

Effect of Different Conditions on the Sorption Behavior of Co^{2+} Using Celatom- ZeoliteY Composite

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Abstract—Composite of Celatom-ZeoliteY (Cel-ZY) was used to remove cobalt ion from an aqueous solution using batch mode. ZeoliteY has successfully superimposed on Celatom FW-14 surface using hydrothermal treatment. The product was synthesized as a novel of hierarchical porous material. It was observed from the results that Cel-ZY has higher ability to remove cobalt ions than the pure ZeoliteY powder (PZY) synthesized under the same conditions. Several parameters were studied in this project to investigate the effect of removal cobalt ion such as pH and initial cobalt concentration. It was clearly observed that the uptake of cobalt ions was affected with increase these parameters. The results proved that the product can be used effectively to remove Co^{2+} ions from wastewater as an environmentally friendly alternative.

Keywords—Adsorption, Celatom-Zeolite, Cobalt ions, Isotherm models.

I. INTRODUCTION

SEVERAL techniques are using for treating industrial and domestic wastewater, such as chemical precipitation, sedimentation, ion exchange, thermal evaporation and reverses osmosis membranes. These techniques (along with others) aim to release decontaminated effluents into the environment and allow the conditioning of waste concentrates for disposal [1], [2]. Adsorption is widely used and considered a most powerful technique according to the low cost, easy technique, efficient, abundance and availability [3]. Activated carbon is considered as the most competitive media to the adsorbent materials as a powder or granular due to its properties such as porous structure, meso and/or micro porous which give high surface area and capacity for the adsorption of undesirable ions and organism molecules. On the other hand, the high cost production and regeneration processes are considered the main drawbacks from the industries and looking for more economic, easier and efficient adsorbent materials.

The cost and efficiency of purification techniques have become increasingly important in implementing industrial waste disposal of alternative ion exchange media [4], [5].

Diatoms are microscopic algae, which are found in every aquatic environment, formed by fragments of armor (skeletons) of diatom algae. Diatomite rock belongs to the group of silica-bearing materials. ¹It has special properties,

such as low density, high porosity, low thermal conductivity [6], high melting point (1400 °C to 1750 °C depending on impurities), being chemically inert [7], high permeability and high surface area [8], [9]. These properties make it very useful for a wide range of applications.

Zeolites are considered one of the most important and naturally abundant ion exchange media [10], [11]. Zeolites are tetrahydrate aluminosilicate framework with very open three dimensional structures. Zeolites are principally comprised of $[\text{SiO}_4]^{-4}$ and $[\text{AlO}_4]^{-5}$ [10], have pores of uniform size from 5 to 13 Å [12]. Cavities and channels are found within Zeolite structures; they form about 50% of the total volume allow cations such as Na^+ , K^+ , Ca^{2+} and Mg^{2+} and water molecules to be held within Zeolites frameworks. These cations have a high degree of mobility and ability to exchange with other cations. In addition, the internal structure of the Zeolite allows for regular arranged pores. These structural properties make it a useful adsorbent for metallic ions and water vapour [11], [13]. However, due to the diffusivity problem of small particles of Zeolite powder, this has caused an inhibition of Zeolite use in the industry.

In this work, Zeolite crystals were superimposed onto Celatom surfaces in this experiment to build a hierarchical structure. This new composite structure of macroporous Celatom/microporous ZeoliteY is suggested as a method to overcome the diffusivity problem of Zeolite powder [14].

II. EXPERIMENTAL WORK

A. Seeding Process

A nano-crystal solution of Zeolite was prepared by grinding a commercial ZeoliteY (supplied by PQ Corporation) for 32h using 1mm ceramic beads (zirconium oxide) ball mill grinder as the grinder media. The ground product was used for seeding Diatomite using the same procedure reported in our previous work with different kinds of seeded carbon [14]. This method is considered more economic in time, energy and cost than the expensive and complex synthesis of colloidal Zeolite seeds [15].

Dynamic Light Scattering (DLS) and Transmission Electron Microscopy (TEM) were used to characterize the fine particle size of ground ZeoliteY in solution.

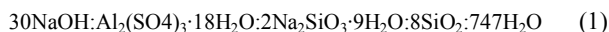
For seeding process the ground ZeoliteY was distributed and attached onto Celatom surface using 6h sonic-bath and 20:1 Celatom-ZeoliteY weight ratio.

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B. Preparation of Zeolite-Y Crystal on Celatom

The hydrothermal treatment of syntheses solution was applied using the molar ratio 1 [14].



Some amount of sodium metasilicate and Celatom were used as silica source. Sodium hydroxide was used to provide cation and alkaline medium. While, aluminum sulphate octadecahydrate was used as aluminum source. The ingredient of the growth gel is presented in Table I.

TABLE I
SHOWS THE AMOUNT OF EACH INGREDIENT FOR THE FORMATION OF THE GROWTH GEL

Component	Mass g	Supplier
NaOH	2.5	Aldrich
$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	1.38	Fisher Scientific
$\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$	1.18	Aldrich
H_2O	28	-----
Celatom	1	-----

Celatom FW-14 was used as silica source using Celatom: silica molar ratio 4:1. [14] It was estimated that the silica in the Celatom provides the exact silica requirement for ZeoliteY.

The mixture was added to fill two-thirds of the volume of an autoclave, sealed tightly and left in the oven for 4h at 100°C. The amount of Zeolite on the diatom surface for sample was estimated by the Celatom weight difference before and after hydrothermal process.

X-Ray powder Diffractometer (XRD), Energy Dispersive X-Ray Analysis (EDAX) and Scanning Electron Microscope (SEM) were used to characterise the pattern, identify the elemental composition and show the morphology of composite Celatom-ZeoliteY. While, Nitrogen adsorption method was used to assess the surface area for Celatom, C-ZY and PZY samples using BET method.

III. BATCH SORPTION STUDIES

Kinetic processes were conducted using batch mode at room temperature and pH 6. 100 ml capacity plastic bottles were used for this purpose. 50 mL of cobalt solutions were mixed with 0.1g Celatom-ZeoliteY. A 600 ppm concentration stock Co^{2+} solution was prepared using $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ [14]. The Co^{2+} solution was diluted many times to get different Co^{2+} concentrations. The mixing speed was kept constant at room temperature for all runs to ensure equal mixing. The samples were taken from the solution after 0.5, 1.5 and 3.5h. After that the composite of Celatom-ZeoliteY was dried overnight at 50°C for different characterisations such as XRD, EDAX and SEM to investigate the integrity of the micro/macropores structure, bulk's composition and surface morphology, respectively.

To study the effect of ZeoliteY on the Celatom surface, C-ZY and pure Zeolite-Y as powder were treated separately at the same conditions described above. The ICP-OSE device

was used to measure the concentrations of Co^{2+} ion before and after the treatment. The machine was calibrated with three standards solutions 2, 8 and 15 ppm Co^{2+} solutions. All samples were diluted to be within this range of concentrations before analysis.

The amount of adsorbed Co^{2+} ions at time t, $q(t)$ (mgCo.g^{-1}) was calculated using (1) [16].

$$q(t) = \frac{C_o - C_t}{m} \cdot V \quad (1)$$

where v and m are the volume of Co^{2+} ions solution (L) and the amount of the adsorbent, respectively. C_o and C_t are the initial concentration and concentration at any time of Co^{2+} ion, respectively.

IV. STUDY THE EFFECT OF pH AND INITIAL CONCENTRATION ON Co^{2+} UPTAKE

Different Co solutions varying pH 2, 4 and 6 were prepared to study the effect of pH variation on the uptake of Co^{2+} ions. Three plastic containers of 100 mL were filled with 50mL from the stock Co^{2+} solution as an initial concentration. 1 M HCl was used to adjust the pH value of solutions. A 0.1g of Cel-ZY was added to the Co^{2+} solutions and mixed for 3h to ensure that the system reached the equilibrium situation at room temperature. Also, the effect of initial Co^{2+} concentrations using 250,350 and 600 ppm was studied using 50 mL Co^{2+} solutions and 0.1g adsorbent media at the pH 5-6 at room temperature.

V. ISOTHERM MODEL (LANGMUIR AND FREUNDLICH EQUATIONS)

According to kinetic experiments, 3h was used to study the isotherm model of Cel-ZY using Langmuir and Freundlich models. For this purpose, 50 mL of Co^{2+} solution with different concentrations were mixed with Cel-ZY as adsorbent media at 25°C and pH 5-6.

Equations (2) and (3) describe the non-linear Langmuir and Freundlich models, respectively [17].

$$q_e = \frac{q_m K_a C_e}{1 + K_a C_e} \quad (2)$$

where q_e is the equilibrium Co^{2+} uptake (mg.g^{-1}), C_e represents the equilibrium concentration (mg.L^{-1}), K_a is sorption equilibrium constant (L.mg^{-1}) and q_m is the maximum adsorption capacity (mg.g^{-1}).

$$q_e = K_F (C_e)^{(1/n)} \quad (3)$$

where K_F and n are the constants of Freundlich isotherm. K_F ($\text{mg.g}^{-1} (\text{L.mg}^{-1})^{1/n}$) is the adsorption capacity of the sorbent and n can be used as an indicator of how favorable the adsorption route Whilst, Equation 4 was used to study the best

fitting to the experimental data with the two data models by calculating the coefficients of determination (r^2) [18].

$$r^2 = \frac{\sum (q_{e,model} - q_{e,av})^2}{\sum (q_{e,model} - q_{e,av})^2 + \sum (q_{e,model} - q_{e,exp})^2} \quad (4)$$

where $q_{e,model}$ is the equilibrium capacity obtained from the isotherm model, $q_{e,exp.}$ is the equilibrium capacity obtained from experiment, and $q_{e,av}$ is the average of q_e .

The values of the separation factor R_L were used to indicate the favorable adsorption using Langmuir constant K_a ($L \cdot mg^{-1}$) as described in (5) [19].

$$R_L = \frac{1}{1 + K_a C_o} \quad (5)$$

where C_o is the highest initial concentration of Cobalt ($mg \cdot L^{-1}$), the value of R_L indicates the type of isotherm to be favorable ($0 < R_L < 1$), unfavorable $R_L > 1$, linear $R_L = 1$ or irresolvable $R_L = 0$.

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V1. RESULTS AND DATA ANALYSIS

A. Results of Product Characterizations, Seeding and Crystal Growth.

ZeoliteY after grinding process was collected and investigated after 32 hr using XRD as shown in Fig. 1. The range of fine particle size was found between 88-270 nm with average range 129 nm using DLS as shown in Fig. 2. TEM results are shown in Fig. 3 to investigate the product of fine particle size of the ground Zeolite powder, which shows good morphology as shown in Fig. 3.

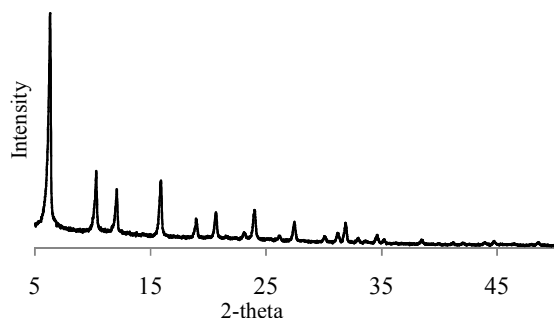


Fig. 1 XRD pattern of suspension of dried ground commercial ZY using ball mill

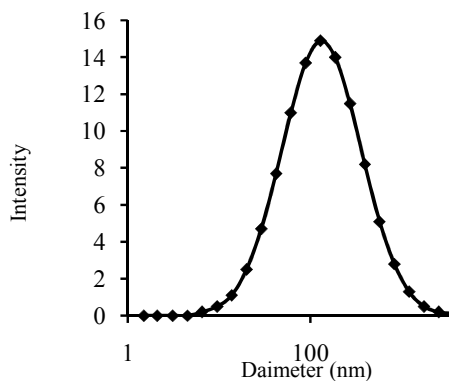


Fig. 2 DLS shows the distribution of particle sizes for ball milled product

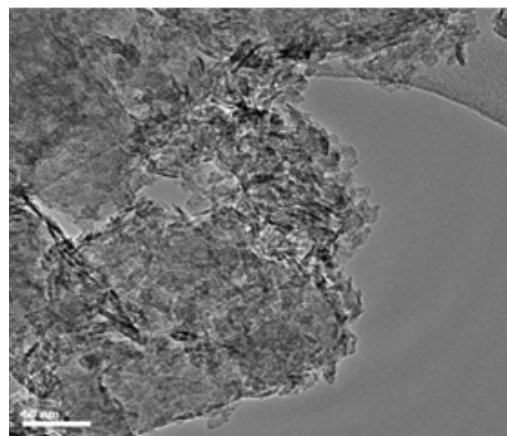


Fig. 3 TEM images show the morphology of ground commercial ZY scale bar = 100 n

It was observed that ZeoliteY has combination on the Celatom surfaces using XRD as shown in Fig. 4. The XRD patterns shows the characteristic reflections of Zeolite Y at 6.12° , 10° , 11.73° and 15.43° [20] presented with the Celatom-ZeoliteY samples, while the reflection at 22° recorded for Celatom. The surface morphology of each samples were observed using SEM before and after the hydrothermal process Fig. 5, the results show good organized porosity and cristanility of ZeoliteY on Celatom surfaces. The pores are arranged and organized like arrays on Celatom surfaces.

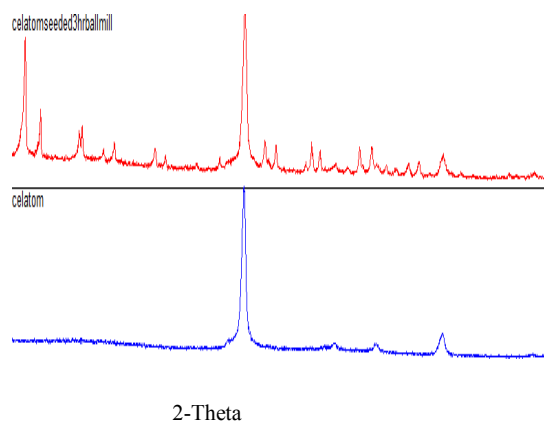
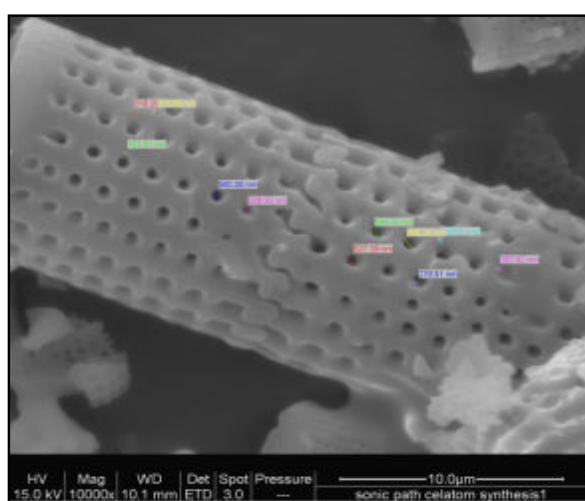
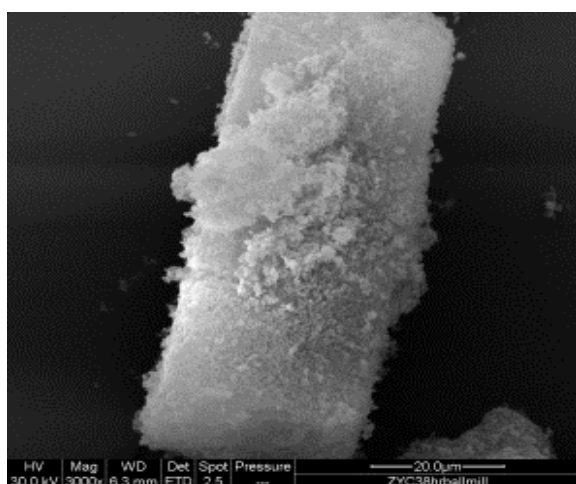


Fig. 4 The X-Ray diffraction pattern of (a-) Pure Celatom and (b-) Celatom-ZY after 4h hydrothermal treatment



(a)



(b)

Fig. 5 Celatom FW-14 (a) - without ZY (scale bar =10 nm) and (b) - in conjunction with ZY (scale bar = 20 nm)

The results of surface area of all samples are shown in Table II were measured by Nitrogen adsorption method.

TABLE II
SHOW THE SURFACE AREA OF THE THREE SAMPLES PURE CELATOM, PZY AND COMPOSITE OF CELATOM-ZY

Materials	BET surface area ($\text{m}^2 \cdot \text{g}^{-1}$)
Pure Celatom	98.4
PZY	27
Celatom-PZY	26.7

B. Results of the Ion Exchange Process

The adsorption of Co^{2+} ions onto Celatom-ZeoliteY media was performed at room temperature. Inglezakis, et al., Panayotova et al., and Doula. El al., [21]-[23] have observed the typical Zeolite isotherm for Pb^{2+} , Cr^{2+} , Fe^{3+} , Cu^{2+} were achieved at room temperature indicating an exothermic character of adsorption process. The batch operation was conducted by varying the adsorbent types (Cel-Y and PZY) while other conditions such as temperature, solution volume, stirring time and initial concentration of Co^{2+} solution were unchanged. SEM images showed the crystals of ZeoliteY on the Celatom surfaces were still stuck after the adsorption process Fig. 6. While, Fig. 7 show that Co ion has appeared clearly in the EDAX spectra after the treatment. The results show that Cel-ZY has achieved a maximum adsorption capacity q_e ($140 \text{ mgCo} \cdot \text{g}^{-1}$) as shown in Fig8. The higher removal capacity of Co^{2+} ions was observed with Cel-ZY due to the high ion-exchange capacity, larger framework channels and higher number of ion-exchange sites of ZeoliteY aided by the present of Celatom. While the PZY powder has been achieved lower than Cel-ZY due to the diffusivity problem of Zeolite-Y without scaffold support as mention in section I. In addition, it was noticed that the uptake of Co^{2+} ions was significantly increased with increasing the time contact, as well as observed on previous work [24]. The first 30 min of the initial stage of the contact time were recorded a fast Co^{2+} ion reduction with both type of adsorbents, suggested due to available vacant sites on the adsorbent solid surfaces at the beginning with the initial Co^{2+} concentration [25], [26] as well as the ion exchange process. A.M. El-Kamash observed that ZeoliteA shows 80-90% sorption of Cs^+ and Sr^{2+} ion occurred within the first 30 min [18].



Fig. 6 Show the ZeoliteY crystals still attached on Celatom surface (scale bar = 50 nm)

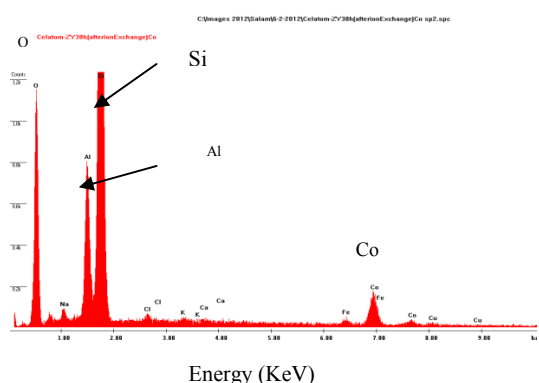


Fig. 7 EDAX spectrum show Co ion appears with Cel-ZY composite

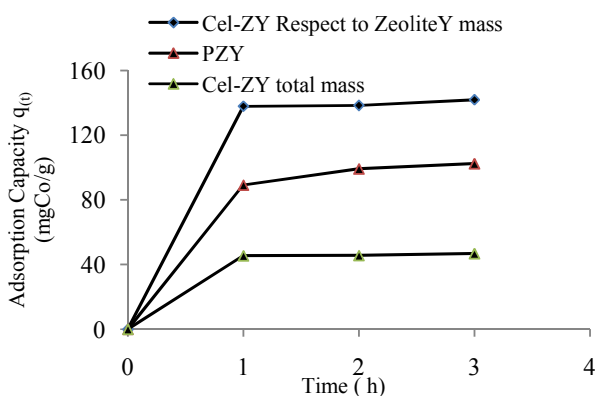


Fig. 8 Effect of contact time on the amount of Co^{2+} ions adsorbed of Cel-ZY, only Celatom, only Zeolite Y on Celatom surface and PZY as adsorbent materials

C. Results of Effect of PH and Initial- Concentration

The effect of pH on the sorption of Co^{2+} ions using prepared Cel-ZY material was investigated over the range from 2 to 6. There was no indication of hydroxide precipitation at this range of pH. The results show the uptake of Co^{2+} ion depending strongly on the pH value in the solution as shown

in Fig. 9. It was clearly noticed that the adsorption of Co^{2+} ion was increased with increasing of the pH value. The lowest absorb of Co^{2+} ion was observed at pH 2.0 suggested due to increase the H^+ ions which make challenging with Co^{2+} ion to occupy the vacant on the solid media. Whilst, the uptake of Co^{2+} ion was increased with increasing the pH value between 4-6. It is approved that mineral acids affect the structure of Zeolite [26]. All next experiments will deal with pH 6 solution. Fig. 10 shows the effect of initial Co^{2+} concentration versus contact time onto Cel-ZY. The initial Co^{2+} concentrations have played an important role on the uptake of Co^{2+} ions with increasing contact time. In addition, as same as all experiments, the equilibrium time was attained between 30-60 min with changing the Co^{2+} concentration from 200 to 600 ppm.

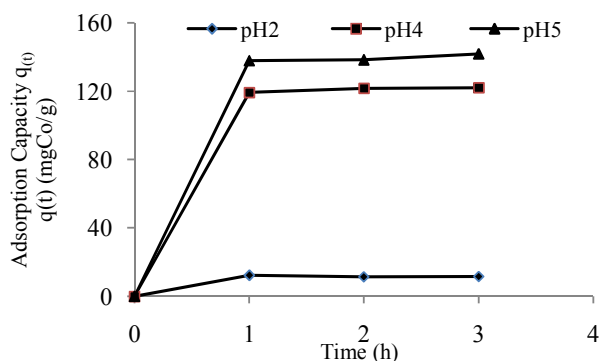


Fig. 9 Effect of contact time on the amount of Co^{2+} uptake onto Cel-ZY at different pH solutions

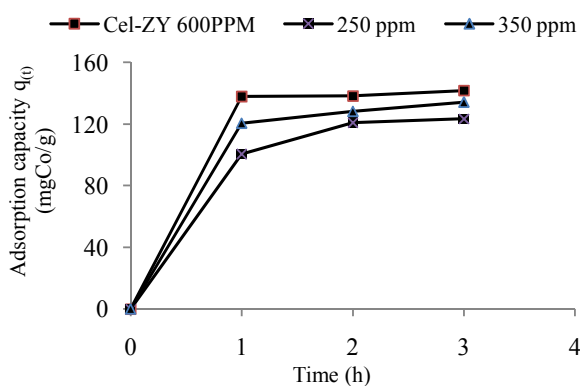


Fig.10 Effect of contact time on the amount of Co^{2+} uptake onto Cel-ZY at the different initial of Co^{2+} Concentrations

D. Results of Adsorption Process

Good fitting was observed for Langmuir and Freundlich models with the experimental data by plotting q_e ($\text{mg} \cdot \text{g}^{-1}$) versus C_e ($\text{mg} \cdot \text{L}^{-1}$). These models were used to express the sorption isotherm of both models to study the uptake of Co^{2+} ions onto Cel-ZY as shown in Fig. 11. The constants of Langmuir and Freundlich equations were calculated in the solver add-in with Microsoft's spreadsheet, Microsoft Excel

[27]. In addition, it was found that the value of separation factor R_L lies between 0 and 1 indicate a favorable adsorption as shown in Fig. 12. The separation factor (R_L) value has been calculated using the Langmuir constant K_a ($L \cdot mg^{-1}$) value of non-linear relationships. The values of Langmuir and Freundlich parameters, coefficients of determination r^2 and dimensionless separation factor (R_L) are listed in Table III.

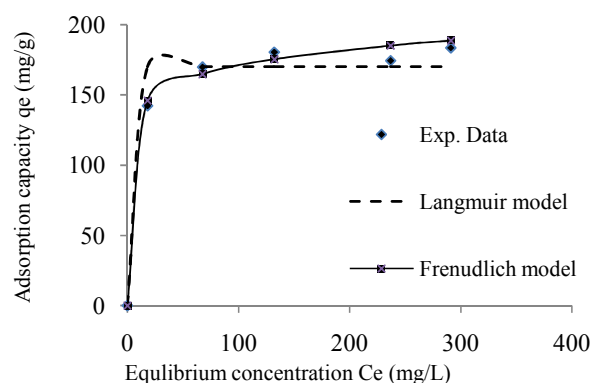


Fig. 11 Langmuir and Freundlich isotherm plots versus experimental data for non-linear relationship for Co^{2+} ions adsorbed (pH 6, 25°C, Cel-ZY 0.1g and interaction time 120 min)

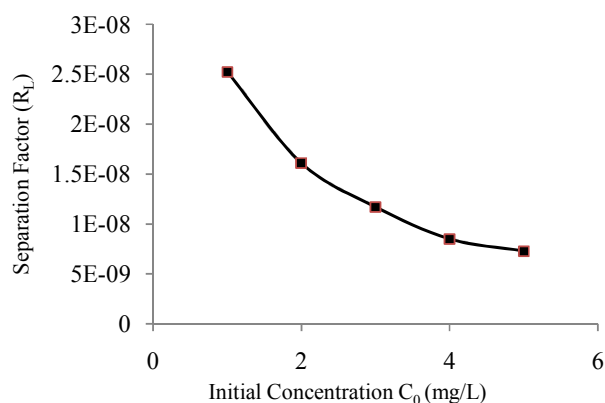


Fig. 12 showing the separation factor R_L vs initial cobalt concentrations. The R_L values were found to be between 0 and 1 using Langmuir constant K_a ($L \cdot mg^{-1}$)

VIII. CONCLUSION

The sorption of Co^{2+} ions on pure ZeoliteY (PZY) and Celatom-ZeoliteY composite (Cel-ZY) was studied. The results showed that these media are capable to remove Co^{2+} ions from the aqueous solution. The maximum adsorption capacity (q_{max}) of composite Cel-ZY was higher than PZY. The results show that the best conditions of experiment are pH 5-6 and high initial concentration.

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TABLE III

FREUNDLICH AND LANGMUIR PARAMETER FOR ADSORPTION OF Co^{2+} IONS AT 25°C CELATOM-ZY 0.1G/25ML; INITIAL Co^{2+} IONS CONCENTRATION FROM 125 TO 600 $MG \cdot L^{-1}$; PH 6 AND 3H AS CONTACT TIME)

Model	K_a ($L \cdot mg^{-1}$)	q_m ($mg \cdot g^{-1}$)	K_F ($L \cdot g^{-1}$)	n	r^2
Non- Linear Langmuir	3223	170.27	-----	-----	0.9976
Non-Linear Freundlich	-----	-----	111.76	10.80	0.9995

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