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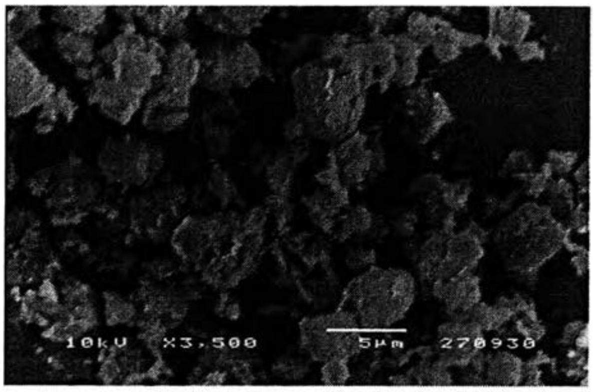
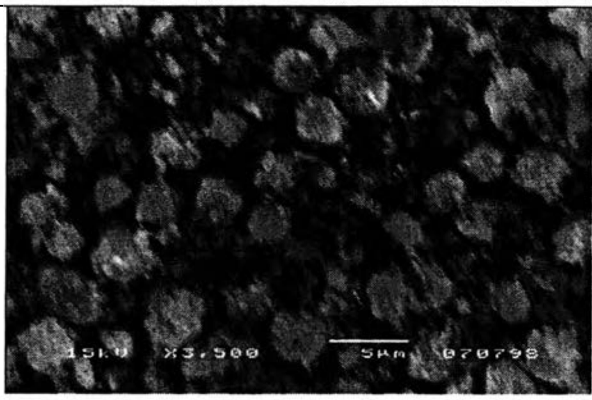
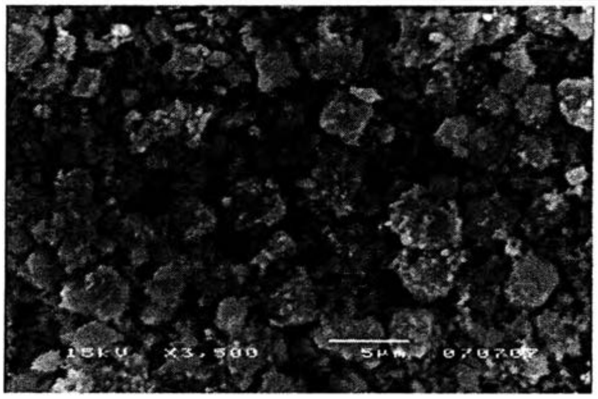
APPENDICES

Appendix A: SEM Images of Molecular Sieve Zeolites

Table A1 SEM images of 1/8″ molecular sieve

Number of batches	**SEM images**
Fresh	 x 3500
5 batches	 x 3500
15 batches	 x 3500

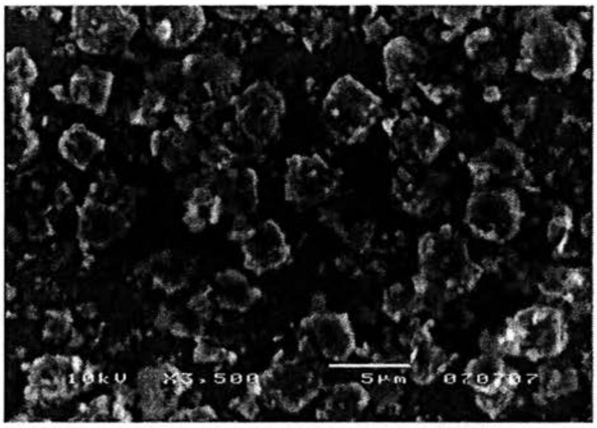
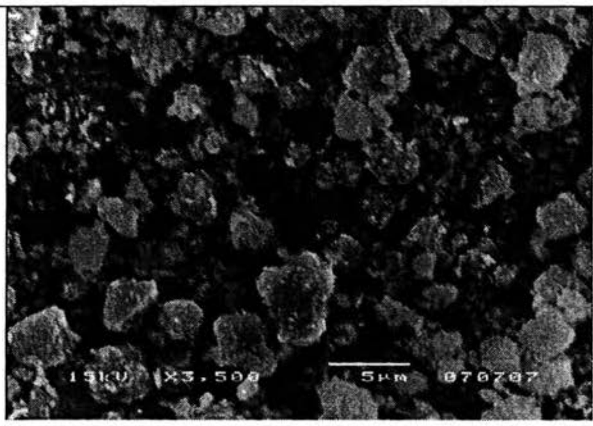
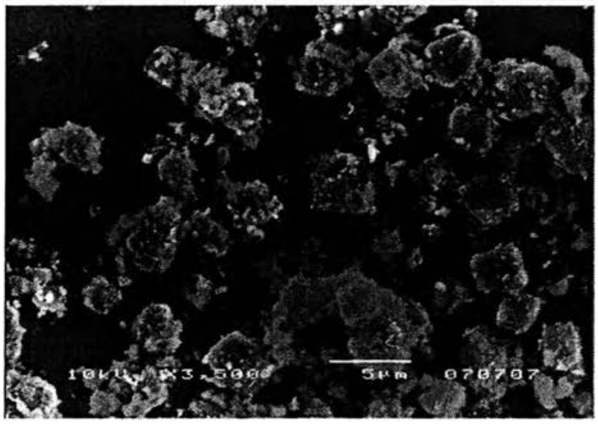
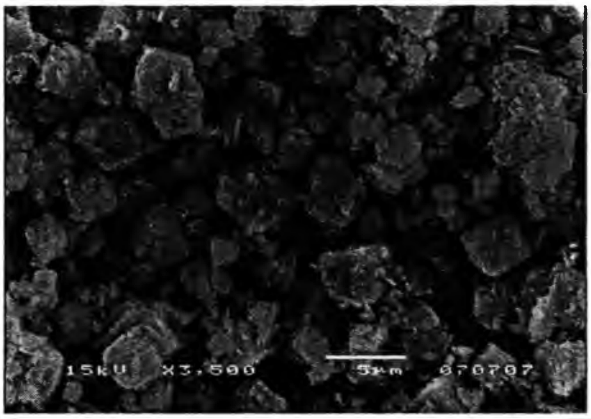
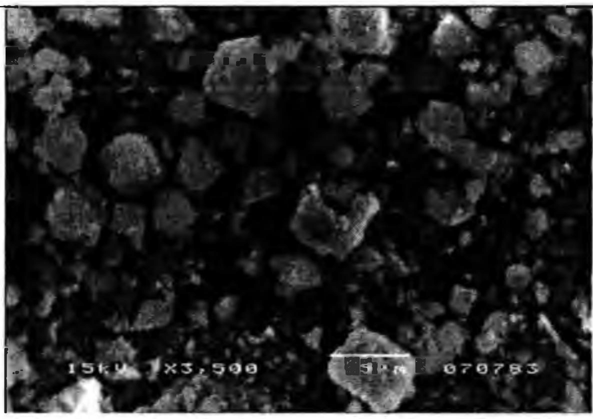
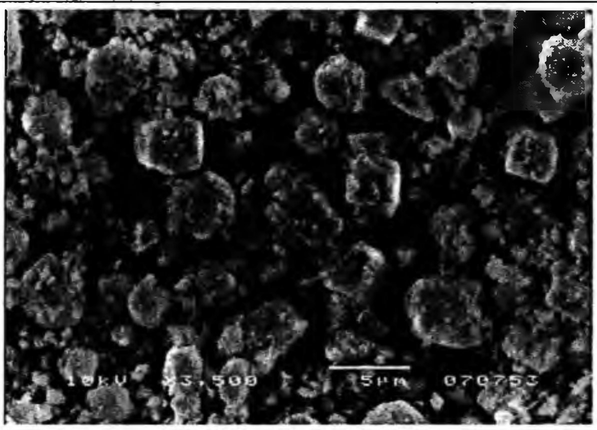
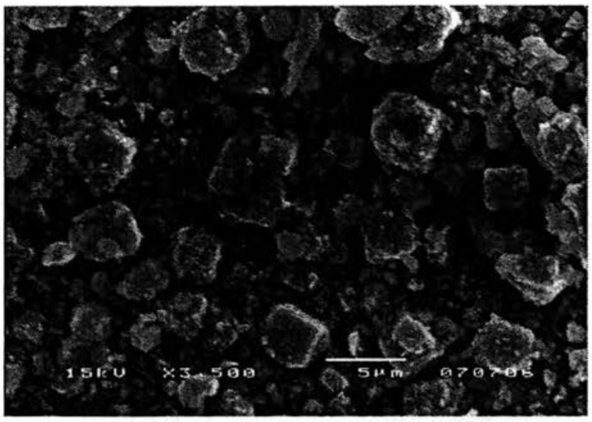
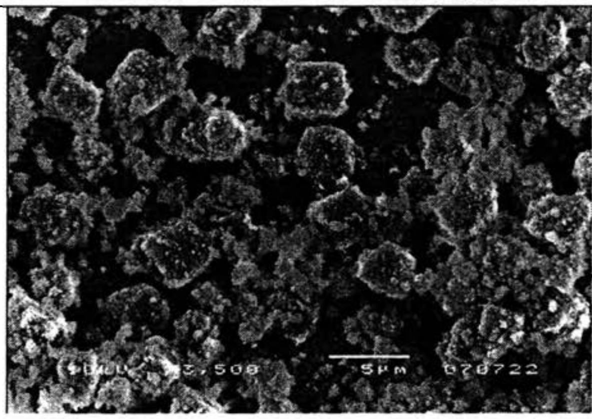
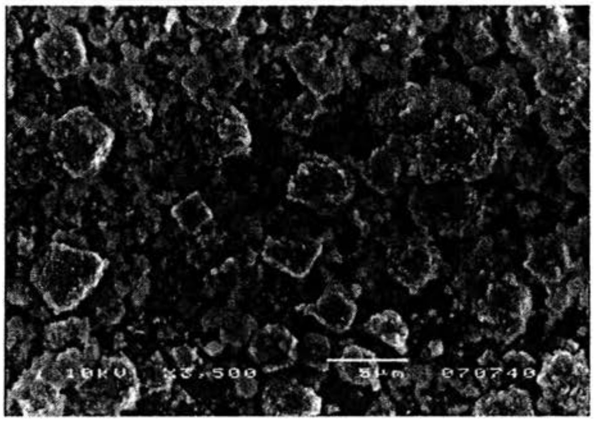
Number of batches	SEM images
25 batches	 x 3500
35 batches	 x 3500
45 batches	 x 3500

Table A2 SEM images of 1/16″ molecular sieve

Number of batches	SEM images
Fresh	 x 3500
5 batches	 x 3500
15 batches	 x 3500

Number of batches	SEM images
25 batches	 x 3500
35 batches	 x 3500
45 batches	 x 3500

Appendix B: Data of Crystal Size Distribution from SEM

Table B1 Data of crystal size distribution of 1/8″ molecular sieve

Crystal size range (micron) \ Number of Batches	%quantity					
	fresh	5 batches	15 batches	25 batches	35 batches	45 batches
0.00-0.49	0	0	0	0	0	0
0.50-0.99	0	0	0	4	2	4
1.00-1.49	0	1	7	26	19	21
1.50-1.99	0	2	24	21	29	35
2.00-2.49	4	22	44	30	35	40
2.50-2.99	47	40	22	15	15	0
3.00-3.49	45	30	3	4	0	0
3.50-3.99	4	4	0	0	0	0
4.00-4.49	0	1	0	0	0	0
Average crystal size (micron)	2.99	2.805	2.195	1.96	1.955	1.8

Table B2 Data of crystal size distribution of 1/16″ molecular sieve

Crystal size range (micron) \ Number of batches	%quantity					
	fresh	5 batches	15 batches	25 batches	35 batches	45 batches
0.00-0.49	0	0	0	0	0	0
0.50-0.99	0	0	2	4	2	2
1.00-1.49	0	3	15	14	20	32
1.50-1.99	5	7	23	30	32	39
2.00-2.49	9	17	42	34	25	17
2.50-2.99	35	33	18	18	20	10
3.00-3.49	33	26	0	0	1	0
3.50-3.99	16	13	0	0	0	0
4.00-4.49	2	1	0	0	0	0
Average crystal size (micron)	3.000	2.82	2.04	1.985	1.965	1.75

Appendix C: Bed Void Fraction

The bed void fraction of both fresh and deactivated adsorbents can be obtained from Figure A1.

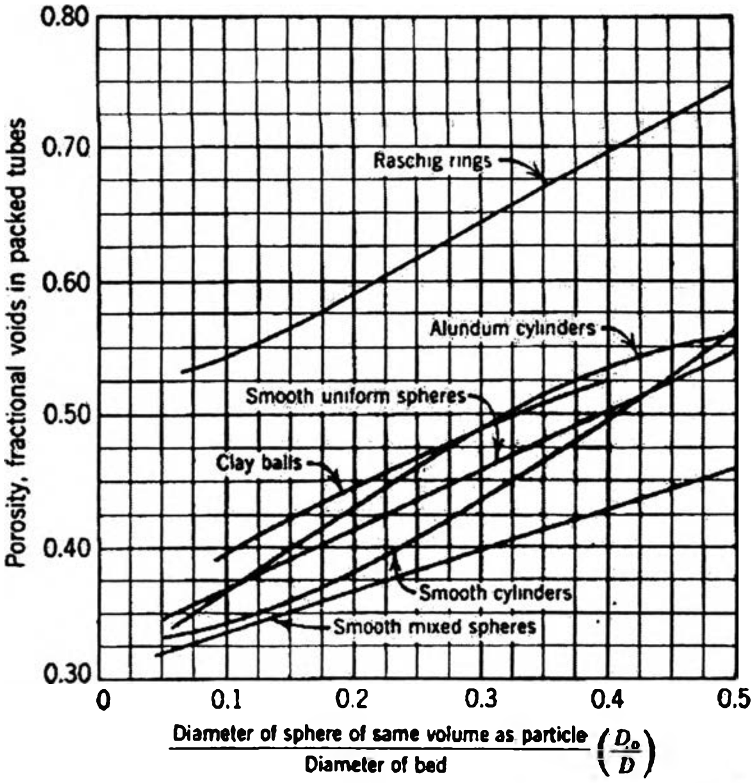


Figure C Porosity as a function of the ration of particle diameter to bed diameter (Leva, 1947).

Appendix D: Mass Transfer Coefficient

The mass transfer coefficient, k, of both fresh and deactivated adsorbents can be calculated by following equation (Murillo *et al.*, 2004).

$$\frac{1}{k} = \frac{R_p}{3k_f}K + \frac{R_p^{\ 2}}{15\varepsilon_p D_e}K \tag{D1}$$

where

k	=	mass transfer coefficient (1/sec)
k_f	=	fluid mass transfer coefficient (m/s)
R_p	=	radius of pellet (m)
K	=	equilibrium constant
ε_p	=	porosity of particle
D_e	=	effective diffusivity (m^2/s)

The effective diffusivity (D_e), which was used in equation D1, is related to Knudsen diffusivity (D_k) and molecular diffusivity (D_m), as follows.

$$\frac{1}{D_e} = \frac{\tau}{\varepsilon_p}\left(\frac{1}{D_m} + \frac{1}{D_k}\right) \quad \text{(D2)}$$

Also, the Knudsen diffusivity (D_k) and molecular diffusivity (D_m) can be obtained from equations D3 and D4, respectively.

$$D_k = 9.7x10^3 r_p \left(\frac{T}{M}\right)^{1/2} \quad \text{(D3)}$$

$$D_m = \frac{0.0018583T^{3/2}(1/M_A + 1/M_B)^{1/2}}{P * \sigma_{AB}^2 \Omega_{AB}} \quad \text{(D4)}$$

r_p	=	mean pore radius (cm)
T	=	absolute temperature (K); and
M	=	molecular weight of diffusing species
M_A	=	average molecular weight of bulk species
M_B	=	molecular weight of adsorbate species
P	=	total pressure
σ_{AB}	=	collision diameter from Lennard-Jones potential; and
Ω_{AB}	=	collision integral

Appendix E: Breakthrough Curve Prediction Program

This program can be used for predict the breakthrough curve by input the degree of deacticvation because the parameters in mass balance equation and the adsorption isotherm were written as a function of the degree of deactivation.

```
        IMPLICIT NONE
        DOUBLE PRECISION RHR,Velo,Alu,Bmol,Smol,DA,Db,Ds
        DOUBLE PRECISION C0,C,q,dt,KC,Kq,time,Csat,RH
        DOUBLE PRECISION v1,v,e_A,e_B,e_C
        INTEGER i,j,imax,jmax,n
        PARAMETER(imax=90,jmax=5000)
        DIMENSION C(imax,jmax),q(imax,jmax),v(imax,jmax)
        DIMENSION KC(4,imax,jmax),Kq(4,imax,jmax)

c       ................INITIAL CONDITION................
        dt = 0.008
        time=0
        j=1                             !at time = 0
        Csat=1.2794E-03
        C(1,j)=C0

        OPEN(9,file='breakthrough.txt')  !open file to receive input values
        READ(9,*)Alu,Bmol,Smol,RHR,Velo
        RH = RHR
        C0 = RH*Csat/100        !inlet concentration (mol/l)
        v1= Velo                ! Superficial velocity
        DA = Alu
        Db     = Bmol
        Ds     = Smol
        e_A=-0.0000002834*DA**2-0.00001597 *DA+0.3698157  !void fraction as
a function of degree of deactivation
        e_B=-0.00000003348 *Db**2-0.000004606*Db+0.3448013
        If(Ds.LE.62.38) then
                e_C=-0.0004604*Ds**0.028037+0.329731
        Else
            e_C=0.3691822-0.001106*Ds+7.44E-06*Ds**2
        END if
    v(1,j)=v1/e_A


    WRITE(*,*)'Input Values'  ! show input values
        WRITE(*,*)'%deactivation of alumina=',DA
        WRITE(*,*)'%deactivation of 1/8"4A Molsiv=',Db
        WRITE(*,*)'%deactivation of 1/16"4A Molsiv=',Ds
```

```
      WRITE(*,*)'%Relative Humidity=',RH
      WRITE(*,*)'Superficial Velocity=',v1,'(cm/s)'
      WRITE(*,*)'----------------------'
      WRITE(*,*)'   Running Program    '
      WRITE(*,*)'     Please Wait      '
      WRITE(*,*)'----------------------'
  OPEN(5,file='velocity.dat')

      DO i=2,imax

        C(i,j)=0
        q(i,j)=0

      END DO

      OPEN(1,file='data1.dat')

      DO i=1,imax
        WRITE(1,101)time,i,j,C(i,j),q(i,j),v(i,j)
      END DO

        Call RK4(j,C,q,v,imax,jmax,KC,Kq,dt,v1,DA,Db,Ds)

      GOTO 20

10    OPEN(2,FILE='DATA2.DAT')

      DO i=2,imax

        READ(2,102)time,C(i,1),q(i,1),v(i,1),(KC(n,i,1),n=1,4)
     1  ,(Kq(n,i,1),n=1,4)

      END DO

20    DO j=2,jmax

        DO i=2,imax

                v(1,j)=v1/e_A

                C(1,j)=C0

          C(i,j)=C(i,j-1)+(dt/6)*(KC(1,i,j-1)+2*KC(2,i,j-1)
     1          +2*KC(3,i,j-1)+KC(4,i,j-1))

          q(i,j)=q(i,j-1)+(dt/6)*(Kq(1,i,j-1)+2*Kq(2,i,j-1)
     1          +2*Kq(3,i,j-1)+Kq(4,i,j-1))
```

```
          END DO

          Call  RK4(j,C,q,v,imax,jmax,KC,Kq,dt,v1,DA,Db,Ds)

        END DO


C       .............The Results.....................

        DO j=1,jmax

          time=time+dt                    !sec

        END DO

        CLOSE(2)
        OPEN(2,file='data2.dat')
        DO i=2,imax

          WRITE(2,102)time,C(i,jmax),q(i,jmax),v(i,jmax)
        1   ,(KC(n,i,jmax),n=1,4),(Kq(n,i,jmax),n=1,4)

          WRITE(5,102)time,C(i,jmax),q(i,jmax),v(i,jmax)

          OPEN(3,file='RESULT.dat')
          IF(i.EQ.imax)THEN
                WRITE(3,102)time,C(i,jmax),q(i,jmax),v(i,jmax)

          ELSE
          END IF

        END DO

        CLOSE(2)
c    ............Check Running Loop...............................

        IF(time.LT.400000) THEN
        GOTO 10
        ELSE
        GOTO 999
        END IF

C      .........Format for Input and Output Statements.......
 99     FORMAT(E15.9,E15.9,E15.9,E15.9,E15.9)
101     FORMAT(F13.3,I3,I6,2E15.9,8E15.9)
102     FORMAT(F13.3,3E15.9,8E15.9)
```

```
999  STOP
       CLOSE(3)
     END

c
*******************************************************************
******
     SUBROUTINE RK4(j,C,q,v,imax,jmax,KC,Kq,dt,v1,DA,Db,Ds)

          IMPLICIT NONE
          DOUBLE PRECISION DA,Db,Ds,v1
          DOUBLE PRECISION CC,qq,C,q,dC_dt,dq_dt,dt,KC,Kq,v
          INTEGER i,j,imax,jmax
          DIMENSION C(imax,jmax),q(imax,jmax),dC_dt(imax,jmax)
          DIMENSION dq_dt(imax,jmax),KC(4,imax,jmax),Kq(4,imax,jmax)
          DIMENSION CC(imax,jmax),qq(imax,jmax),v(imax,jmax)

c         ...............Define Parameter......................

          !v1= Velo             ! Superficial velocity
          !DA = Alu
          !Db    = Bmol
          !Ds    = Smol

     DO i=1,imax

            CC(i,j)=C(i,j)
            qq(i,j)=q(i,j)

      END DO

          Call ODEs_EQ(j,imax,jmax,CC,qq,dC_dt,dq_dt,v,v1,DA,Db,Ds)

      DO i=2,imax

            KC(1,i,j)=dC_dt(i,j)
            Kq(1,i,j)=dq_dt(i,j)
            CC(i,j)=CC(i,j)+(dt/2)*KC(1,i,j)
            qq(i,j)=qq(i,j)+(dt/2)*Kq(1,i,j)

       END DO

            Call ODEs_EQ(j,imax,jmax,CC,qq,dC_dt,dq_dt,v,v1,DA,Db,Ds)

       DO i=2,imax
```

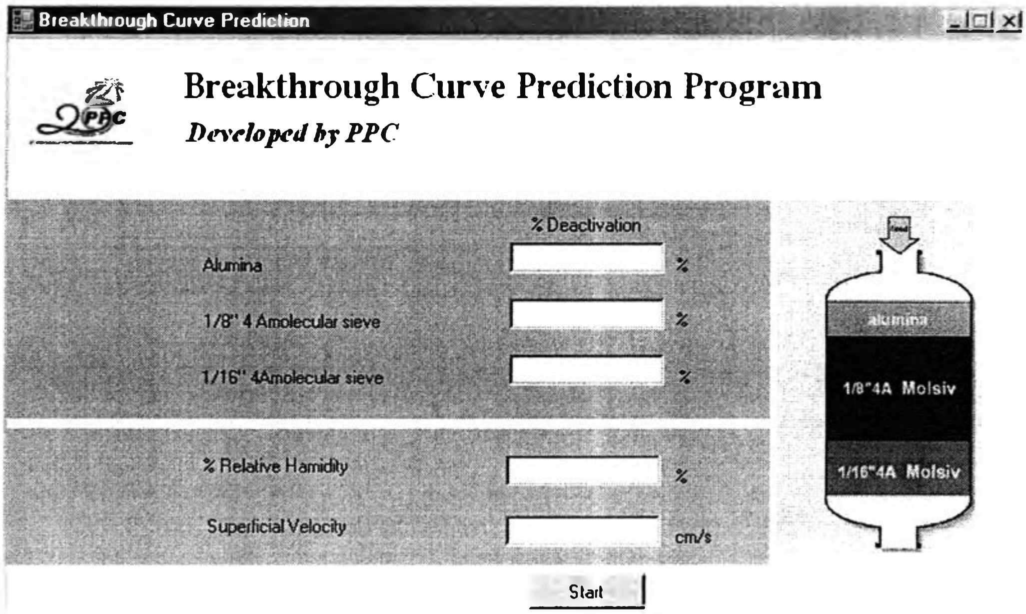
```
          KC(2,i,j)=dC_dt(i,j)
          Kq(2,i,j)=dq_dt(i,j)

          CC(i,j)=CC(i,j)+(dt/2)*KC(2,i,j)
          qq(i,j)=qq(i,j)+(dt/2)*Kq(2,i,j)

      END DO

          Call ODEs_EQ(j,imax,jmax,CC,qq,dC_dt,dq_dt,v,v1,DA,Db,Ds)

      DO i=2,imax

          KC(3,i,j)=dC_dt(i,j)
          Kq(3,i,j)=dq_dt(i,j)

          CC(i,j)=CC(i,j)+(dt)*KC(3,i,j)
          qq(i,j)=qq(i,j)+(dt)*Kq(3,i,j)

      END DO

          Call ODEs_EQ(j,imax,jmax,CC,qq,dC_dt,dq_dt,v,v1,DA,Db,Ds)

      DO i=2,imax

          KC(4,i,j)=dC_dt(i,j)
          Kq(4,i,j)=dq_dt(i,j)

       END DO

       Return

       End

c
*******************************************************************
******
    SUBROUTINE ODEs_EQ(j,imax,jmax,c,q,dC_dt,dq_dt,v,v1,DA,Db,Ds)

        IMPLICIT NONE
        DOUBLE PRECISION
c,q,dC_dt,dz,L,d2C_dz2,DL_A,v1,e_A,e_B,e_C,dq_dt
        DOUBLE PRECISION k1,k2,k3
        DOUBLE PRECISION
dC_dz,qstar,a1,a2,a3,b1,db_A,db_B,db_C,DL_B,DL_C
        DOUBLE PRECISION Csat,b2,t1,d1,b3,t2,d2,RT,Pa,Psat,P0
        DOUBLE PRECISION v,dv_dz,Ct
        DOUBLE PRECISION rd_A,rd_B,rd_C
```

```
      DOUBLE PRECISION DA,Db,Ds
      INTEGER i,j,imax,jmax
      DIMENSION C(imax,jmax),q(imax,jmax),dC_dt(imax,jmax)
       DIMENSION d2C_dz2(imax,jmax),dC_dz(imax,jmax),qstar(imax,jmax)
      DIMENSION dq_dt(imax,jmax),v(imax,jmax),dv_dz(imax,jmax)

      !v1= Velo            ! Superficial velocity
      !DA = Alu
      !Db    = Bmol
      !Ds    = Smol


c     ...............Define Parameter......................

      L =8.8                                  ! Total bed length
      dz = L/ (imax-2)                        ! Step size for length
      Ct=0.040902639                          ! P/RT
      RT=24.45388                             ! RT
      Pa=1.0133E+08                           ! atmospheric pressure
      P0=1.01325E+06

c  ..........Parameter of Adsorber Zone-A (Activated Alumina)................

      db_A =0.73743                           ! Bulk density of adsorbent
Zone-A
      DL_A=0.028249704                   ! Axial dispersion through Zone-A
      e_A=-0.0000002834*DA**2-0.00001597*DA+0.3698157 !Void fraction
ofZone-A
      rd_A=(-0.0053*DA**2-0.1761*DA-195.93)/10


c  ..........Parameter of Adsorber Zone-B (UI-94 1/8")................

      db_B=0.66529                       ! Bulk density of adsorbent Zone-B
      DL_B=0.027733066                   ! Axial dispersion through Zone-B
      e_B=-0.00000003348*Db**2-0.000004606*Db+0.3448013 !Void fraction of
C     Zone-B
      rd_B=(-0.0026461*Db**2-0.0098614*Db-283.2747)/10


c     ........Parameter of Adsorber Zone-C (UI-94 1/16")................

      db_C =0.66529                           ! Bulk density of adsorbent
Zone-C
```

```
      DL_C=0.027170115                    ! Axial dispersion through Zone-C
      If(Ds.LE.62.38) then       ! Void fraction of Zone-C
            e_C=-0.0004604*Ds**0.028037+0.329731
            rd_C=(-53.02706*Ds**0.0287672-1167.399)/10

      Else
            e_C=0.3691822-0.001106*Ds+7.44E-06*Ds**2
            rd_C=(3637.953-134.6133*Ds+0.9053535*Ds**2)/10
      END if
c    ........Adsorption Isotherm Constant Parameter.........
      k1 =-0.000000001345*DA**2-0.0000003543*DA+0.00006169   ! Effective
      overall mass transfer coeficient
      k2 =-0.0000000008449*Db**2-0.0000003555*Db+0.00004525
      k3 =-0.000000007212*Ds**2-0.0000007993*Ds+0.0001557
      j=j
c    ..........Zone-A (Silica gel)................
      Csat=1.2794E-03
      a1=1.197121-0.0290791*DA+0.0001773*DA**2    ! For Freundlich-
Isotherm
      if(DA.LE.67.9) then
            b1= 2.09E-05*DA**2.510129+0.8289536
      Else
            b1=-0.0005461*DA**2+0.0834425*DA-1.48687
      END if
      DO i=2,4

         qstar(i,j)=a1*((100*C(i,j)/Csat)**b1)

         dq_dt(i,j)=k1*(qstar(i,j)-q(i,j))

         d2C_dz2(i,j)=(1/(dz**2))*(C(i+1,j)-2*C(i,j)+C(i-1,j))

         dC_dz(i,j)=(1/(2*dz))*(C(i+1,j)-C(i-1,j))

         dv_dz(i,j)=-(v1*rd_A)/(e_A*P0*((2*rd_A*(i-1)*dz/P0)+1)**1.5)

          v(i,j)=dz*(dv_dz(i,j))+v(i-1,j)

      dC_dt(i,j)=DL_A*d2C_dz2(i,j)-v(i,j)*dC_dz(i,j)
    1  -((1-e_A)/e_A)*dq_dt(i,j)*db_A/1.8-C(i,j)*dv_dz(i,j)


      END DO
c    ..........Zone-B (Mol Siv 1/8")................

      Psat=3169904.00
```

```
      a2=-1.269777*Db**0.5740309+17.50962
      b2=70.87607*Db**0.3887716+20.02354
      t1=-1.038514*Db**0.1542384+2.902765
      d1=0.0425293*Db**0.4721149+0.1048701
      P0=P0*((2*rd_A*0.3/P0)+1)**0.5
      DO i=5,60

            qstar(i,j)=(a2*b2*C(i,j)/Csat)/(((1+(b2*C(i,j)/ Csat)**t1)**
     1      (1/t1))*(1-c(i,j)/Csat)**d1)

            dq_dt(i,j)=k2*(qstar(i,j)-q(i,j))

           d2C_dz2(i,j)=(1/(dz**2))*(C(i+1,j)-2*C(i,j)+C(i-1,j))

           dC_dz(i,j)=(1/(2*dz))*(C(i+1,j)-C(i-1,j))

            dv_dz(i,j)=-(v(4,j)*rd_B)/(P0*((2*rd_B*(i-4)*dz/P0)+1)**1.5)

            v(i,j)=dz*(dv_dz(i,j))+v(i-1,j)

            v(5,j)=v(5,j)*e_A/e_B

      dC_dt(i,j)=DL_B*d2C_dz2(i,j)-v(i,j)*dC_dz(i,j)
     1 -((1-e_B)/e_B)*dq_dt(i,j)*db_B/1.8-C(i,j)*dv_dz(i,j)


      END DO
c   ..........Zone-C (Mol Siv 1/16")................
      a3=-1.441778*Ds**0.5831572+18.0277
      b3=15.51344*Ds**0.7242306+24.18842
      t2=-1.740397*Ds**0.1264964+3.877282
      d2=0.0262151*Ds**0.7678798+0.1262725
      Psat=3169904.00
      P0=P0*((2*rd_B*5.6/P0)+1)**0.5
      DO i=61,89

            qstar(i,j)=(a3*b3*C(i,j)/Csat)/(((1+(b3*C(i,j)/ Csat)**t2)**
     1      (1/t2))*(1-c(i,j)/Csat)**d2)

            dq_dt(i,j)=k3*(qstar(i,j)-q(i,j))

            d2C_dz2(i,j)=(1/(dz**2))*(C(i+1,j)-2*C(i,j)+C(i-1,j))

            dC_dz(i,j)=(1/(2*dz))*(C(i+1,j)-C(i-1,j))

            dv_dz(i,j)=-(v(60,j)*rd_C)/(P0*((2*rd_C*(i-60)*dz/P0)+1)**1.5)
```

```
              v(61,j)=v(61,j)*e_B/e_C

              v(i,j)=dz*(dv_dz(i,j))+v(i-1,j)

              dC_dt(i,j)=DL_C*d2C_dz2(i,j)-v(i,j)*dC_dz(i,j)
1             -((1-e_C)/e_C)*dq_dt(i,j)*db_C/1.8-C(i,j)*dv_dz(i,j)


      END DO

      i=imax
         qstar(imax,j)=qstar(imax-1,j)

         dq_dt(imax,j)=dq_dt(imax-1,j)

         d2C_dz2(imax,j)=0

         dC_dz(imax,j)=0

         dC_dt(imax,j)=dC_dt(imax-1,j)

         dv_dz(imax,j)=dv_dz(imax-1,j)

         v(imax,j)=v(imax-1,j)

      Return

      End
```



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