adsorbent and the apparent energy of adsorption, E_D . The plots of $\ln q_e$

against ϵ^2 yielded straight lines and indicates a good fit of the isotherm to the experimental data as shown in Figure 3.

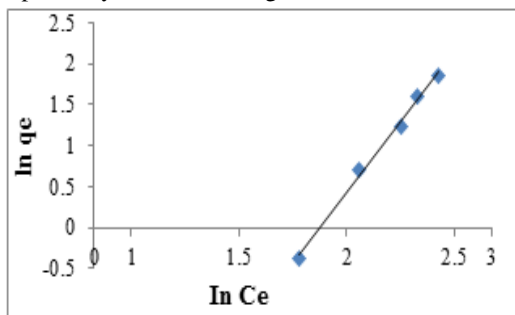


$$(W = 0.3 \text{ g/50ml, pH} = 3.0), \epsilon^2 = \left[RT \ln \left(1 + \frac{1}{C_e} \right) \right]^2$$

Fig. 3: Plot of D-R isotherm for AR adsorption on OP

The linear regression coefficient, R^2 as shown in Table 1 was found to be 0.980 and the values of B_D and Q_D were calculated from slope and the intercept are shown respectively. The estimated constant, E_D (0.156 kJmol^{-1}) being less than 8 kJmol^{-1} is an evidence that the process was physisorption in nature (Spiff *et al.*, 2004).

Halsay adsorption isotherm: The Halsay constants K_{Ha} and n_{Ha} were evaluated from the slope and the intercept of the linear plot of $\ln q_e$ versus $\ln C_e$, respectively as shown in Figure 4.



$$(W = 0.3 \text{ g/50ml, pH} = 3.0)$$

Fig. 4: Plot of Halsay isotherm for AR adsorption on OP

The related Halsay isotherm R^2 value was calculated and presented in Table 1. The high R^2 value of 0.993 and shows an excellent fit of the isotherm for the experimental adsorption data. This finding implies that the process obeys the Halsay isotherm model which simply means there is a multilayer coverage of the heteroporous OP adsorbent surface.

Table 1: Calculated adsorption equilibrium parameters for the adsorption of AR onto OP

| Adsorption Isotherm Model | Parameters | Value |
|-------------------------------|--|------------------------|
| Langmuir Isotherm | q_m (mgg ⁻¹) | 11.50 |
| | K_L (L/g) | 1.526 |
| | R^2 | 0.944 |
| Freundlich Isotherm | K_F (mg/g(mg/L) ^{n_F}) | 1.56×10^{-4} |
| | n_F | 3.44 |
| | R^2 | 0.993 |
| Dubinin-Radushkevich Isotherm | B_D (mol ² /kJ ²) | 2.080×10^{-5} |
| | Q_D (mol/g) | 14.17 |
| | E_D (kJmol ⁻¹) | 0.156 |
| | R^2 | 0.980 |
| Halsey Isotherm | K_{Ha} (mg/L) | 6.540 |
| | n_{Ha} | -0.291 |
| | R^2 | 0.993 |

Conclusion: Conclusively, the equilibrium data agreed with all the four isotherms models thereby showing a very good correlation with the experimental data. This further implies that adsorption of AR onto the OP adsorbent was a complex process; as such it can be well described using any of these four models. By exhibiting excellent adsorptive property towards AR dye, orange peels which are often regarded as waste materials can serve as good and substitute for commercial activated carbon with more economic advantage.

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