

# *Chapter V*

## *Adsorption Studies Employing GDAC*

This chapter deals with the results pertaining sequestration of DB2, RR152 and Cu(II) by Goat Dung Activated Carbon(GDAC), an animal based waste material.

### 5.1 BET and BJH Studies

Table 5.1 summarizes BET total surface area, pore volume and average pore-size distribution of GDAC. The surface area of GDAC is calculated as 253.8 m<sup>2</sup>/g from BET plot (Figure 5.1) indicating appreciable sorption capacity. The measured pore size distribution as evident from figure 5.2 reveals the mesoporous nature of GDAC. The adsorption - desorption profiles of GDAC belong to the type IV hybrid-shape as (Figure 5.3) defined by the International Union of Pure and Applied Chemistry (IUPAC) classification.

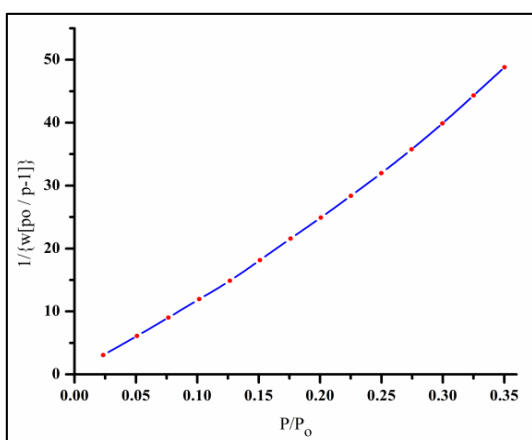


Figure 5.1 BET Plot

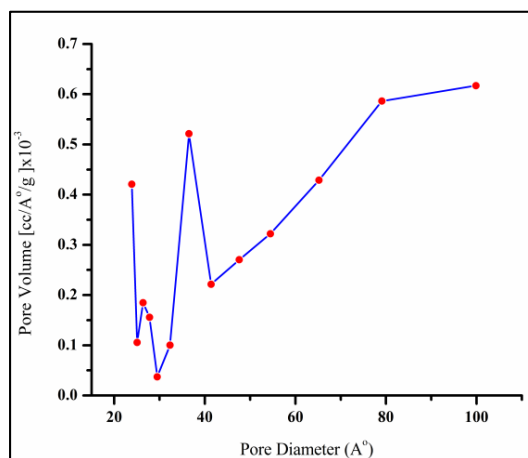


Figure 5.2 BJH Plot

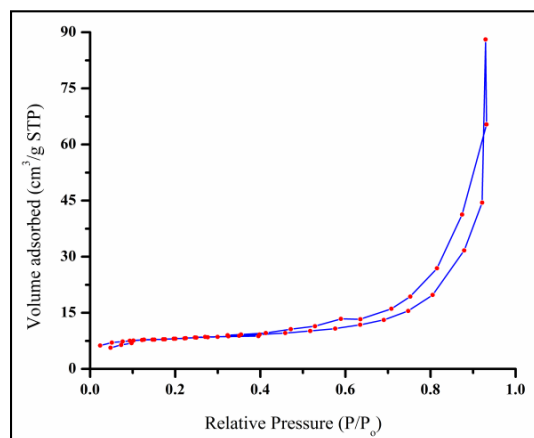


Figure 5.3 Adsorption/Desorption Isothermal Plot

## 5.2 Physico - Chemical Characterization

Lower ash content and higher bulk density values of GDAC reflects the better tendency of the prepared carbon to remove inorganic contaminants, also preventing the suspension<sup>161</sup>. Minimal water soluble and acid soluble nature of GDAC favour extended sorption characteristics of the latter. Neutral zero point charge expresses the flexibility of the material to function as an effective sorbent under both acidic and alkaline conditions with higher carbon content. The other parametric values are align with PJBAC characteristics as discussed in chapter IV. The numerical expressions pertaining to 5.1 & 5.2 discussions are listed in table 5.1.

**Table 5.1 Physico -- Chemical Characterisation**

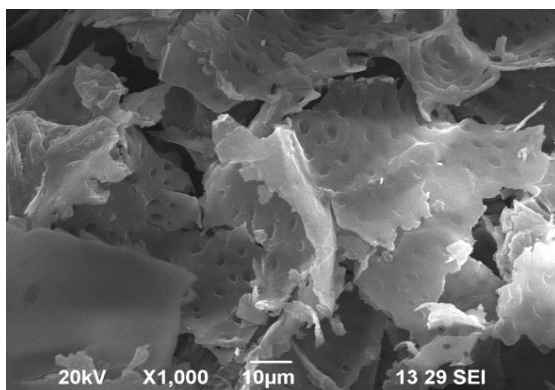
| <b>Properties</b>                | <b>GDAC</b> |
|----------------------------------|-------------|
| pH of 1 % solution               | 6.52        |
| Conductivity                     | 0.12        |
| Ash content (%)                  | 4.10        |
| Moisture (%)                     | 6.50        |
| Volatile matter (%)              | 13.2        |
| Acid soluble matter (%)          | 3.81        |
| Water soluble matter (%)         | 4.20        |
| Bulk density (g/mL)              | 0.39        |
| Specific gravity                 | 1.19        |
| Porosity (%)                     | 47.21       |
| Methylene blue value (mg/g)      | 551         |
| Iodine number (mg/g)             | 732         |
| PHzpc                            | 6.0         |
| Surface area (m <sup>2</sup> /g) | 253.8       |
| Mean Pore diameter (A°)          | 65.42       |
| Carbon (%)                       | 69.2        |
| Hydrogen (%)                     | 1.44        |
| Nitrogen (%)                     | 2.84        |
| Sulphur (%)                      | 4.17        |
| Oxygen (%)                       | 18.25       |
| Fixed carbon (%)                 | 70.2        |
| Yield (%)                        | 56.1%       |
| <b>Surface acid groups</b>       |             |
| Phenolic                         | 0.72        |
| Carboxylic                       | 1.02        |
| Lactonic                         | 0.42        |

## 5.3 Morphological Studies

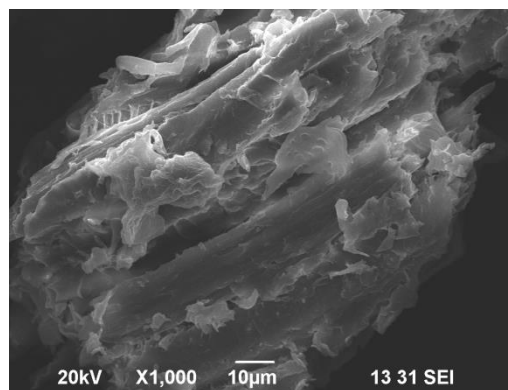
### 5.3.1 SEM and EDAX Analyses

Appreciable pores are noticed in the layered structure of unloaded GDAC (Figure 5.4), which have been found to be minimized in figures 5.5, 5.6 and 5.7, subjective to sorption of DB2, RR152 and Cu(II) respectively.

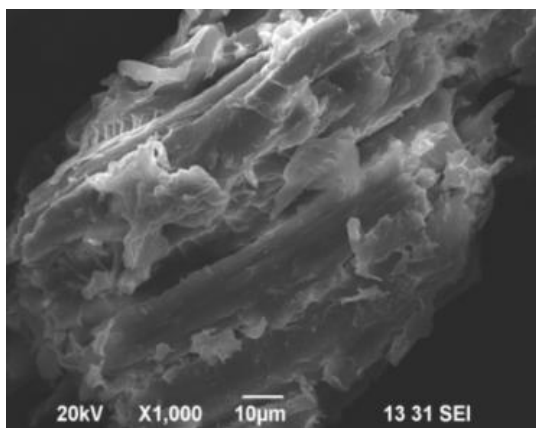
The EDAX spectra of GDAC (Figure 5.8) and its copper loaded counterpart (Figure 5.9) exhibit similar peaks as observed for PJBAC.



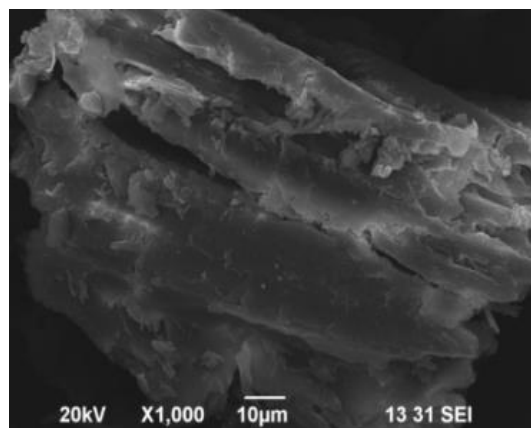
**Figure 5.4 SEM Image-  
Unloaded GDAC**



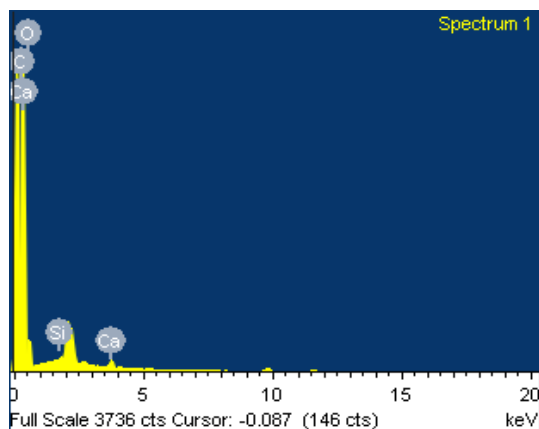
**Figure 5.5 SEM Image DB2  
Loaded GDAC**



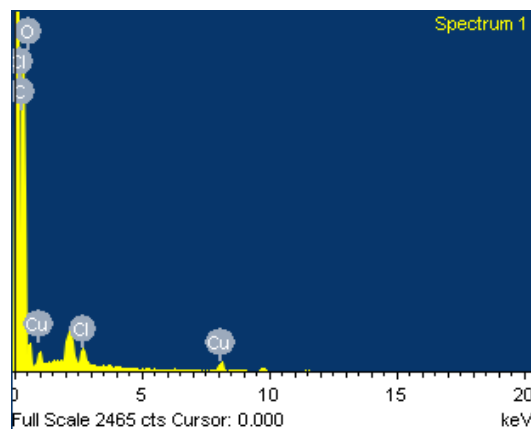
**Figure 5.6 SEM Image -RR152  
Loaded GDAC**



**Figure 5.7 SEM Image- Cu(II)  
Loaded GDAC**



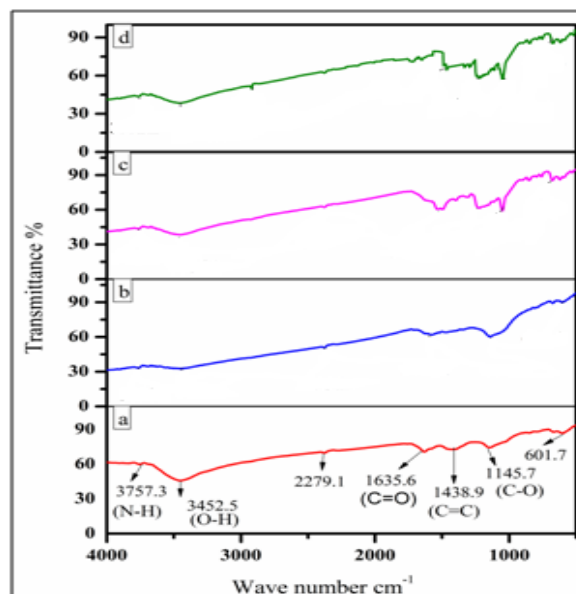
**Figure 5.8 EDAX Spectrum-  
Unloaded GDAC**



**Figure 5.9 EDAX Spectrum – Cu(II)  
Loaded GDAC**

### 5.3.2 FTIR Spectral Analysis

Significant specific peak shifts and additional peak appearances related to stretching vibrations and functional groups are seen in the sorbates' loaded FTIR spectra (Figure 5.10 b,c,d) against the unloaded one (Figure 5.10 a). These observations are noted to be similar to that of PJBAC systems.

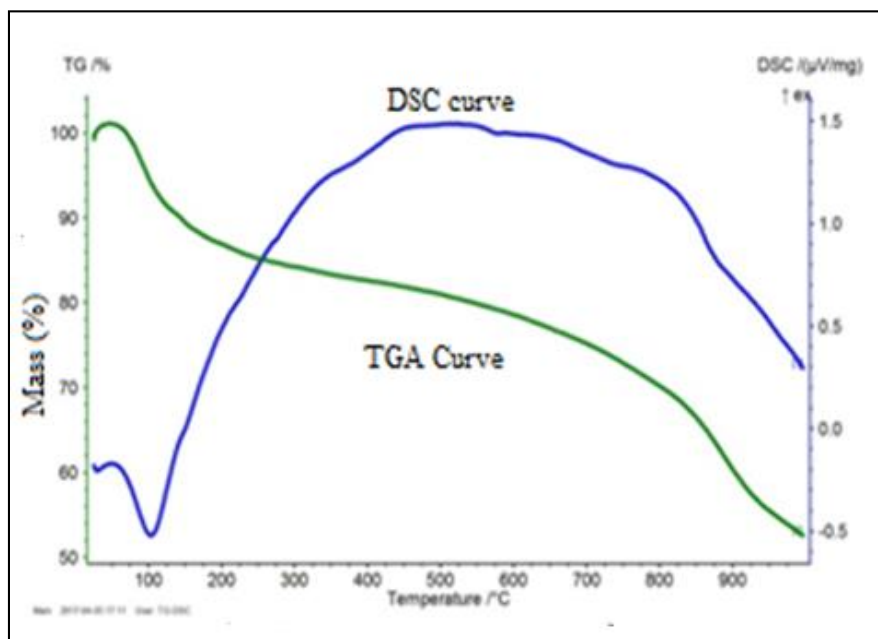


**Figure 5.10 FT-IR Spectrum (a) Unloaded GDAC, (b) DB2 Loaded GDAC,  
(c) RR152 Loaded GDAC and (d) Cu (II) Loaded GDAC**

### 5.3.3 TGA and DSC Analysis

TGA-DSC curves of GDAC (Figure 5.11) imply a marked reduction (TGA) in the weight of the sample from 75°C to 150°C, later, a slow decline in mass was observed followed by a measurable increase in weight loss upto 1000°C, from which thermal degradation of few structures is evidenced.

DSC curve pattern of GDAC is found to be identical with that of PJBAC, favouring similar characteristics. The yield obtained was 56%.



**Figure 5.11 TGA-DSC Curve**

### 5.4 Effect of Concentration and Contact Time

The amounts of DB2, RR152 and Cu(II) adsorbed by GDAC at varying initial concentrations and time slots are shown in tables 5.2 - 5.4 and the corresponding equilibrium curves are depicted in figures 5.12 - 5.14. From the tabulated values, it is obvious that the amounts of sorbates adsorbed vary linearly with the initial concentrations of dyes and Cu(II), which might be due to the repulsive forces acting between the adsorbate molecules on the solid surface and in the bulk phase, the existing vacant surface sites remaining unoccupied.

Also, at an initial stage of time frames, a rapid uptake of ions is envisaged, the trends being similar to that of PJBAC screening. Reports on the utilization of fly ash and saw dust under equivalent conditions, had been mentioned as registered in the present study<sup>162,163</sup>. An equilibrium contact time of 60, 90 and 15 minutes have been fixed for DB2, RR152 and Cu(II) sorption.

**Table 5.2 Effect of Initial Concentration and Contact Time - DB2**

| System   | Time (min) | Amount Adsorbed (mg/g) |         |         |          |          |          |
|----------|------------|------------------------|---------|---------|----------|----------|----------|
|          |            | 25mg/L                 | 50 mg/L | 75 mg/L | 100 mg/L | 125 mg/L | 150 mg/L |
| DB2-GDAC | 10         | 5.8                    | 12.1    | 16.4    | 18.9     | 20.2     | 21.2     |
|          | 20         | 7.0                    | 13.3    | 18.6    | 22.8     | 24.2     | 24.0     |
|          | 30         | 7.4                    | 14.8    | 20.2    | 24.6     | 27.9     | 28.5     |
|          | 40         | 7.6                    | 15.0    | 21.3    | 27.2     | 29.7     | 31.7     |
|          | 50         | 7.8                    | 15.3    | 23.0    | 29.2     | 31.6     | 35.4     |
|          | 60         | 8.0                    | 16.0    | 23.4    | 30.6     | 37.7     | 44.4     |
|          | 90         | 8.0                    | 15.9    | 23.4    | 30.6     | 37.7     | 44.4     |

Adsorbent dose 150 mg; Agitation time: 60 min; pH: 6; Temperature: 303K.

**Table 5.3 Effect of Initial Concentration and Contact Time - RR152**

| System     | Time (min) | Amount Adsorbed (mg/g) |         |         |          |          |          |
|------------|------------|------------------------|---------|---------|----------|----------|----------|
|            |            | 25mg/L                 | 50 mg/L | 75 mg/L | 100 mg/L | 125 mg/L | 150 mg/L |
| RR152-GDAC | 10         | 3.682                  | 7.696   | 11.76   | 15.61    | 19.39    | 20.95    |
|            | 20         | 3.970                  | 7.888   | 12.02   | 15.93    | 19.94    | 21.89    |
|            | 30         | 4.240                  | 8.394   | 12.20   | 16.45    | 20.39    | 22.38    |
|            | 40         | 4.375                  | 8.709   | 12.44   | 16.94    | 20.99    | 23.10    |
|            | 50         | 4.476                  | 8.935   | 12.64   | 17.26    | 21.30    | 24.45    |
|            | 60         | 4.662                  | 9.075   | 13.32   | 17.36    | 21.46    | 24.51    |
|            | 90         | 4.696                  | 9.110   | 13.51   | 17.71    | 21.63    | 25.21    |
|            | 120        | 4.696                  | 9.110   | 13.51   | 17.71    | 21.63    | 25.21    |

Adsorbent dose : 250 mg; Agitation time: 90 min; pH: 6; Temperature: 303K.

Table 5.4 Effect of Initial Concentration and Contact Time - Cu(II)

| System      | Time (min) | Amount Adsorbed (mg/g) |        |         |         |         |
|-------------|------------|------------------------|--------|---------|---------|---------|
|             |            | 4 mg/L                 | 8 mg/L | 12 mg/L | 16 mg/L | 20 mg/L |
| Cu(II)-GDAC | 3          | 1.19                   | 2.81   | 5.38    | 7.81    | 12.5    |
|             | 6          | 1.44                   | 3.56   | 6.38    | 8.56    | 13.1    |
|             | 9          | 1.69                   | 3.88   | 6.81    | 8.88    | 14.2    |
|             | 12         | 1.94                   | 4.00   | 6.94    | 9.00    | 14.8    |
|             | 15         | 2.44                   | 4.75   | 7.00    | 9.19    | 16.4    |
|             | 18         | 2.06                   | 4.19   | 7.06    | 9.19    | 16.3    |
|             | 21         | 2.00                   | 4.25   | 7.00    | 9.25    | 16.2    |

Adsorbent dose 80 mg; Agitation time: 15 min; pH: 6; Temperature: 303K.

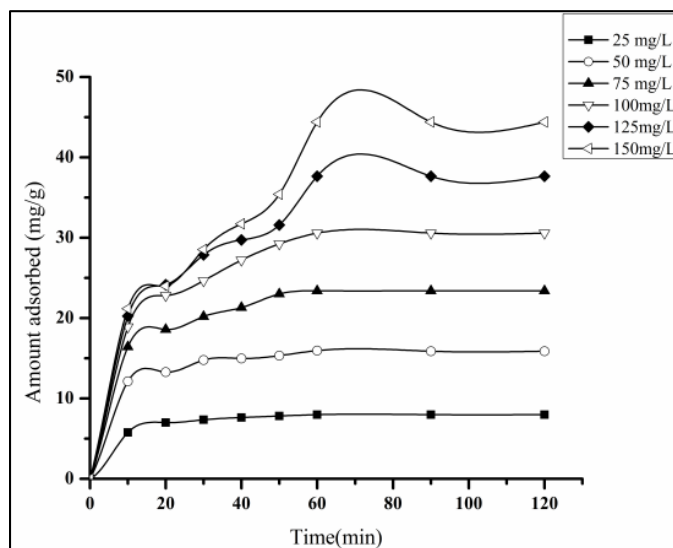
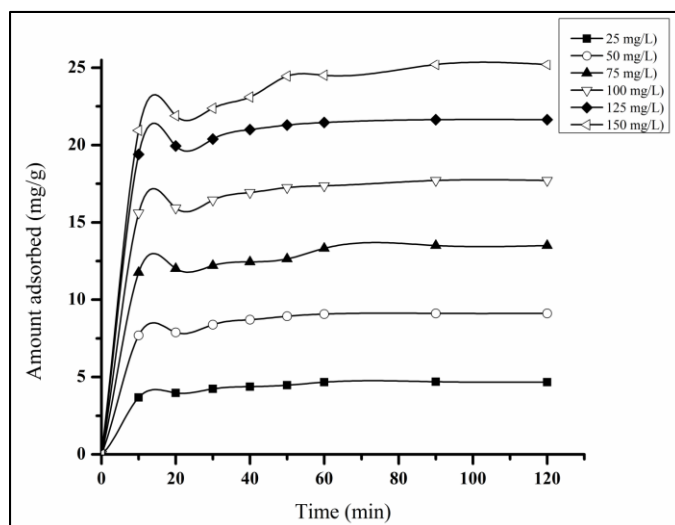
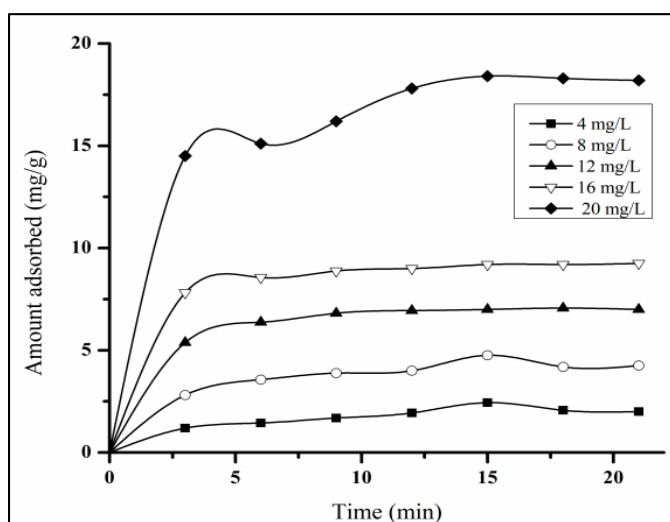


Figure 5.12 Effect of contact time and Initial Concentration - DB2





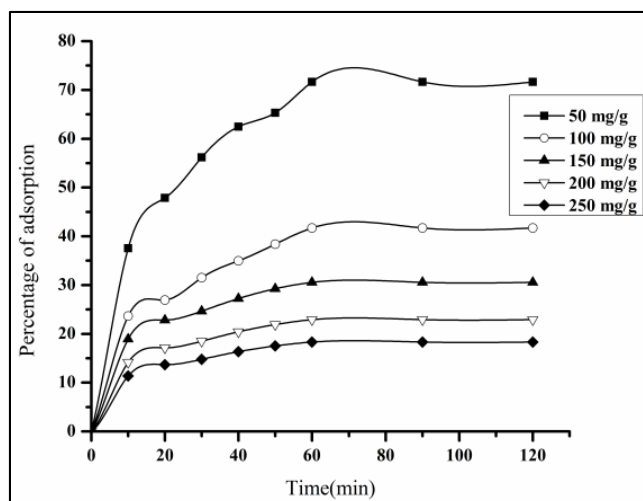
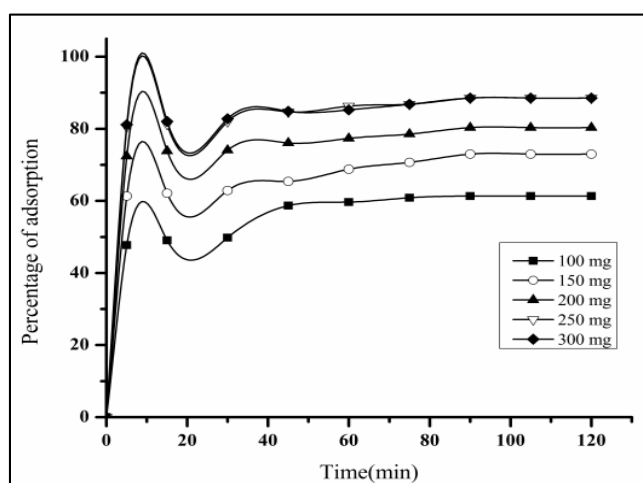
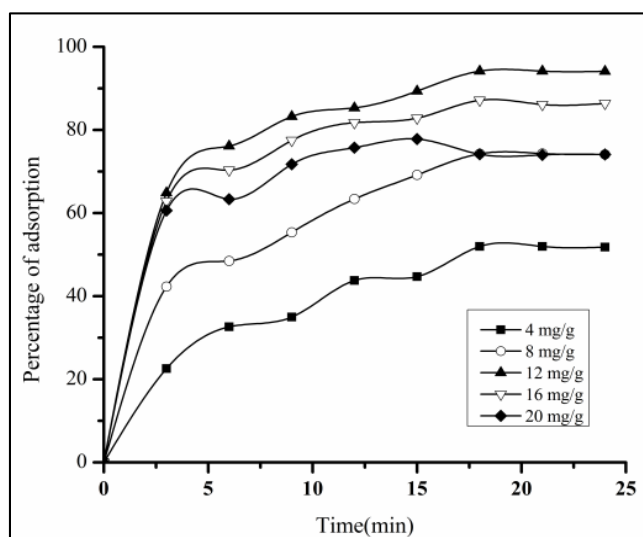
**Figure 5.13 Effect of contact time and Initial Concentration- RR152**



**Figure 5.14 Effect of contact time and Initial Concentration - Cu(II)**

### 5.5 Effect of Dosage

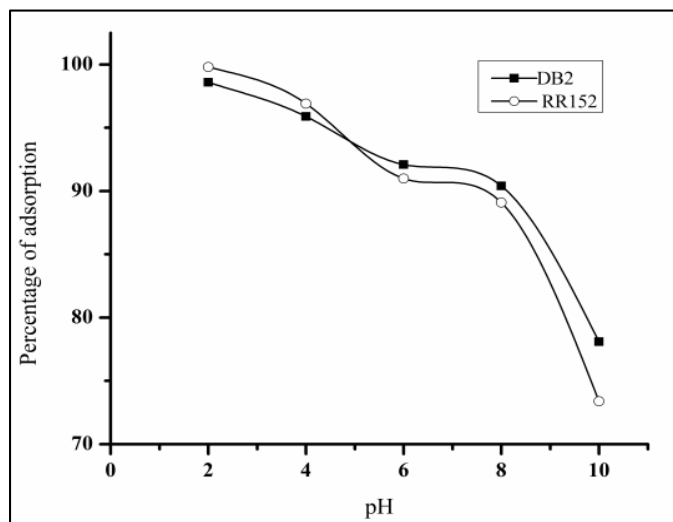
Increments in GDAC doses reflected an increase in the sorption capacity to trap the dye molecules and metal ion upto specified time limits as shown in figures 5.15-5.17, beyond which linear plateaus are observed. Thus, the minimal dosages of 150 mg, 250 mg and 80 mg have been found sufficient for the maximum removal the three adsorbate species viz., DB2, RR152 and Cu(II). Insignificant removal beyond the optimized dosages could be due to overlapping of adsorption sites at higher dose environments<sup>164,165</sup>.

**Figure 5.15 Effect of Dosage - DB2****Figure 5.16 Effect of Dosage - RR152****Figure 5.17 Effect of Dosage - Cu(II)**

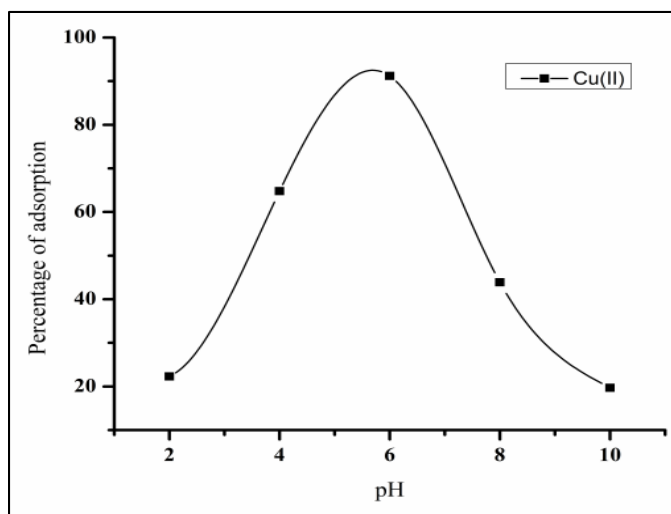
## 5.6 Effect of pH

Identical sloping curves are observed for both the dyes as evident from figure 5.18, where a maximum removal (DB2: 98.6%, RR152: 99.3%) had occurred at pH 2. This shall be due to the electrostatic interaction between the positively charged adsorbent surface and the negatively charged DB2 and RR152 anions. The declines of the curves at basic pH environments reflect the non-interaction of like charged (negative) anionic species and surface sites<sup>166,167</sup>.

Cu(II) removal was observed to be trivial at low pH, possibly due to the competition between  $H^+$  and  $Cu^{2+}$  ions to get sorbed on the sorption sites, preferentially. A maximum removal had occurred at pH 6, obvious from the inverted parabola depicted in figure 5.19. However, a dip in the curve at basic pH may correspond to the precipitation of  $Cu(OH)_2$ <sup>168</sup>. Similar findings were reported in the removal of copper using Wheat straw<sup>169</sup>



**Figure 5.18 Effect of pH -DB2 & RR152**



**Figure 5.19 Effect of pH - Cu(II)**

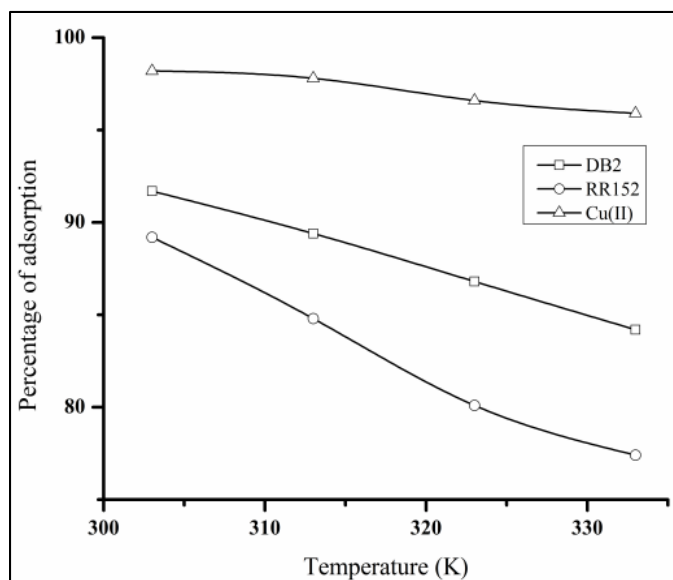
### 5.7 Effect of Temperature

All the three systems recorded a reduction in the species removal (Table.5.5) at higher temperatures, supported by the slanting straight lines (Figure 5.20) indicating the decline. The inverse relation shall be due to the weak bond formation<sup>170</sup> between sorbates and GDAC.

**Table 5.5 Effect of Temperature**

| System       | Conc. of the solution mg/L | Adsorbent dose mg | Percentage of adsorption |      |      |      |
|--------------|----------------------------|-------------------|--------------------------|------|------|------|
|              |                            |                   | 303 K                    | 313K | 323K | 333K |
| DB2-GDAC     | 100                        | 150               | 91.7                     | 89.4 | 86.8 | 84.2 |
| RR152- GDAC  | 100                        | 250               | 89.2                     | 84.8 | 80.1 | 77.4 |
| Cu(II) -GDAC | 20                         | 80                | 98.2                     | 97.8 | 96.6 | 95.9 |

Contact time: 60 min (DB2); 90 min (RR152); Cu(II): 15 min; pH: 6



**Figure 5.20 Effect of Temperature**

### 5.8 Effect of Cations/ Anions/ Co-ions

The influence of various ions viz., cations, anions and co-ions on the removal of Cu(II) from aqueous solutions is shown in table 5.6.  $Mg^{2+}$  ions inhibit Cu(II) removal prior to  $K^+$  and  $Na^+$ . This may be explained by ionic radii factor reported as  $Mg^{2+}$ :0.72 Å,  $K^+$ :1.02Å,  $Na^+$ :1.38 Å. Smaller ionic radii of  $Mg^{2+}$  implies greater degree of hydration in turn facilitates its extended availability to get sorbed ahead of other influencing cations, thus competing with  $Cu^{2+}$  ions. Amidst, the two anions and co-ions, the inhibition of  $Cl^-$  and  $Cr^{6+}$  is greater, as observed in PJBAC systems.

Table 5.6 Effect of Cations/ Anions/ Co-ions - Cu(II)

| Adsorbent | % removal of Cu <sup>2+</sup> in the absence of ions | Percentage Removal |                  |                  |                 |                 |                               |                  |                  |
|-----------|--|--------------------|------------------|------------------|-----------------|-----------------|-------------------------------|------------------|------------------|
|           |  | Conc (mg/L)        | Cations          |                  |                 | Anions          |                               | Co-ions          |                  |
|           |  |                    | Mg <sup>2+</sup> | Mg <sup>2+</sup> | Na <sup>+</sup> | Cl <sup>-</sup> | NO <sub>3</sub> <sup>2-</sup> | Zn <sup>2+</sup> | Cr <sup>6+</sup> |
| GDAC      | 94.1   | 100                | 71.31            | 82.95            | 89.12           | 76.25           | 85.22                         | 93.33            | 88.45            |
|           |  | 200                | 70.29            | 79.58            | 87.54           | 75.02           | 83.21                         | 92.65            | 85.28            |
|           |  | 300                | 68.23            | 77.36            | 85.77           | 72.31           | 81.56                         | 91.58            | 84.52            |
|           |  | 400                | 67.61            | 74.81            | 83.54           | 71.21           | 79.35                         | 89.92            | 83.69            |
|           |  | 500                | 66.11            | 73.28            | 81.25           | 68.52           | 77.48                         | 87.02            | 80.35            |

Metal ion concentration: 20 mg/L; contact time: 18 min; pH:6 ; Temperature: 303K

### 5.9 Desorption and Regeneration Studies

Desorption of DB2, RR152 and Cu(II) from the loaded GDAC followed a similar trend, reported in chapter IV(4.9). The corresponding adsorption/desorption cycles are expressed in the bar charts (Figure 5.21-5.23).

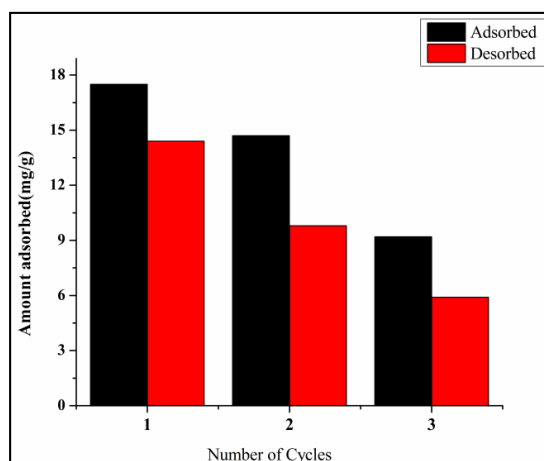


Figure 5.21 Regeneration- DB2

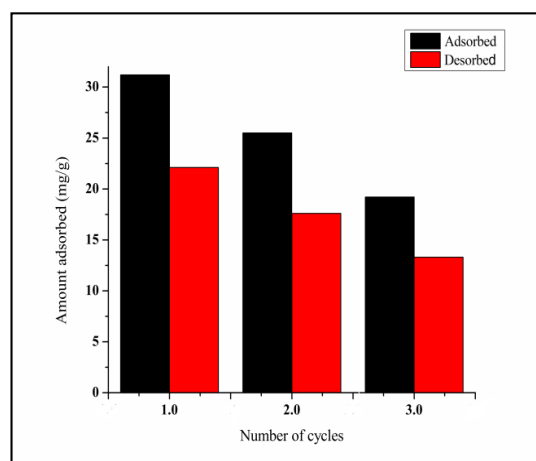
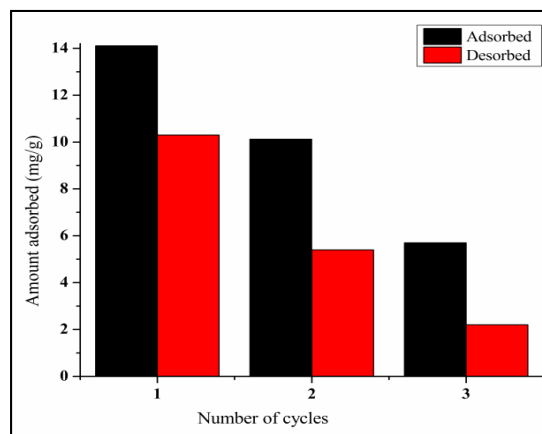


Figure 5.22 Regeneration- RR152



**Figure 5.23 Regeneration- Cu(II)**

### 5.10 Adsorption Isotherm

Adsorption capacities of GDAC in attaining the equilibrium concentrations of DB2, RR152 and Cu(II) are listed in tables 5.7-5.9 accounting for the Langmuir, Freundlich, Tempkin and DKR plots. Equilibrium concentrations are found to be directly proportional to the initial concentrations of the prepared aqueous solutions.

**Table 5.7 Equilibrium/Isothermal Data- DB2**

| Conc. of Dye Solutions (mg/L) | $C_e$ | $q_e$ | $C_e/q_e$ | $\log C_e$ | $\log q_e$ | $\ln C_e$ | $\ln q_e$ | $\varepsilon^2 \times 10^8$ | $R_L$  |
|-------------------------------|-------|-------|-----------|------------|------------|-----------|-----------|-----------------------------|--------|
| 25                            | 1.1   | 8.0   | 0.1381    | 0.0414     | 0.9013     | 0.0953    | 2.075     | 16.54                       | 0.2485 |
| 50                            | 2.4   | 15.9  | 0.1513    | 0.3802     | 1.2005     | 0.8755    | 2.764     | 7.700                       | 0.1419 |
| 75                            | 4.8   | 23.4  | 0.2051    | 0.6812     | 1.3692     | 1.5686    | 3.153     | 2.273                       | 0.0993 |
| 100                           | 8.2   | 30.6  | 0.2680    | 0.9138     | 1.4857     | 2.1041    | 3.421     | 1.840                       | 0.0763 |
| 125                           | 12.0  | 37.7  | 0.3186    | 1.0792     | 1.5760     | 2.4849    | 3.629     | 0.407                       | 0.0620 |
| 150                           | 16.8  | 44.4  | 0.3784    | 1.2253     | 1.6474     | 2.8214    | 3.793     | 0.212                       | 0.0522 |

**Table 5.8 Equilibrium/Isothermal Data- RR152**

| Conc. of Dye Solutions (mg/L) | $C_e$ | $q_e$ | $C_e/q_e$ | $\log C_e$ | $\log q_e$ | $\ln C_e$ | $\ln q_e$ | $\varepsilon^2 \times 10^8$ | $R_L$  |
|-------------------------------|-------|-------|-----------|------------|------------|-----------|-----------|-----------------------------|--------|
| 25                            | 0.67  | 4.7   | 0.1426    | 0.1761     | 0.6721     | -0.4005   | 1.548     | 12.94                       | 0.1952 |
| 50                            | 2.70  | 9.1   | 0.2967    | 0.6532     | 0.9595     | 0.9933    | 2.208     | 6.301                       | 0.1082 |
| 75                            | 5.76  | 13.5  | 0.4267    | 0.8751     | 1.1461     | 1.7509    | 2.603     | 1.627                       | 0.0748 |
| 100                           | 7.60  | 17.7  | 0.4289    | 1.0569     | 1.2538     | 2.0281    | 2.875     | 0.970                       | 0.0572 |
| 125                           | 13.2  | 21.6  | 0.6086    | 1.2253     | 1.3393     | 2.5779    | 3.075     | 0.340                       | 0.0463 |
| 150                           | 20.3  | 25.2  | 0.8049    | 0.1761     | 0.6721     | 3.0106    | 3.228     | 0.147                       | 0.0389 |

**Table 5.9 Equilibrium/Isothermal Data- Cu(II)**

| Conc. of Metal Solutions (mg/L) | $C_e$ | $q_e$ | $C_e/q_e$ | $\log C_e$ | $\log q_e$ | $\ln C_e$ | $\ln q_e$ | $\varepsilon^2 \times 10^8$ | $R_L$  |
|---------------------------------|-------|-------|-----------|------------|------------|-----------|-----------|-----------------------------|--------|
| 4                               | 0.10  | 2.44  | 0.0410    | -1.000     | 0.387      | -2.3026   | 0.8919    | 364.96                      | 0.1452 |
| 8                               | 0.40  | 4.75  | 0.0842    | -0.398     | 0.677      | -0.9163   | 1.5581    | 99.62                       | 0.0783 |
| 12                              | 0.80  | 7.00  | 0.1143    | -0.097     | 0.845      | -0.2231   | 1.9459    | 41.74                       | 0.0536 |
| 16                              | 1.30  | 9.19  | 0.1415    | 0.114      | 0.963      | 0.2624    | 2.2182    | 20.66                       | 0.0407 |
| 20                              | 1.800 | 16.4  | 0.1676    | 0.255      | 1.057      | 0.5878    | 2.4336    | 12.39                       | 0.0328 |



### 5.10.1 Langmuir Isotherm

Figures 5.24 and 5.25 shows that plots of  $C_e/q_e$  vs  $C_e$ , which are observed to be straight lines. Langmuir constants  $q_m$  and  $b$  are listed in table 5.10 had been obtained from the slopes and intercepts of the straight lines.  $R_L$  values for DB2, RR152 and Cu(II) systems between 0.03-0.24 imply favourable adsorption.

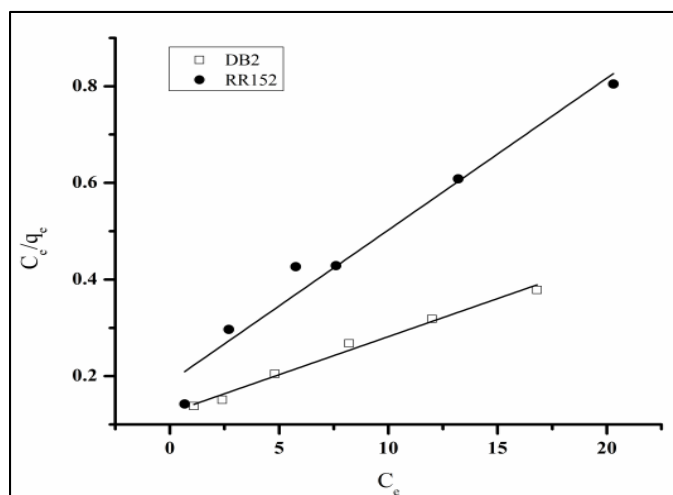


Figure 5.24 Langmuir Plot - DB2 & RR152

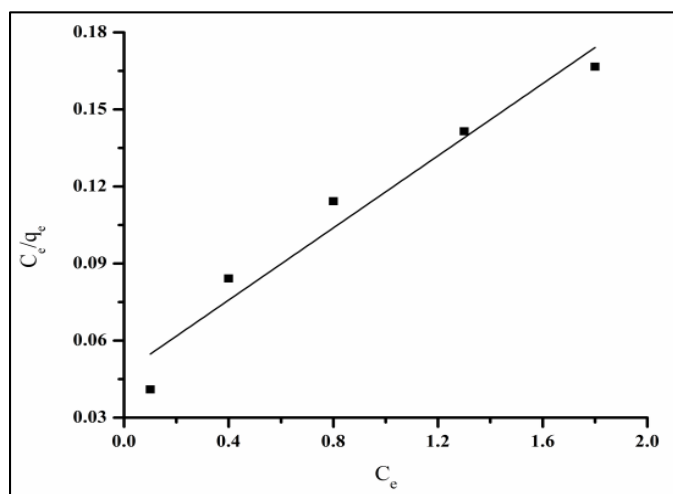


Figure 5.25 Langmuir Plot - Cu(II)

### 5.10.2 Freundlich Isotherm

Appreciable  $K_F$  and lower  $1/n$  values (Table 5.10) obtained from the Freundlich plots (Figure 5.26) are indicative of excellent chelating property of GDAC. The linearity of plots with correlation co-efficients nearness to unity, suggested the fit in of the system to Freundlich isotherm model.

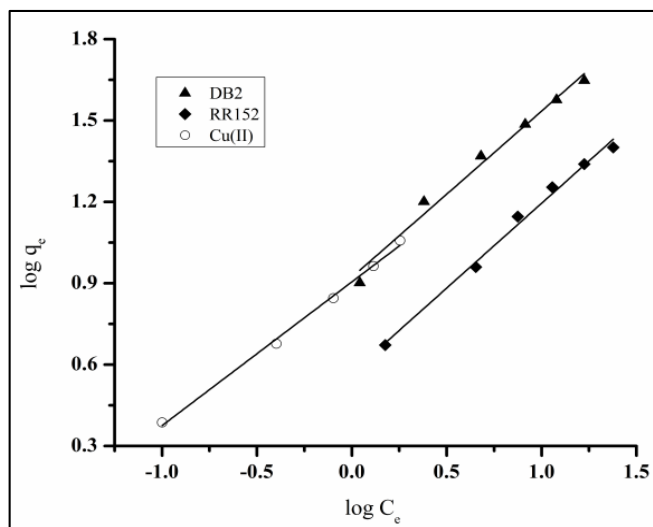


Figure 5.26 Freundlich Plot

### 5.10.3 Tempkin Isotherm

Tempkin isotherms plotted for GDAC systems (Figure 5.27) reflect identical line patterns as that of PJBAC systems, recording high correlation coefficient values, which imply decreasing heats of adsorption against increasing coverage<sup>171</sup>.

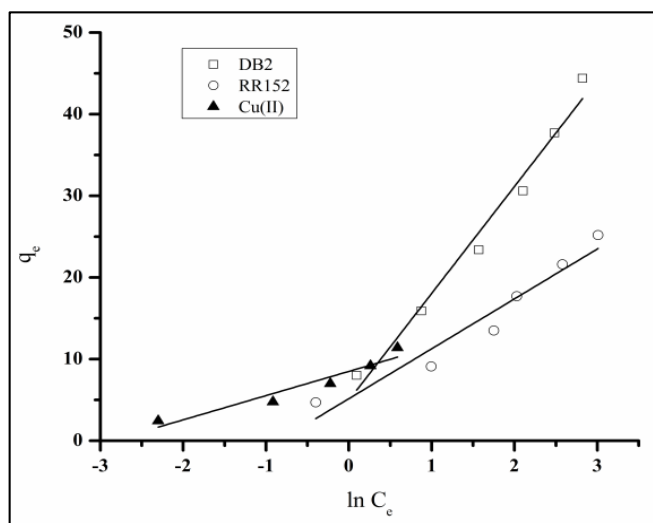


Figure 5.27 Tempkin Plot

#### 5.10.4 Dubinin–Kaganer-Radushkevich Isotherm Model

Figures 5.28 and 5.29 refer to the plots of  $\ln q_e$  vs  $\varepsilon^2$  from which  $q_s$  and  $E$  were calculated (Table 5.10). The appropriate 'E' values favour the type of physical adsorption<sup>172</sup>. The correlation coefficient value of metal system is found to be lesser than that for dye molecules, the reason could be higher affinity of dye molecules towards active sites of GDAC.

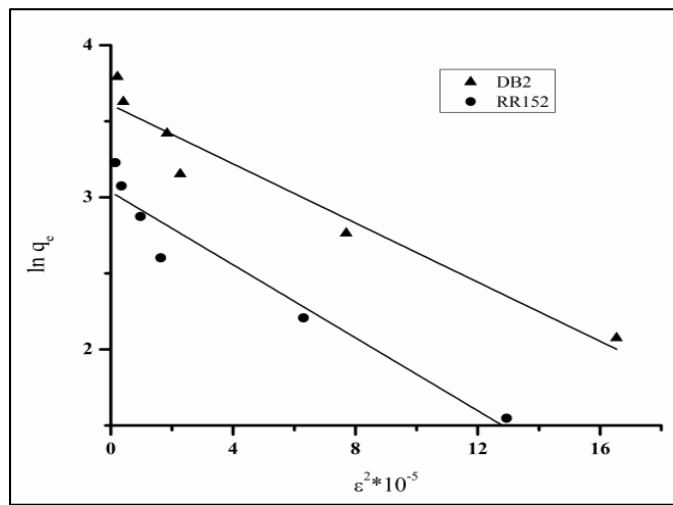


Figure 5.28 DKR plot - DB2 & RR152

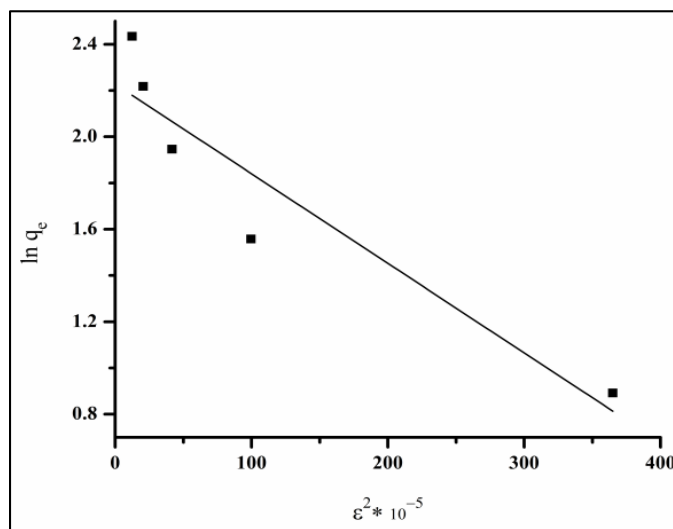


Figure 5.29 DKR plot - Cu(II)

### 5.10.5 Comparison of Isotherm Models

The calculated adsorption capacity ( $q_m$ ) of Langmuir isotherm greater than  $K_F$  and  $q_s$  constants indicate better sorption capacity corresponding to monolayer adsorption. This above statement is favoured by  $A_T$  and  $B_T$  values (Tempkin constants). Also, appreciable  $1/n$  values which infer the sorption intensity both mono/ multilayer sorptions to be obeyed<sup>173</sup>.

**Table 5.10 Isothermal Constants**

| <b>Isotherm Parameters</b> | <b>DB2- GDAC</b> | <b>RR152 – GDAC</b> | <b>Cu(II) – GDAC</b> |
|----------------------------|------------------|---------------------|----------------------|
| <b>Langmuir Isotherm</b>   |                  |                     |                      |
| $q_m$ (mg/g)               | 46.66            | 22.26               | 14.24                |
| $b$ (L/g)                  | 0.1209           | 0.1649              | 1.472                |
| $R^2$                      | 0.9889           | 0.9974              | 0.9954               |
| <b>Freundlich Isotherm</b> |                  |                     |                      |
| $K_F$ (mg/g)               | 8.356            | 3.707               | 8.035                |
| $n$                        | 1.634            | 1.603               | 1.888                |
| $R^2$                      | 0.9848           | 0.9926              | 0.9871               |
| <b>Tempkin Isotherm</b>    |                  |                     |                      |
| $A_T$ (L/g)                | 1.4808           | 1.2006              | 1.0929               |
| $b_T$                      | 192.3            | 413.02              | 849.3                |
| $R^2$                      | 0.9809           | 0.9418              | 0.9259               |
| <b>DKR Isotherm</b>        |                  |                     |                      |
| $q_s$ (mg/g)               | 36.86            | 20.79               | 9.279                |
| $E$ (kJ/mol)               | 2.276            | 2.043               | 3.581                |
| $R^2$                      | 0.943            | 0.939               | 0.885                |

### 5.11 Adsorption Kinetics

Pseudo first order and pseudo second order kinetic models were applied to the DB2-GDAC, RR152-GDAC and Cu(II) -GDAC systems.

The experimental data in reference to the kinetic models listed in tables 5.11, 5.12 and 5.13 for the three systems, from which the corresponding plots derived are shown in figures 5.30-5.33. The kinetic lines and their corresponding constants (Table 5.14) are observed to be in line their related kinetic models being discussed in the previous chapter. Thence, GDAC systems obey pseudo second order kinetic model.

**Table 5.11 Sorption Kinetics - DB2**

| Time (min) | 50 (mg/L)                             |                  | 100 (mg/L)                            |                  | 150 (mg/L)                            |                  |
|------------|---------------------------------------|------------------|---------------------------------------|------------------|---------------------------------------|------------------|
|            | log (q <sub>e</sub> -q <sub>t</sub> ) | t/q <sub>t</sub> | log (q <sub>e</sub> -q <sub>t</sub> ) | t/q <sub>t</sub> | log (q <sub>e</sub> -q <sub>t</sub> ) | t/q <sub>t</sub> |
| 10         | 1.578                                 | 0.825            | 1.909                                 | 0.529            | 2.110                                 | 0.472            |
| 20         | 1.565                                 | 1.506            | 1.887                                 | 0.876            | 2.100                                 | 0.834            |
| 30         | 1.547                                 | 2.028            | 1.877                                 | 1.217            | 2.084                                 | 1.052            |
| 40         | 1.544                                 | 2.671            | 1.862                                 | 1.469            | 2.073                                 | 1.261            |
| 50         | 1.540                                 | 3.262            | 1.849                                 | 1.712            | 2.059                                 | 1.352            |
| 60         | 1.532                                 | 3.761            | 1.842                                 | 1.963            | 2.024                                 | 1.413            |

Adsorbent dose: 150 mg; pH: 6; Temperature: 303K

**Table 5.12 Sorption Kinetics - RR152**

| Time (min) | 50 (mg/L)                             |                  | 100 (mg/L)                            |                  | 150 (mg/L)                            |                  |
|------------|---------------------------------------|------------------|---------------------------------------|------------------|---------------------------------------|------------------|
|            | log (q <sub>e</sub> -q <sub>t</sub> ) | t/q <sub>t</sub> | log (q <sub>e</sub> -q <sub>t</sub> ) | t/q <sub>t</sub> | log (q <sub>e</sub> -q <sub>t</sub> ) | t/q <sub>t</sub> |
| 10         | 1.504                                 | 0.313            | 1.820                                 | 0.151            | 2.015                                 | 0.097            |
| 20         | 1.496                                 | 0.639            | 1.806                                 | 0.313            | 2.007                                 | 0.197            |
| 30         | 1.479                                 | 0.995            | 1.795                                 | 0.481            | 1.998                                 | 0.301            |
| 40         | 1.465                                 | 1.369            | 1.780                                 | 0.664            | 1.980                                 | 0.419            |
| 50         | 1.443                                 | 1.801            | 1.763                                 | 0.863            | 1.963                                 | 0.545            |
| 60         | 1.424                                 | 2.259            | 1.739                                 | 1.095            | 1.922                                 | 0.617            |
| 90         | 1.424                                 | 2.259            | 1.739                                 | 1.095            | 1.922                                 | 0.714            |

Adsorbent dose: 250 mg; pH: 6; Temperature: 303K

Table 5.13 Sorption Kinetics - Cu(II)

| Time (min) | 4 (mg/L)           |         | 12 (mg/L)          |         | 20 (mg/L)          |         |
|------------|--------------------|---------|--------------------|---------|--------------------|---------|
|            | $\log (q_e - q_t)$ | $t/q_t$ | $\log (q_e - q_t)$ | $t/q_t$ | $\log (q_e - q_t)$ | $t/q_t$ |
| 3          | 3.350              | 4.615   | 7.875              | 0.727   | 9.875              | 0.296   |
| 6          | 2.880              | 5.333   | 6.875              | 1.171   | 9.375              | 0.565   |
| 9          | 2.410              | 5.669   | 6.000              | 1.500   | 9.063              | 0.823   |
| 12         | 2.063              | 6.194   | 5.688              | 1.901   | 8.813              | 1.073   |
| 15         | 1.563              | 6.154   | 5.000              | 2.143   | 8.563              | 1.311   |
| 18         | 1.938              | 8.727   | 4.938              | 2.549   | 8.625              | 1.582   |
| 21         | 2.000              | 10.500  | 5.000              | 3.000   | 8.688              | 1.856   |

Adsorbent dose: 80 mg; pH: 6; Temperature: 303K

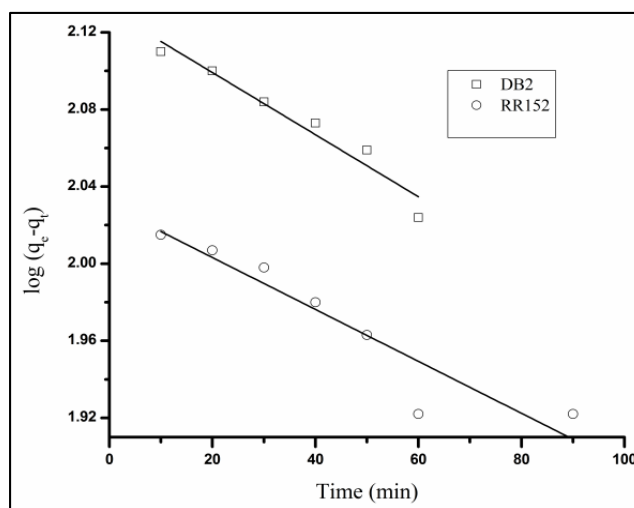


Figure 5.30 First Order Kinetics - DB2 &amp; RR152

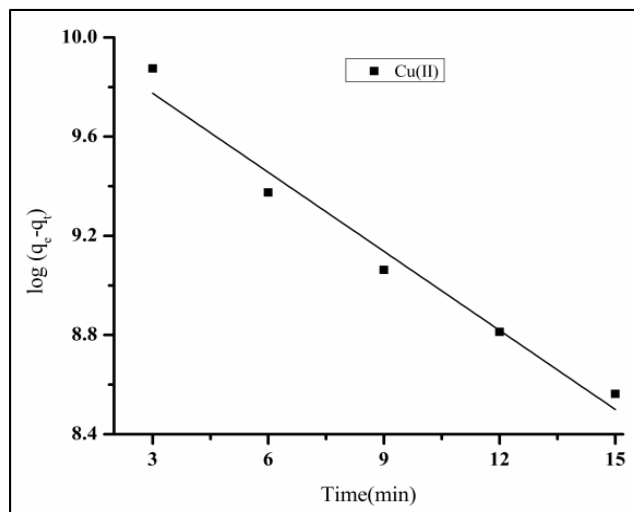


Figure 5.31 First Order Kinetics - Cu(II)

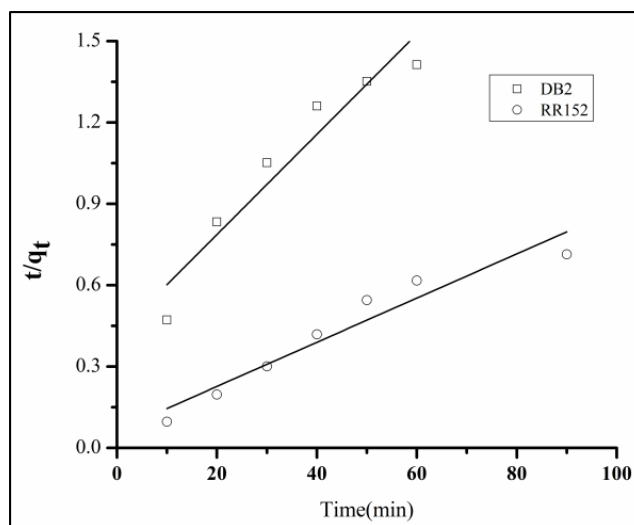


Figure 5.32 Second Order Kinetics- DB2 & RR152]

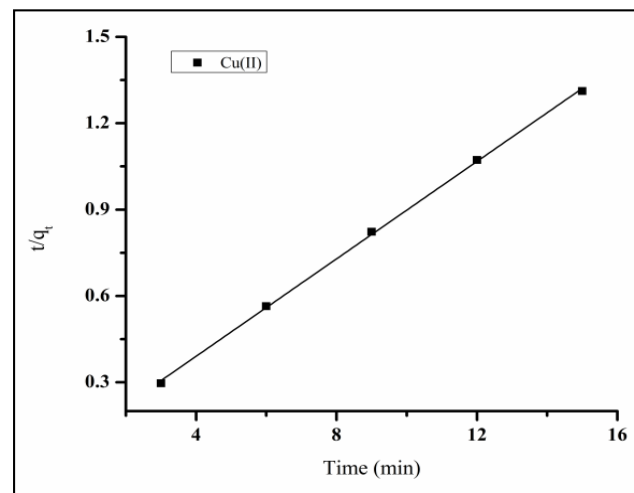


Figure 5.33 Second Order Kinetics - Cu(II)

Table 5.14 Comparison of Pseudo-First-order/ Pseudo-Second-order Kinetic Constants

| Conc. of metal Ions (mg/L) | $q_e$ exp. (mg/g) | Pseudo-first-order kinetics |  |        |       | Pseudo-second-order kinetics |                                  |        |      |
|----------------------------|-------------------|-----------------------------|--|--------|-------|------------------------------|----------------------------------|--------|------|
|                            |                   | $q_e$ cal. (mg/g)           | $k_1 \times 10^{-2}$ ( $\text{min}^{-1}$ ) | $R^2$  | SSE   | $q_e$ cal. (mg/g)            | $k_2 \times 10^{-3}$ (g/ mg min) | $R^2$  | SSE  |
| <b>DB2 – GDAC</b>          |                   |                             |  |        |       |                              |                                  |        |      |
| 50                         | 15.9              | 5.63                        | 0.0024                                     | 0.9274 | 5.40  | 16.5                         | 0.017                            | 0.9993 | 1.78 |
| 100                        | 30.6              | 11.2                        | 0.0031                                     | 0.9777 | 7.43  | 33.0                         | 0.004                            | 0.9973 | 3.92 |
| 150                        | 44.6              | 14.6                        | 0.0037                                     | 0.9334 | 9.81  | 53.5                         | 0.001                            | 0.9730 | 6.12 |
| <b>RR152 – GDAC</b>        |                   |                             |  |        |       |                              |                                  |        |      |
| 50                         | 9.1               | 2.1                         | 0.008                                      | 0.888  | 4.72  | 9.2                          | 0.002                            | 0.999  | 2.32 |
| 100                        | 17.7              | 11.8                        | 0.006                                      | 0.936  | 5.99  | 17.8                         | 0.011                            | 0.998  | 4.56 |
| 150                        | 25.2              | 16.2                        | 0.004                                      | 0.941  | 10.65 | 25.6                         | 0.014                            | 0.999  | 6.87 |
| <b>Cu(II) – GDAC</b>       |                   |                             |  |        |       |                              |                                  |        |      |
| 4                          | 2.44              | 0.701                       | 4.606                                      | 0.9625 | 2.01  | 2.6197                       | 0.004                            | 0.8794 | 1.00 |
| 12                         | 7.21              | 4.562                       | 6.429                                      | 0.9589 | 3.85  | 8.438                        | 0.034                            | 0.9890 | 2.14 |
| 20                         | 11.4              | 9.214                       | 7.895                                      | 0.9665 | 5.86  | 11.82                        | 0.137                            | 0.9993 | 3.73 |

### 5.11.1 Elovich Model

Elovich constants  $\alpha$ ,  $\beta$  (Tables 5.15 & 5.16) referring to initial sorption rate and extent of surface coverage respectively were calculated from the intercepts and slopes of Elovich plots (Figure 5.34). The decrease in  $\beta$  and increase in  $\alpha$  values implicit greater sorption with initial concentration.



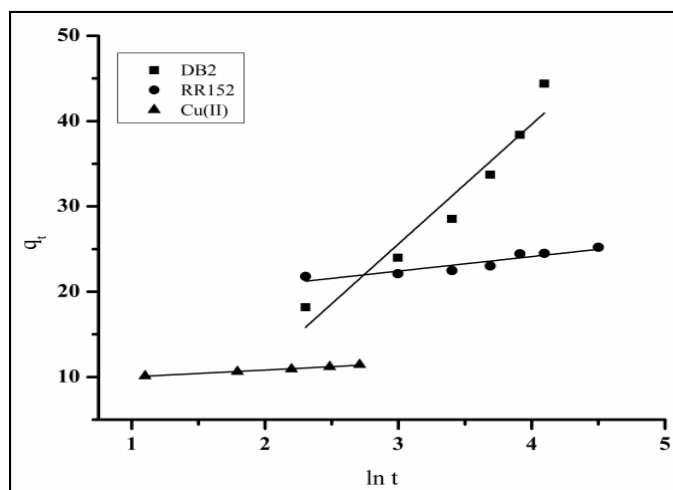


Figure 5.34 Elovich Model

Table 5.15 Elovich Constants - DB2 &amp; RR152

| Conc. of dye solution | DB2 – GDAC |         |       | RR152 – GDAC |         |       |
|-----------------------|------------|---------|-------|--------------|---------|-------|
|                       | $\alpha$   | $\beta$ | $R^2$ | $\alpha$     | $\beta$ | $R^2$ |
| 25                    | 4.197      | 3.873   | 0.835 | 1.008        | 2.886   | 0.845 |
| 50                    | 8.758      | 2.621   | 0.877 | 5.594        | 2.238   | 0.871 |
| 75                    | 9.641      | 1.992   | 0.900 | 8.090        | 1.716   | 0.946 |
| 100                   | 7.644      | 1.167   | 0.916 | 11.509       | 1.433   | 0.972 |
| 125                   | 11.355     | 0.810   | 0.922 | 12.595       | 0.827   | 0.926 |
| 150                   | 16.764     | 0.222   | 0.894 | 17.310       | 0.503   | 0.841 |

$\alpha$ : (mg/g min),  $\beta$ : (g/mg)

**Table 5.16 Elovich Constants - Cu(II)**

| Conc. of Metal solution<br>(mg/L) | Cu(II) – GDAC |         |       |
|-----------------------------------|---------------|---------|-------|
|                                   | $\alpha$      | $\beta$ | $R^2$ |
| 4                                 | -0.862        | 1.862   | 0.846 |
| 8                                 | 0.607         | 1.703   | 0.868 |
| 12                                | 2.364         | 1.608   | 0.972 |
| 16                                | 4.212         | 1.020   | 0.978 |
| 20                                | 9.423         | 0.681   | 0.938 |

$\alpha$ : (mg/g min),  $\beta$ : (g/mg)

### 5.11.2 Intra Particle Diffusion Model

Intraparticle diffusion rate constants ( $K_i$  and  $C$ ) were calculated (Tables 5.17 & 5.18) from the slopes and intercepts of the plots  $qt$  vs  $t^{1/2}$  (Figures 5.35-5.37). The initial inclined portions of the lines represent external surface adsorption followed by intraparticle diffusion as implied by the equilibrium plateau region. Similar results were observed in the findings of Monser et al<sup>174</sup>.

**Table 5.17 Intraparticle Diffusion Constants -DB2 & RR152**

| Conc of Dye Solution<br>(mg/L) | DB2-GDAC                         |       | RR152 – GDAC                     |       |
|--------------------------------|----------------------------------|-------|----------------------------------|-------|
|                                | $K_i$ (mg/g min <sup>1/2</sup> ) | $C$   | $K_i$ (mg/g min <sup>1/2</sup> ) | $C$   |
| 25                             | 6.343                            | 0.047 | 3.295                            | 0.040 |
| 50                             | 12.68                            | 0.090 | 7.744                            | 0.039 |
| 75                             | 17.12                            | 0.177 | 11.08                            | 0.062 |
| 100                            | 20.00                            | 0.293 | 15.11                            | 0.070 |
| 125                            | 20.26                            | 0.460 | 17.93                            | 0.104 |
| 150                            | 19.49                            | 0.654 | 21.33                            | 0.095 |

Table 5.18 Intraparticle Diffusion Constants - Cu(II)

| Conc of metal ion (mg/L) | Cu(II) – GDAC                    |        |
|--------------------------|----------------------------------|--------|
|                          | $K_i$ (mg/g min <sup>1/2</sup> ) | C      |
| 4                        | 0.3839                           | 0.2024 |
| 8                        | 2.0893                           | 0.2559 |
| 12                       | 4.1607                           | 0.3214 |
| 16                       | 6.1252                           | 0.3452 |
| 20                       | 8.2054                           | 0.1324 |

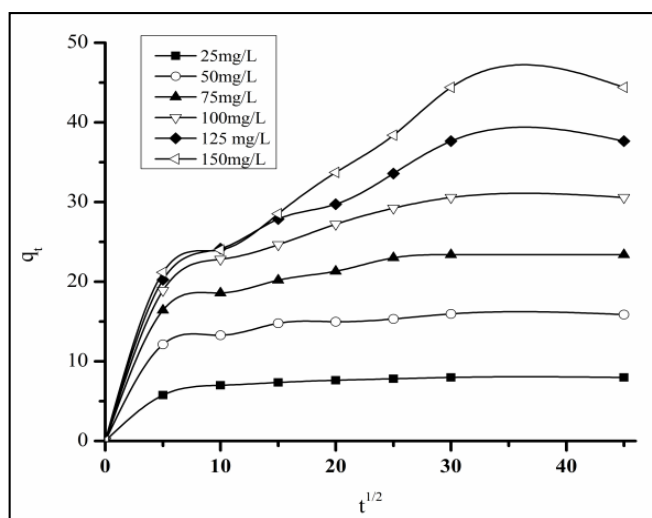


Figure 5.35 Intraparticle Diffusion Model – DB2

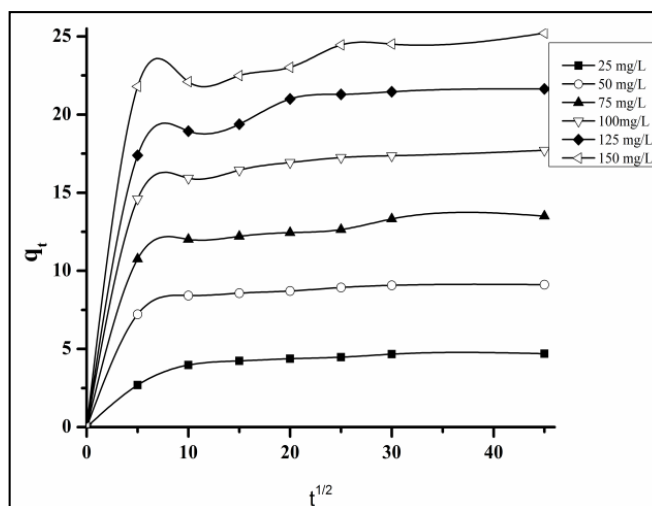


Figure 5.36 Intraparticle Diffusion Model -RR152

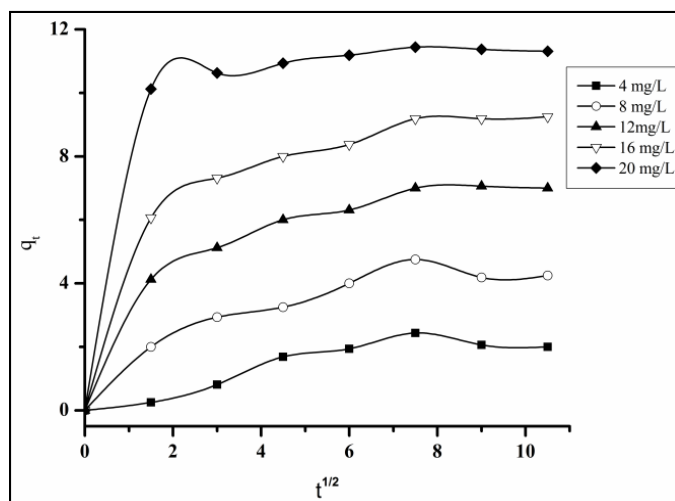


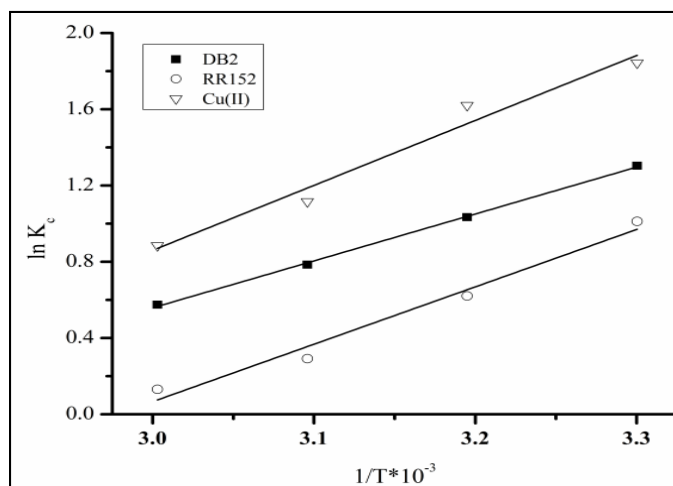
Figure 5.37 Intraparticle Diffusion Model - Cu(II)

### 5.12 Thermodynamics and Equilibrium studies

The thermodynamic parameters,  $\Delta G^\circ$ ,  $\Delta H^\circ$  and  $\Delta S^\circ$  were deduced from the Van't Hoff plots (Figure 5.38). The negative values of  $\Delta G^\circ$  and  $\Delta H^\circ$  (Table 5.19) corresponding to the spontaneous/exothermic nature of the sorption process<sup>175</sup>. The positive  $\Delta S^\circ$  values are indicative of randomness at the solid/solution interface<sup>176</sup>. It is also inferred that the reaction system is spontaneous at higher temperatures as evident from higher  $\Delta G^\circ$  values.

Table 5.19 Thermodynamic Constants [GDAC]

| Temp (K) | DB2 – GDAC                        |                   |                   | RR152- GDAC                       |                   |                   | Cu(II)- GDAC                      |                   |                   |
|----------|-----------------------------------|-------------------|-------------------|-----------------------------------|-------------------|-------------------|-----------------------------------|-------------------|-------------------|
|          | $-\Delta G \times 10^{-3}$ kJ/mol | $\Delta H$ kJ/mol | $\Delta S$ kJ/mol | $-\Delta G \times 10^{-3}$ kJ/mol | $\Delta H$ kJ/mol | $\Delta S$ kJ/mol | $-\Delta G \times 10^{-3}$ kJ/mol | $\Delta H$ kJ/mol | $\Delta S$ kJ/mol |
| 303      | 0.3284                            |                   |                   | 0.2549                            |                   |                   | 0.6592                            |                   |                   |
| 313      | 0.2690                            | -2.460            | 6.822             | 0.1614                            | -3.011            | 8.965             | 0.4979                            | -3.407            | 9.362             |
| 323      | 0.2107                            |                   |                   | 0.0784                            |                   |                   | 0.3304                            |                   |                   |
| 333      | 0.1591                            |                   |                   | 0.0362                            |                   |                   | 0.2278                            |                   |                   |



**Figure 5.38 Vant Hoff's plot (RR152)**

### 5.13 Batch Equilibration Studies –Textile Effluent samples vs Derived Carbons

The prepared activated carbons have been upscaled to field levels based on their optimized results reported in chapters IV & V. Two textile effluent samples with excess concentrations of DB2 and RR152 were identified and collected from Texwell (P) Ltd located at Tirupur, Tamil Nadu, India. These samples with 700 mg/L concentration of DB2 dye molecules (after serial dilutions) were experimentally verified by batch mode under fixed conditions: 100 mg/L initial concentration, contact time of (PJBAC-DB2: 60 min; RR152:30 min & GDAC- DB2:60 min; RR152: 90 min). The adsorption reactions had been tested at varied dose environments (100 mg- 400 mg: 50 mg interval) to ensure the required appropriate doses. The residual concentrations were analysed at 540 and 420 nm using UV-Visible spectrophotometer for DB2 and RR152 respectively. The effluent samples were observed to be colourless with the neutral pH against their coloured solutions before treatment. The doses were fixed as 200 mg/300 mg for DB2/RR152 with the removal of 89.2/90.2% in case of PJBAC and 300 mg/450 mg for GDAC with 86.6/84.3% removal as for DB2/RR152 respectively.

The efficacies of PJBAC/GDAC in the removal of Cu(II) from synthetic solution have been explored, at an initial concentration (20 mg/L), contact time (PJBAC: 18 min; GDAC: 15 min) and different doses (20mg-120mg). The synthetic solution for Cu(II) was prepared by dissolving the chemicals in double distilled water as follows: (i) 2.6826

g of  $\text{CuCl}_2$ , (ii) 2.828 g of  $\text{K}_2\text{Cr}_2\text{O}_7$ , (iii) 0.7218 g of  $\text{Zn}(\text{NO}_3)_2$ , (iv) 0.01443 g of  $\text{KNO}_3$  (v) 0.0508 g of  $\text{NaCl}$  (vi) 0.07836 g of  $\text{Mg Cl}_2$  and 0.0382 g of  $\text{KCl}$  and made upto one litre. The corresponding compositions of various ions present in the prepared synthetic solution are listed in table 7.1. A dose of 100mg (PJBAC) and 120mg (GDAC) were required to remove 91.2 % and 90.1% of  $\text{Cu}(\text{II})$  respectively.

**Table 5.20 Composition of synthetic solution-Cu(II)**

| <b>Components<br/>(mg/L)</b>              | <b>Concentration<br/>(mg/L)</b> |
|---|---------------------------------|
| $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ | 20.00                           |
| Sodium                                    | 20.00                           |
| Potassium                                 | 20.00                           |
| Magnesium                                 | 20.00                           |
| Nitrate                                   | 20.00                           |
| Chloride                                  | 20.00                           |
| Zinc                                      | 20.00                           |
| Chromium                                  | 20.00                           |

From the observation made in this chapter, it is found that PJBAC and GDAC express excellent sorption characteristics towards effluent samples, at higher dose level than required for aqueous solutions of respective chosen species. This could be due to few other ions/species in the effluent sample which exhibit marked interferences.

#### **5.14 Statistical Analyses**

The optimized experimental data for the adsorption systems is validated with statistics software tool. Mean, Standard deviation (SD), Standard error of mean values (SE) calculated from descriptive analysis are listed in Table 5.21 and 5.22. A higher descriptive value is observed for DB2 supports the maximum adsorption exhibited by the same, for both PJBAC and GDAC.

The negative correlation values concerning the effects of dosage, pH, initial concentrations and contact time intervals in the case of dye removal indicate a decline in amounts adsorbed at higher parametric values. However, in the case of copper removal, positive correlation values are observed favouring the adsorption capacity to be directly proportional with the influential factors. The probability values ( $P$ )  $< 0.05$  imply the equilibrium data has been well correlated with the statistical results. The  $F > F_{crit}$  values of ANOVA signify the deviation between the sorbed and unadsorbed species of sorption systems. The calculated statistics confirms the results of batch equilibration data.

**Table 5.21 Statistical Analyses – PJBAC**

| System       | parameter      | Descriptive |        |        | Pearson Correlation | P      | ANOVA  |        |
|--------------|----------------|-------------|--------|--------|---------------------|--------|--------|--------|
|              |                | Mean        | SD     | SE     |                     |        | F      | F crit |
| DB2-PJBAC    | Initial.Conc.  | 39.61       | 20.42  | 8.339  | -0.9997             | 0.0060 | 5.2813 | 4.964  |
|              | Dosage         | 41.52       | 20.070 | 10.035 | -0.9711             | 0.0417 | 6.1033 | 5.9873 |
|              | pH             | 45.16       | 1.9295 | 0.8629 | -0.9833             | 0.0003 | 5.587  | 5.317  |
| RR152-PJBAC  | Initial. Conc. | 20.48       | 10.518 | 4.2943 | -0.999              | 0.0031 | 11.726 | 4.964  |
|              | Dosage         | 35.21       | 19.698 | 8.8094 | -0.9062             | 0.0288 | 9.9269 | 5.3176 |
|              | pH             | 23.19       | 1.4846 | 0.6639 | -0.9743             | 0.0057 | 9.15   | 5.317  |
| Cu(II)-PJBAC | Initial. Conc. | 9.829       | 5.4013 | 2.4155 | 0.9974              | 0.0043 | 7.3404 | 5.312  |
|              | Dosage         | 16.318      | 6.555  | 2.9316 | 0.9753              | 0.0310 | 9.1474 | 5.317  |
|              | pH             | 11.36       | 0.9872 | 0.7831 | 0.3568              | 0.0217 | 5.5466 | 5.317  |

Table 5.22 Statistical Analyses - GDAC

| System          | parameter      | Descriptive |        |        | Pearson<br>Correlation | P      | ANOVA  |        |
|-----------------|----------------|-------------|--------|--------|------------------------|--------|--------|--------|
|                 |                | Mean        | SD     | SE     |                        |        | F      | F crit |
| DB2-<br>GDAC    | Initial.Conc.  | 26.65       | 13.623 | 5.5615 | -0.9996                | 0.0032 | 9.3617 | 4.9646 |
|                 | Dosage         | 37.02       | 21.264 | 9.5097 | -0.9324                | 0.0317 | 9.5226 | 5.3176 |
|                 | pH             | 30.83       | 1.6860 | 0.7540 | -0.9909                | 0.0001 | 10.09  | 5.317  |
| RR152-<br>GDAC  | Initial. Conc. | 15.31       | 7.7265 | 3.1543 | -0.9990                | 0.0031 | 13.913 | 4.964  |
|                 | Dosage         | 21.416      | 6.333  | 2.8323 | -0.9829                | 0.0047 | 5.352  | 4.964  |
|                 | pH             | 18.36       | 1.3106 | 0.5861 | -0.9864                | 0.0017 | 6.200  | 5.317  |
| Cu(II)-<br>GDAC | Initial. Conc. | 6.956       | 3.5351 | 1.5811 | 0.9994                 | 0.0077 | 9.423  | 5.317  |
|                 | Dosage         | 18.1        | 10.955 | 4.899  | 0.9020                 | 0.0441 | 7.8373 | 5.317  |
|                 | pH             | 10.68       | 1.578  | 0.599  | 0.3801                 | 0.0249 | 5.804  | 5.317  |