Kinetic and Isotherm study of Sudan Black B removal

Hamid Reza Moazzen, Mohammad Ali Moazzen, Ali Faghihi-Zarandi and Eghbal Sekhavati

1Department of Chemistry, Islamic Azad University, Firozabad Branch, Firozabad, Iran.
2Department of Chemistry, Islamic Azad University, Firozabad Branch, Firozabad, Iran.
3Department of Occupational Health, School of Public Health, Kerman University of Medical Sciences, Kerman, Iran.
4Larestan School of medical Sciences, Larestan, Iran

ABSTRACT

Cadmium hydroxide nano particle loaded on activated carbon (Cd(OH)2-NP-AC) efficiently used for the removal of Sudan Black B. In batch studies the optimum values of variable was set as: pH 1.0, 0.03 g Cd(OH)2-NP-AC at contact time of 30 etc. this adsorbent useful for removal of Sudan Black B for at least 20 mg of adsorbent. After optimization of variable, the experimental equilibrium data was analyzed by different conventional models such as Langmuir, Freundlich, Tempkin and Dubinin–Radushkevich and based on the adsorbent correlation coefficient and error analysis the suitability of Langmuir model for interpretation of equilibrium data with high adsorption capacity. The adsorption of Sudan Black B was endothermic and feasible in nature. The removal data versus time was analyzed by different kinetic models and it was found that low quantity of adsorbent (<0.03 g) is suitable for removal of large amount of Sudan Black B in short time (<30 min) the adsorption process following pseudo second order kinetics and involvement of particle diffusion mechanism.

INTRODUCTION

Generally, dyes applied in industries like textile, paints, pulp and paper, carpet and printing. There is growing interest and demands in textiles industry for application of synthetic organic dyes for coloring textile fibers such as cotton and polyester. These dyes and organic pollutant containing waste water lead to generation and creation of certain health hazards and environmental pollution. Dye effluents are aesthetic pollutants, while their colors via hinder light penetration in the receiving water bodies, disturb the biological processes. On the other hand, dye containing waste water may possess chemicals exhibit toxic effects toward microbial populations and can be toxic and/or carcinogenic to mammalian animal [1]. EPA imposed threshold limit on the concentrations of discharged pollutant arrived from aqueous effluents of dyestuff manufacturing and textile industries [2]. Sudan Black B (C26H24N4O) (Fig.1) is a nonfluorescent, relatively thermostable xanthene (fat-soluble dye) diazo dye used for staining of neutral triglycerides and lipids on frozen sections and some lipoproteins on paraffin sections and used for Sudan staining.

Fig. 1: structure of Sudan Black B.

Sudan Black B is applicable for staining all material in addition to liquid Sudan Black B used for fingerprint enhancement and recognition of fats contaminated with oil and grease. In differentiating hematological disorders Sudan black will stain myeloblasts but not lymphoblasts [3,4]. Among different branch of dyes such as
anionic, cationic, non-ionic and zwitterionic Cationic dyes are more toxic than anionic dyes [5,6]. Various and extensive procedure efficiency applied for dye removal and elimination the discharged effluents to decrease their ecosystem environment impact. These methods include adsorbtion onto inorganic or organic matrices, decolourization by photo-catalysis or photo-oxidation processes, microbiological decomposition, chemical oxidation, ozonation and coagulation [7]. Adsorption as widely used procedure generally lead to quantitative removal of dyes with lesser hazards. The biggest limitation for adsorption application the high cost of available adsorbents for commercial application. This limitation and disadvantage can be overcome using regenerable and high surface area atom to be able for quait inexpensive [8]. Adsorption is superior to all other dye removal techniques in view of efficiency, capacity and large scale applicability, regeneration and recycling potential of adsorbents. Some commercial and traditional systems are based on using activated carbon dyes wastewater [9-13]. However, the high cost of activated carbon and high removal times restricts its comprehensive and universal application. There is more focus on development and designing new adsorbents with high surface area and areas to be able for quantitative dye removal in short time with high adsorption capacity. These entire requirements will be benefited by decreasing and synthesis of nanomaterials and nanoparticles. In this paper, the adsorption of SBB from aqueous solutions onto Cd(OH)2-NP-AC adsorbent has reported. Equilibrium adsorption isotherms were measured and the experimental data were analyzed to commonly used models including Langmuir, Freundlich, Tempkin and Dubinin- Radushkevich Isotherm equations.

Experimental:

Instruments and Reagents:

Sudan Black B (SBB) (United States, Sigma-Aldrich) stock solution was prepared by dissolving require amount of their solid material in double distilled water. The test solutions daily were prepared by diluting their stock solution to the desired concentrations. The concentration of Sudan Black B (SBB) was determined at 596-605 nm respectively. The pH measurements were done using pH/Ion meter model-682 (Metrohm, Switzerland, swiss) and absorption studies were carried out using Jusco UV-Visible spectrophotometer model V-570.

Batch Adsorption Experiments:

Concentration of Sudan Black B (SBB) in was estimated accurately using the calibration curve obtained at the same condition concentrations. The dye adsorption capacities of adsorbent were determined at the time intervals in the range of 0-30 min at room temperatures (10–60 °C) after 30 min. The effect of initial pH on adsorbtion was examined 20 mg L\(^{-1}\) in the pH range of 1-6 (adjusted by the addition of HCl or KOH). The actual value of adsorbed dye to each step and finally equilibrium can be calculated based on well known following equation:

\[
q_e = \left( x_0 - C_e \right) \frac{V}{W}
\]

where \(C_i\) and \(C_e\) are the initial and equilibrium dye concentrations in solution, respectively (mg L\(^{-1}\)). \(V\) the volume of the solution (l) and \(W\) is the mass (g) of the adsorbent used.

Preparation of Cd(OH)\(_2\)-NP-AC:

The Cadmium hydroxide nanoparticles was loaded on activated carbon (Cd(OH)\(_2\)-NP) as follow: 100mL of 0.01 mol L\(^{-1}\) Cd(CH\(_3\)COO)\(_2\) solution was added to the 2 mol L\(^{-1}\) ammonia solution and the mixture was stirred until appearance of a white by 2 g was initially observed, which subsequently dissolved back into solution upon the further addition of the NH\(_3\) solution. The above solution was uniformly mixed with the activated carbon in ultrasonic bath and the mixture was maintained at pH of ca.12 at room temperature for 5 days. This phenomenon lead to resulting in the direct growth of the Cd(OH)\(_2\)-NP-AC in the solution. Following neutralization, the adsorbent was dried under air and used for further characterization.

RESULTS AND DISCUSSION

Characterization of the Cd(OH)\(_2\)-NP-AC:

The optical properties and ability of Cd(OH)\(_2\)-NP-AC for UV-Vis absorption (Fig.2) show distinct and distinguished peak.

The band gap of Cd(OH)\(_2\)-NP was calculated from plotting \((\alpha h\nu)^2\) vs \(\nu\) (Fig. 2) was found to be about 3.35 eV is larger than the direct band gap of bulk Cd(OH)\(_2\) that was 3.2 xV[14]. The Cd(OH)\(_2\)-NP-AC identity was recognized by powder XRD patterns (Fig. 3).

The five broad peaks observed in the diffractogram around 29.45°, 34.55°, 48.85°, 57.85° and 60.53° belong to the planes (100), (011), (012), (003) and (200) which show hexagonal structure of lattice structure of Cd(OH)\(_2\)-NW [15]. The match of obtained diffraction pattern with hexagonal Cd(OH)\(_2\) (JCPDF No. 73-0969) show the formation of Cd(OH)\(_2\)-NPs. Field emission scanning electron microscopy (FE-SEM) image of the Cd(OH)\(_2\)-NP-AC (Fig. 4) show formation of large quantity of Cd(OH)\(_2\) nanowires with micrometer lengths and diameters of 80 ±10 nm.
Fig. 3: X-ray diffraction (XRD) pattern of the Cd(OH)$_2$ nanowires.

Fig. 4: Typical FE-SEM image of the Cd(OH)$_2$ nanowires grown on a glass.

The SBB removal percentage on Cd(OH)$_2$-NP-AC was studied at different adsorbent amount in the range of 0.04 g at 20 mg/L SBB concentration, pH (1) and (25±1°C) at 30 min. As it is observed (Fig.5) by raising the amount of adsorbent till 0.6 g/L due to increase in the number of vacant site and diffusion (driving force of adsorption) the rate of SBB transfer to adsorbent surface significantly increase.

Fig. 5: Effect of amount of ( Cd(OH)$_2$ -NW-AC) on the removal of SBB.

Effect of Contact Time:

The effect of contact time on the removal percentage of SBB at 20 mg/L at various stirring time in the range of 0-30 min investigated. The available adsorption results reveal show that initial fast sorption rate becomes slower at higher time and reach to equilibrium at 30 min (Fig. 6).

At initial step of removal process due to huge number of vacant site the diffusion driving force of transport lead to increase in the mass transfer. Therefore, it is much easier for the adsorbate to reach the adsorption site and after a lapse of time, the number of active sites becomes less and the adsorbent becomes crowded inside the particles [16, 17]. For the initial concentrations of 20 mg/L, the equilibrium was achieved within 30 min, respectively [18].
Effect of Ph:
The pH of the solution affects the surface charge of the adsorbents as well as the degree of ionization of the materials present in the solution. The hydrogen ion and hydroxyl ions are adsorbed quite strongly. Therefore, the dye as ionic species adsorption of other ions is affected by the pH of the solution. The change of pH affects the adsorptive process via influencing the dissociation of functional groups and the active sites of adsorbent, which leads to shift in reaction kinetics and equilibrium characteristics of the absorption process (Fig. 7).

Effect of initial SBB concentration:
Concentrations ranging from 10-20 mg/L of SBB were investigated with fixed amounts of adsorbent at room temperatures. The SBB extent of adsorption increases with rising its initial concentration, so that by increase in concentration of the adsorbate exhibits a prominent increase in its. Maximum and quantitative removal percentage of dye molecule occurs up to initial concentration of 20mg/L at the same conditions that may be attributed to the saturation of all vacant site of adsorbent.

Effect of ionic strength:
For almost all the treatment strategies, the effect of typical wastewater contaminants on decolorization efficiencies is very important [21]. Generally, presence certain additives and ionic strength adjuster such as soluble salts can either accelerate or retard dye adsorption processes. Usually sodium chloride used as stimulator in dyeing processes by affecting the electrostatic interaction of opposite charges in adsorbents and the dye molecules, and an increase higher salt concentration lead to reducing the amount removal percentage on the other hand, salts via increasing the fraction of dissociation of the dye molecules facilitate their removal percent. The attraction interaction is responsible for adsorption of acid dyes by such adsorbents. So, the ionic strength may be another important factor in the adsorption of certain dyes onto chitosan [22-26]. The influence of ionic strength at various concentration of NaCl investigate by conducting a set of similar and it was found that by increasing the sodium chloride concentration till 0.25 mol/L removal percentage increase.

Kinetic parameters of adsorption:
The kinetic parameters (helpful for determination of the rate controlling and mass transfer step) give important information for selection application of on efficient low cost with high adsorption capacity adsorbent. To uptake some information the influence of contact time on the adsorption process was investigated and the
time dependency removal data was fitted by different conventional models such as pseudo-first-order, pseudo-second-order [15], Elovich [16] and intraparticle diffusion [17] models. The judgment for examination of model suitability is based on agreement between experimental and the model-predicted adsorption capacity values and the correlation coefficients (R², values close or equal to 1 and the relatively higher value shows the applicability of the model).

Pseudo-first-order equation The adsorption kinetic data were described by the Lagergren pseudo-first-order model [27] is commonly expresses in linear form as follows:

$$\log (q_e - q_t) = \log (q_e) - k_1 t / 2.303$$  \hspace{1cm} (2)

Generally by Plotting the log ($q_e - q_i$) versus t (linear relationship) $k_1$ and $q_e$ can be evaluated from the slope and intercept of the respective line respectively. If the intercept is not close to $q_e$ means then the reaction is not likely to be first-order reaction even the obtained line and plot has high correlation coefficient [28,29]. However, this model is applicable for fitting and interpretation of adsorption data and phenomena at initial stages (rapid adsorption) but cannot be applied for the entire adsorption process. Additionally, the calculated $q_e$ value significantly for from experimental $q_e$ values (Table 1) which indicates unsuitability of first-order reaction for fixing experimental data.

Pseudo-second-order equation Due to insufficiently of first order kinetic model for explanation of adsorption over whole data it is necessary that experimental data be fitted by Pseudo-second-order model [30] that in linear expresses as follows:

$$t/q_t = 1/ (k_2 q_e) + t/q_e$$  \hspace{1cm} (3)

It was seen that the plots of $t/q_t$ versus t give a straight line that show its suitability and applicability for fitting and interpretation of experimental data. The $k_2$ and equilibrium adsorption capacity ($q_e$) values was evaluated from the intercept and slope of this line and respective value is presented in Table 1. The values of R² and close of experimental and theoretical $q_e$ indicate applicability of this model in comparison to other models for explanation of adsorption process.

Table 1: The Elovich constants obtained from the slope and the intercept of the straight line.

<table>
<thead>
<tr>
<th>Model</th>
<th>Equation</th>
<th>Plot parameters</th>
<th>C-BOHID, NW. a C</th>
</tr>
</thead>
<tbody>
<tr>
<td>First-Order Kinetic</td>
<td>$q_t = q_e (1-e^{-k_1 t})$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\log (q_e - q_t) = \log (q_e) - k_1 t / 2.303$</td>
<td>$k_1$</td>
<td>0.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$q_e$ (calc.)</td>
<td>14.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R²</td>
<td>0.827</td>
</tr>
<tr>
<td>Second-Order Kinetic</td>
<td>$t/q_t = 1/(k_2 q_e) + t/q_e$</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$k_2$</td>
<td>38.07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$q_e$ (calc.)</td>
<td>32.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R²</td>
<td>0.993</td>
</tr>
<tr>
<td>Intraparticle Diffusion</td>
<td>$q_t = K_d t^{1/2} + C$</td>
<td>$K_{int}$</td>
<td>2.079</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C</td>
<td>16.62</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R²</td>
<td>0.818</td>
</tr>
<tr>
<td>Elovich</td>
<td>$q_t = 1/\beta \ln (a \beta) + 1/\beta \ln (t)$</td>
<td>$\beta$</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td>a</td>
<td>81.24</td>
</tr>
<tr>
<td></td>
<td></td>
<td>R²</td>
<td>0.911</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30.784</td>
</tr>
</tbody>
</table>

**Elovich kinetic equation:**

The Elovich equation [30] as another rate equation based on the adsorption capacity in linear form is as follows:

$$q_t = 1/\beta \ln (a \beta) + 1/\beta \ln (t)$$  \hspace{1cm} (4)

Plot of $q_t$ versus ln(t) should yield a linear relationship if the Elovich is applicable with a slope of $1/\beta$ and an intercept of $1/\beta \ln (a \beta)$. The Elovich constants obtained from the slope and the intercept of the straight line reported in Table 1. The correlation coefficients R² are higher than 0.911 show suitability of model for evaluation of adsorption process.
The intraparticle diffusion model:

Generally, most of adsorption process follows intraparticle diffusion [31] other kinetic model in addition to study the rate-limiting step for SBB adsorption onto Cd(OH)2-NW-AC. This model is based on well known following equation:

$$q_t = K_{diff} t^{1/2} + C$$  \hfill (5)

The values of $K_{diff}$ and $C$ (Table 1) were calculated from the slope and intercept of the plot of $q_t$ versus $t^{1/2}$. $C$ value is related to the thickness of the boundary layer and $K_{diff}$ is the intraparticle Diffusion rate constant (1/2 mg/g min). These models give two lines and rate constant ($K_{diff}$) directly evaluated from the slope of the second regression line, while the first one represent surface adsorption (start of adsorption) and the second show intraparticle diffusion.

Adsorption equilibrium study:

The experimental adsorption equilibrium data provides some insight into the adsorption mechanism, the surface properties and affinity of the adsorbent for adsorbate [32-34]. A constant agitation speed of 350 rpm, 0.03g of adsorbent at room temperature (25°C) was maintained for adsorption experiments. Equilibrium data was fitted by Langmuir, Freundlich and Tempkin isotherms Langmuir equation [34] is represented in the linear form as:

$$\frac{C_e}{q_e} = \frac{1}{kQ_m} + \frac{C}{Q_m}$$  \hfill (6)

The value of $Q_m$, $k_1$ and the correlation coefficient for this model calculated from the slope and intercept of line obtained by plotting $C/q$ vs. $C$ and their values are presented in Table 2. The high correlation coefficients of this model show its applicability for interpretation of experimental equilibrium data. It seems that SBB first layer adsorb on the surface of adsorbent via attraction force and further layer of adsorbent molecule is impossible due to electrostatic repulsive force. The linear form of Freundlich isotherm is expressed as [35]:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e$$  \hfill (7)

The values of $K$ and $1/n$ is determined from the intercept and slope of linear plot of $\log q$ versus $\log C_e$, respectively. The value of $n$ varies with the heterogeneity of adsorbent for favorable adsorption process the value of $n$ should be less than 10 and higher than unity [36]. The linear form of Tempkin isotherm [37, 38] is presented as follows:

$$q_e = B_1 \ln K_T + B_1 \ln C_e$$

Where $B_1 = R T/b$, $T$ is the absolute temperature in Kelvin, $R$ the universal gas Constant (8.314 J K$^{-1}$ mol$^{-1}$). Values of $B_1$ and $K_T$ were calculated from the Plot of $q_e$ against $C_e$ (Table 2).

Fitting the experimental data in three isotherm models and considering the higher values of correlation coefficients ($R^2 > 0.99$) show that Langmuir isotherm model is the best model to explain the SBB adsorption over Cd(OH)2-NW-AC.

Table 2: Values of $B_1$ and $K_T$ were calculated from the Plot of $q_e$ against $C_e$.

<table>
<thead>
<tr>
<th>Isotherm</th>
<th>Equation</th>
<th>Plot</th>
<th>parameters</th>
<th>$C_d$ (mg/g)</th>
<th>$K_F$ (L/mg)</th>
<th>$q_e$ (mg/g)</th>
<th>$K_T$ (L/mg)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Langmuir</td>
<td>$C_e/q_e = 1/(kQ_m)$ + $C_q/Q_m$</td>
<td>A plot shows a straight line of $1/Q_m$ and an intercept of $1/(kQ_m)$.</td>
<td>$q_e$</td>
<td>66.67</td>
<td>0.34</td>
<td>0.995</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Freundlich</td>
<td>$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e$</td>
<td>The values of $K_f$ and $1/n$ were obtained from the slope and intercept of linear plot of $\log q$ versus $\log C_e$, respectively.</td>
<td>$R^2$</td>
<td>0.504</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tempkin</td>
<td>$q_e = B_1 \ln K_T + B_1 \ln C_e$</td>
<td>values of $B_1$ and $K_T$ were calculated from the plot of $q_e$ against $C_e$.</td>
<td>$R^2$</td>
<td>15.19</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Subba and</td>
<td>$\ln q_e = \ln K_c + e^{1/k_c}$</td>
<td>The slope of the plot of $\ln q_e$ versus $C$ gives $K_c$ (mol$^{-1}$). The intercept yields the adsorption capacity, $Q_e$ (mg g$^{-1}$).</td>
<td>$R^2$</td>
<td>43.64</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Guatekuvic</td>
<td>$K_T = (1/2RT) \ln (1 + 1/C_e)$</td>
<td></td>
<td></td>
<td>31-7</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$K_T = (1/2RT) \ln (1 + 1/C_e)$
Conclusions:
An adsorption experiment of SBB under different experimental conditions in bath mode has been conducted and the influence of variables such as amount of adsorbent, SBB concentration, contact time and pH of the solution on its removal percentage has been investigated. Higher dye removal was found within 30 min of the start of every experiment that under the optimum experimental pH of 1–6. The proposed adsorption system has The removal process follow Langmuir model with maximum adsorption capacity of 66.67 mg/g.

The rate of SBB from bulk to the adsorbent surface follow pseudo second order kinetic model with involvement of inter particle diffusion model.
1) Using small amount of Cd (OH)2 -NW-AC, the high amount (0.03 g) and removal percentage (higher of 95%) SBB significantly can be removal in short time (30 min).

REFERENCES
[22] Chiou, M.S., H.Y. Li. 2003. Adsorption behavior of reactive dye in aqueous solution on chemical cross-
linked chitosan beads, Chemosphere, 50: 1095-105.


