Thermodynamics and Kinetics of Adsorption of Alizarin Yellow from Aqueous Solutions on Saccharum spontaneum

A. Lakshmi Narayanan, Dr. M. Dhamodaran, Dr. J. Samu Solomon

Abstract—Saccharum spontaneum is used for the removal of the industrial dye (alizarin yellow R) from aqueous solution. The effects of contact time, temperatures, initial concentrations and pH values have been investigated. Langmuir and Freundlich isotherms are fitted on the experimental data of adsorption of the studied system. Depending on the results obtained from the effect of temperatures, the thermodynamic parameters (ΔG°, ΔH° and ΔS°) are estimated. The work also included kinetic study conducted by applying two kinetic models, the pseudo first and second order equations. The results proved that, the studied system follows the pseudo second order model indicated by the agreement between the experimental and calculated values of adsorption capacity (qe) at equilibrium. The concentration of the adsorbed dye is determined spectrophotometrically.

Index Terms—Saccharum spontaneum, alizarin yellow R, Langmuir and Freundlich isotherms, ΔG°, ΔH° and ΔS°, adsorption, etc...

I. INTRODUCTION

Dyes are widely used in textile, paper, plastic, food and cosmetic industries. The discharge of the excess of dyes into the environment with the wastewater of such industries represents a great reason of pollution in which its treatment becomes a vital task. The level of pollution by such dyes even it was in a very low concentration is highly visible and will affect aquatic life as well as food web. The color compounds are not only aesthetically displeasing but also inhibiting sunlight penetration into the stream and affecting aquatic ecosystem. Dyes usually have complex aromatic molecular structures which make them more stable and difficult to biodegrade, furthermore many dyes are toxic to some micro organisms and may cause direct destruction or inhibition of their catalytic capabilities. There are various conventional methods of removing dyes including coagulation, flocculation, ion exchange oxidation or ozonation and membrane separation. These methods are not widely used due to their high cost and economic disadvantage. Chemical and electro chemical oxidations, coagulation are generally not feasible on large scale industries. In contrast adsorption technique is by far the most versatile and widely used. The most common know adsorbent materials are: alumina, silica, metal hydroxides and activated carbon as proved by many researchers. Removal of dyes by activated carbon and mineral clay is economically favorable and technically easier.

In this study, the adsorption of alizarin yellow R from aqueous solution on the surface of carbonised Saccharum spontaneum as a natural adsorbent is investigated. It grows as wasteland weed. It is considered as valuable medicinal herb in traditional systems of medicine in India. It is popular folk medicine. According to Ayurveda, roots are sweet, astringent, emollient, refrigerant, diuretic, lithotriptic, purgative, tonic, aphrodisiac and useful in treatment of dyspepsia, burning sensation, piles, sexual weakness, gynaecological troubles, respiratory troubles etc. Alizarin yellow is a mordant dye, suitable for the dyeing of wool and nylon. It usually exists as a sodium salt. In its pure form, it is a rust-colour solid. Its molecular formula is C 13 H 8 N 3 NaO5 (Na salt), its molecular mass is 309.21 g mol⁻¹ and its λ max is 370 nm. It is a slightly brown powder soluble in cold water. It causes irritation in the eyes, skin, digestive tract, and respiratory tract.

Saccharum spontaneum

Alizarin yellow R
II. EXPERIMENTAL WORK

A. Instrumentation
The pH was adjusted with a digital pH meter (Jenway Model 3320) using HCl (0.1 mol L⁻¹) and NaOH (0.1 mol L⁻¹). Alizarin yellow was estimated with a UV/VIS spectrophotometer (Labomed UVD 3500) at λmax 370 nm.

B. Preparation of adsorbent
Stems of Saccharum spontaneum, collected from the karaikal coastal area, was crushed with laboratory-scale crushers, powdered with a disk pulveriser, and sieved to 0-63 mesh (ASTM). The powdered adsorbent was washed, dried at 105 °C for 10 h in an oven, and stored in high-density polythene (HDPE) bags. The proximate analysis of the coal was carried out by using standard methods (ASTM D 5142-90). Powdered adsorbent was soaked in HCl (0.1 mol L⁻¹) for 24 h, followed by filtering and washings with distilled water. Afterwards, it was dried in an oven at 105 °C for 10 h and stored in HDPE bags.

C. Chemicals
All chemicals used during experimental work were of analytical grade and were used as such without purification. Alizarin yellow (Fluka), HCl (E.Merck 11.6 M), Double distilled water was used for the preparation of all types of solution and dilution when required.

D. Instrumentation
Balance ER-120A (AND), Electric grinder (Kenwood), pH meter HANNA pH 211 (with glass electrode), UV/VIS spectrophotometer (Labomed, Inc. Spectro UV-Vis double beam UVD =3500).

E. Standard Solutions
1.0 g of Alizarin yellow was taken in 1000 mL measuring flask and dissolved in double distilled water, making volume up to the mark. This was 1000 ppm stock solution of dye. Standard solutions of dye were prepared by successive dilution of stock solution.

F. Adsorption Experiments
The adsorption studies were carried out at 30 ± 1 °C. pH of the solution was adjusted with 0.1 N HCL. A known amount of adsorbent was added to sample and allowed sufficient time for adsorption equilibrium. Then the mixture were filtered and the remaining dye concentration were determined in the filtrate using (Spectro UV-Vis Double Beam UVD-3500, Labomed.Inco) at λmax = 370 nm. The effect of various parameters on the rate of adsorption process were observed by varying mesh size of adsorbent contact time, t , initial concentration of dye Co, adsorbent amount, initial pH of solution and temperature. The solution volume (V) was kept constant 50 mL. The dye adsorption (%) at any instant of time was determined by the following equation:

Dye adsorption (%) = (Co –Ce) × 100/ Co

Where Co is the initial concentration and Ce is the concentration of the dye at equilibrium. To increase the accuracy of the data, each experiment was repeated three times and average values were used to draw the graphs.

G. Isotherm studies
A series of experiments were carried out for isothermal and kinetic study of Saccharum spontaneum adsorption of alizarin yellow dye. Langmuir (eq :1), Freundlich (eq :2), Redlich-peterson(eq :3) and Dubinin-Kaganer-Radushkevich (DKR) (eq :4) were plotted by using standard straight-line equations and corresponding parameters were calculated from their respective graphs.

\[
\frac{Ce}{K} = \frac{1}{K_{L} + Ce} \quad (1)
\]

\[
\log qe = \log K_{F} + \frac{1}{n} \log Ce \quad (2)
\]

\[
qe = \frac{K_{R} Ce}{(1+bRCe)} \quad (3)
\]

\[
\log qe = \log Xm – \beta \varepsilon^{2} / 2.303 \quad (4)
\]

Ce is the equilibrium concentration of the adsorbate (mg/L) and X is the amount of adsorbate adsorbed (mg/g). KL indicates monolayer adsorption capacity (mg/g). KF is the Langmuir equation constant(L/mg). Kp and 1/n are constants for a given adsorbate and adsorbent at a particular temperature and bT (KJ/mol) is adsorption potential of the adsorbent. KF, b, β are Redlich Peterson constants. Xm is maximum sorption acacity; β is mean sorption energy and ε is sorption potential in DKR isotherms.

III. RESULTS AND DISCUSSION

Adsorption of Alizarin Yellow R dye on Saccharum spontaneum was studied through batch mode, making use of different variables like adsorbent dosage, pH of the medium, contact time, initial concentration of Alizarin Yellow R dye and temperature. The size of adsorbent particles were maintained constant at below 63µm. Experiments were carried out so that the effect of any one variable was studied, keeping all others constant. This was repeated with all the other variables.

A. Effect of particle Size
The effect of adsorbent’s particle size was studied in the range of 0-200 microns mesh particle (0-63, 63-125, 125-200) for checking the maximum adsorption of Alizarin Yellow R and the smallest mesh particle (0-63) was shown to be best for adsorption, as particles with smallest size presents a larger surface area and the results are shown in Fig. 1.

B. Effect of adsorbent dosage
The adsorbent dosage is an important parameter, which influences the extent of dye uptake from the solution and thus the effect as shown in Fig. 2. It was evident that the amount of dye uptake increases from 72.11 % with 50mg adsorbent up to 98.69% with 200mg adsorbent. Prior to that, it is apparent that the percent removal of Alizarin Yellow R dye increases as the adsorbent dosage increases from 50mg up to 200mg due to the limited
availability of the number of adsorbing species for a relatively larger number of surface sites on the adsorbent at higher dosage of adsorbent. It is plausible that with higher dosage of adsorbent there would be greater availability of exchangeable sites from dye. Besides, Fourest and Roux suggested that the reduction in adsorbent dosage in the suspension at a given dye concentration enhances the dye/adsorbent ratio, and thus increases the dye uptake per unit adsorbent, as long as the latter is not saturated. However, in some cases, the adsorption capacity decreased sharply with the increasing of adsorbent dosage these results may due to the overlapping of the adsorption sites as a result of overcrowding of adsorbent particles. Moreover, the high adsorbent dosage could impose a screening effect of the dense outer layer of the cells, thereby shielding the binding sites from dye. The effect of the mass of the adsorbent in the adsorption of Alizarin Yellow R dye was studied at the optimum pH 1.0 and at room temperature (30°C). 50 ml of a solution of Alizarin Yellow R dye with an initial concentration of 50 mg/L was mixed with 50.0 mg of the adsorbent and the mixture was shaken for 180 minutes. After centrifugation, the amount of Alizarin Yellow R dye in the supernatant was estimated quantitatively. From this the percentage of dye adsorbed on the adsorbent was deduced. This procedure was repeated with 100, 150, 200 and 250 mg of the adsorbent and the results are recorded in figure 2. With the adsorbent dosage of 200 mg or more, adsorption reached the maximum. Hence adsorbent dosage was fixed at an optimum amount of 150 mg.

C. Effect of pH

The acidity of solution pH is one of the most important parameters controlling the uptake of dyes from wastewater and aqueous solutions. The uptake and percentage removal of dye from the aqueous solution are strongly affected by the pH of the solution as illustrated in Fig. 3. The uptake of dye decreases from 99.66 % to 28.13% when the pH increases from pH 1 to pH 6 , sorption is noted to decrease significantly 99.66% adsorption capacity at pH 1. After that the capacity of adsorption decreases deeply in pH range of 7 to 9. The maximum adsorption observed at low pH (pH 1) may be due to the fact that the higher concentration and higher mobility of H^+ ions present favoured the preferential adsorption of Alizarin Yellow R dye compared to hydrogen ions. It would be plausible to suggest that at lower pH value, the surface of the adsorbent is surrounded by hydronium ions (H^+), thereby replacing by the dye from the binding sites of the sorbent. In contrast, as the pH decreases, more negatively charged surface becomes available thus facilitating greater dye removal. It is commonly agreed that the sorption of dye cations decreases with increasing pH (Fig 3) as the dye species become high stable in the solution. However, at higher pH values (pH 7, pH 8 and pH 9) there is a decrease in the adsorption capacity. This is due to the occurrence of dye precipitation.

D. Effect of contact time

Figure 4 reveals that the curve is smooth and continuous, alizarin Yellow R dye to saturation, suggesting possible monolayer coverage of the dye on Saccharum spontaneum. Nearly 60.54% adsorption has taken place within 30 minutes of contact time with the adsorbent which indicates the efficiency of Saccharum spontaneum as adsorbent. More time is required for attainment of equilibrium. In this study, all the batch experiments were carried out for a time interval of 180 minutes.

E. Effect of initial concentration

Figure 5 show that adsorption capacity decreases from 95.56% to 61.91% as the dye concentration increases from 10 to 60 mg/L. The trend is that of the result of the progressive decrease in the electrostatic interaction between the Alizarin Yellow R dye and the absorbent active sites. Moreover, this can be explained by the fact that less adsorption sites were being covered as the dye concentration decreases. Besides, lower initial concentrations to an increase in the affinity of the Alizarin Yellow R dye towards the active sites. The decline in the adsorption capacity is due to the availability of smaller number of surface sites on the adsorbent for a relatively larger number of adsorbing species at lower concentrations. The experimental results of adsorption of Alizarin Yellow R dye on Saccharum spontaneum at various initial concentrations are shown in figure 5. It reveals that, the actual amount of dye adsorbed per unit mass of Saccharum spontaneum decreased with increase in dye concentration. Adsorption is maximum when the initial concentration of Alizarin Yellow R dyes were 10 mg/L. As the concentration increases, all the adsorption sites are being filled up and there remains unadsorbed dye, hence the decrease in percentage adsorption. This result is in favour of only monolayer coverage and suggests the application of the Langmuir isotherm model. Since 96.02% adsorption occurs when the initial concentration was 10 mg/L, Saccharum spontaneum appears to be very effective adsorbent in removing even traces of dye.
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**Adsorption isotherms**

Isotherm parameters, evaluated from the linear plots of equations (1–4) are illustrated in Table 1. (Fig. 6a and 6.b). The $K_L$ (sorption equilibrium constant) value for the Langmuir isotherm, ie. 3.424 mg/g indicated the high adsorption capacity of biosorbent toward dye adsorption. This is in turn supported by the values of the dimensionless separation factor ($R_L$), which are less than 1. The $R^2$ (correlation coefficient) value 0.935 indicated that the Langmuir isotherm is good for explaining the dye adsorption. The $R^2$ value calculated for the Freundlich isotherm was found to be 0.924, indicating that the experimental data can be explained by the Freundlich isotherm. The $K_F$ (ultimate adsorption capacity) value as calculated from the Freundlich isotherm was 3.0338 mg/g. The values of Freundlich constant, $n$, are much greater than 1, implying that the adsorption process is governed by physisorption only. The $R^2$ value calculated for the Redlich-peterson isotherm was found to be 0.947, indicating that the experimental data can be explained by the Redlich-peterson isotherm. The $β$ value as calculated from this isotherm was 0.670. The Dubinin–Kaganer–Radushkevich (DKR) model was adopted to describe the single-solute adsorption isotherms. The $R^2$ value calculated for the DKR isotherm was found to be 0.999, indicating that the experimental data can be explained by the DKR isotherm poorly. The $β$ value as calculated from this isotherm was 0.347. The values of desorption constant, $β$, in the Redlich-Peterson and the Dubinin-Kaganer-Radushkevich isotherms is a measure of the desorption constant. Its values are less than 1, indicating favourable adsorption. The sorption energy $ε$ in the DKR isotherm is a valuable parameter to distinguish between physisorption and chemisorptions. Lower values suggest physisorption is more.

<table>
<thead>
<tr>
<th>$K_L$</th>
<th>$q_0$</th>
<th>$b_L$</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.424658</td>
<td>13.33333</td>
<td>0.256849</td>
<td>0.935</td>
</tr>
<tr>
<td>N</td>
<td>R²</td>
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</tr>
<tr>
<td>3.033891</td>
<td>9.090909</td>
<td>0.924</td>
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</tr>
<tr>
<td>$β$</td>
<td>$B$</td>
<td>$q_0$</td>
<td>$R^2$</td>
</tr>
<tr>
<td>0.670173</td>
<td>0.324</td>
<td>2.108628</td>
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<td>$β$</td>
<td>$b_R$</td>
<td>$K_R$</td>
<td>$R^2$</td>
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<td>0.347</td>
<td>2.881844</td>
<td>0.657061</td>
<td>0.999</td>
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</table>

**Fig. 4**

F. Kinetics

Kinetics of adsorption is a characteristic responsible for the efficiency of adsorption. Since the initial sorption rate plays a crucial role, adsorption was measured at time intervals 10, 20, 30, 40, 50 and 60 minutes. The kinetics of adsorption of Alizarin Yellow R dye on Saccharum spontaneum was followed by the use of four models: Lagergren’s pseudo-first order kinetics

![Fig. 5](image)

**Fig. 5**

![Fig. 6a](image)

**Table 1**

![Fig. 6b](image)

**Fig. 6b**
Pseudo-second order kinetics.
The Elovich kinetics
The intra-particle diffusion model.
The kinetics parameters are given in table 2(Fig. 7).
Analysis of the kinetics parameters shows that there is no
 correlation between theoretical and experimental qe values
for the Lagergren’s first order kinetics and hence the
 adsorption process is not likely to be of the first order. The
 $R^2$ values for the second order(eq 5) kinetics shows high
 precision suggesting that second order kinetics is a best fit.

$$\log (qe-qt) = \log qe - (K1t / 2.303)$$

<table>
<thead>
<tr>
<th>I Order</th>
<th>K1</th>
<th>Qe</th>
<th>$R^2$</th>
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</thead>
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<tr>
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<td>0.006909</td>
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<tr>
<td>II Order</td>
<td>qe</td>
<td>K2</td>
<td>$R^2$</td>
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<td></td>
<td>3.184713</td>
<td>0.01267</td>
<td>0.976</td>
</tr>
<tr>
<td>Int part</td>
<td>Kp</td>
<td>C</td>
<td>$R^2$</td>
</tr>
<tr>
<td>diff</td>
<td>0.10900</td>
<td>1.3800</td>
<td>0.905</td>
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<tr>
<td>Elovich</td>
<td>$\beta$=0.472</td>
<td>$\alpha$=0.3340</td>
<td>$R^2$=0.860</td>
</tr>
</tbody>
</table>

Table 2

$\Delta G_0 = -RT\ln K$  \hspace{1cm} 6

$\ln K_c = (\Delta S_0/R) - (\Delta H_0/RT)$  \hspace{1cm} 7

Here, $K$ denotes the distribution coefficient for the
adsorption. $R$ is the universal constant and $T$ is the absolute
temperature in Kelvin. The negative value of $\Delta G_0$ at the
studied temperature range indicated that the sorption of
alizarin yellow on sorbent was thermodynamically feasible
and spontaneous. The increase in the value of $\Delta G_0$ with
temperature further showed the increase in feasibility of
sorption at the elevated temperature for Saccharum spontaneum.
In other words, sorption is endothermic in nature.
The positive value of $\Delta H_0$ for Saccharum spontaneum
showed that the sorption was endothermic. The positive value of
$\Delta S_0$ showed an increased randomness at the solid alizarin
yellow solution interface during the adsorption of alizarin
yellow, reflecting the affinity of Saccharum spontaneum for
alizarin yellow.

Activation energies for adsorption of alizarin yellow on
adsorbent was calculated using the Arrhenius equation (eq
8),plotted in Fig 8 and tabulated in table 4.The activation
energy obtained(Table 4) in this case indicate that physical
forces are involved in the sorption mechanism and sorption
feasibility.

Arrhenius equation
$$\log K = \log A - (EA / 2.303 RT)$$

<table>
<thead>
<tr>
<th>$\Delta G_0$</th>
<th>$\Delta H_0$</th>
<th>$\Delta S_0$</th>
<th>Log 10 $K_a$</th>
<th>1/T</th>
</tr>
</thead>
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<td>22.785</td>
<td>64.14293</td>
<td>0.243038</td>
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</tr>
<tr>
<td>-1771.97</td>
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<td>0.29582</td>
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<td>-2094.4</td>
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<td>0.338555</td>
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<td>-2441.77</td>
<td></td>
<td></td>
<td>0.382859</td>
<td>0.003002</td>
</tr>
</tbody>
</table>

Table 4

The thermodynamic parameters for the adsorption of
Alizarin Yellow R dye on Saccharum spontaneum are given
in table 4. For the adsorption of dye on Saccharum spontaneum,
the free energy values are all negative confirming that the process is spontaneous even at room
temperature. The entropy change is positive and explains the
increase in randomness of the process. The endothermic
nature of the adsorption process is evident from the positive
values of enthalpy change. Presumably, the randomness
factor ($T\Delta S$) overcomes the energy factor ($\Delta H$) and makes the
overall process spontaneous ($\Delta G$ negative). Activation
energies for adsorption of Alizarin Yellow R dye on
adsorbent was calculated using the Arrhenius equation (eq
6-8), plotted in Fig 8 and tabulated in table 8b.The activation
energy obtained in this case, indicate that physical forces are
involved in the sorption mechanism and sorption feasibility.
Temperature has an important effect on the rate of adsorption. The percentage of dye adsorption was studied as a function of temperature in the range of 30-60 °C. It was observed that adsorption yield increase with increase in temperature. The minimum adsorption was 84% at 30 °C and maximum adsorption was 87.87% at 60 °C for 50 ppm initial concentration of dye solution.

K. FT-IR Study

The action of oxidizing Oxygen on the surface of the carbonaceous precursor causes formation of surface oxides. Their structure have not been investigated completely because of the greater number of possible surface groups. The most common Oxygen groups on the surface are carboxylic, lactonic and phenolic. These groups have acidic character, which can be relatively easily determined by titration methods that are based on titrations using bases of different strengths. The method of Boehm has been followed to find the density of functional groups present on the carbon surface. FT-IR (SHIMADZU) spectra of the activated carbon samples before and after adsorptions are shown in figures (10a &10b) respectively. The spectra provide the evidences for the presence of surface groups on the adsorbent’s surface as established by Boehm. Notable differences among them are the peak intensities. The carbons have marked differences in the intensities of nearly all the absorption bands, reflecting that the density of corresponding functional groups differ a lot. After adsorption some peaks is vanished due to desorption in to adsorbate and few peaks are slightly shifted to higher or lower wave numbers due to electrostatic forces. There are no new peaks after adsorption confirmed the absence of formation of new compounds shown.

L. SEM analysis

The surface morphology of Saccharum spontaneum was examined using Scanning Electron Microscopy (SEM), before and after adsorption and the corresponding SEM micrographs were obtained at an accelerating voltage of 15 kV (Hitachi SE 900) at 5000× magnification and are presented in figures 11a and 11b. At such magnification, theSaccharum spontaneum particles showed rough areas of surface within which micropores were clearly identifiable.
The study indicates that activated carbon prepared from *Saccharum spontaneum* could be used as an effective adsorbent material for the treatment of alizarin yellow dye in aqueous solution. The adsorption of alizarin yellow dye on activated carbon is found to be pH, initial concentration and dose dependent. The optimum conditions of alizarin yellow dye uptake obtained from this study are: pH 1.0, initial concentration 10 mg/L and biomass loading of 150mg. In addition, the correlation of Langmuir adsorption isotherm fits the experimental data most accurately. It was determined that the maximum adsorption capacity is 95.56 %. The material is not only economical, but also is an agricultural waste product. Hence activated carbon derived from *Saccharum spontaneum* would be useful for the economic treatment of wastewater containing alizarin yellow dye metal ions. There are peaks after adsorption confirmed adsorption alizarin yellow dye on adsorbent surface.

**REFERENCES**


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**IV. CONCLUSION**

The X-ray Diffraction Studies of the adsorbent *Saccharum spontaneum*, before and after adsorption of dye, were carried out using Rigaku Corporation, Japan X-ray Diffractometer 40KV / 30mA, Model D/Max ULTIMA III. The diffraction patterns are shows in figure 12 a and 12 b. It is evident from the figures that there is no appreciable change in the spectra of adsorbent before and after adsorption. This may be due to the fact that adsorption does not alter the chemical nature of the surface of the adsorbent. The adsorption is governed by weak Van der Waals forces and is physical in nature.