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Application of Marble Slurry a Low Cost Waste Material for the Removal of Co(II) Ions from Synthetic Aqueous Solutions

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Abstract: The present paper deals with the equilibrium adsorption of Co(II) by marble slurry. The adsorption follows Langmuir, Freundlich and Tempkin isotherms. The maximum monolayer coverage (Q_o) from Langmuir isotherm model has been found to be 322.58 mg/g, separation factor indicating a favorable adsorption experiment is 0.031. Adsorption intensity (1/n) has been calculated using Freundlich isotherm,which indicates favorable adsorption and correlation, values are 4.65 L/g, and 0.991 respectively. The heat of adsorption process has also been estimated using Tempkin isotherm model and found to be 5.07, which widely proves that the adsorption experiments followed both physical and chemical adsorption processes.

Keywords: Marble slurry, Cobalt(II) ions, Adsorption isotherm, equilibrium adsorption.

1. INTRODUCTION

Cobalt is a most common metal ion useful for human being[1]. Cobalt is used in making super alloys and pigments. Cobalt is an essential element in humans and animals as constituents of vitamin B_{12}. Cobalt is used in treatment for anemia, because it stimulates red blood cell production. Short time exposure to high level of cobalt by inhalation in human and animals results in respiratory effects such as edema, hemorrhage of the lungs cardiac effect, congestion of the liver and kidney. Cobalt is also found in effluents of large number of industries which is major source of cobalt pollutant in water. Several methods for removal of heavy metals such as ion exchange, biodegradation, solvent extraction, oxidation and adsorption have been reported[2-4]. Removal of heavy metals using waste inorganic adsorbents is a good technique because of economic material, easy handling and little use of technology. Several studies reveal that few inorganic adsorbents and bioadsorbents are effective in the removal of heavy metal ions[5-7]. Some commonly reported inorganic adsorbents are fly ash[8-10], Fuller earth[11], clarified sludge[12], red mud[13], lime stone[14-15] etc. Thus there is need for development of efficient low cost and environment friendly methods to remove heavy metals from effluents.

In our earlier study marble slurry has been found to possess excellent adsorption efficiency for removal of Cr(III)[16]. Thus, present study has been centered upon marble slurry waste as adsorbent. During the processing of marble a lots of fine marble slurry is generated which is left as a waste material. It is creating a serious threat to surrounding areas. The present work is designed to develop marble slurry as useful and cheap adsorbent for removal of Cobalt from effluents.

2. EXPERIMENTAL

2.1 Apparatus

Atomic absorption spectrophotometer (Elico SL 168) has been used to determine the concentration of Cobalt ions in various aqueous solutions. The pH studies were performed using pocket-sized pH meter (pH 600 Milwaukee). An auto stop magnetic stirrer (model DIGMAG) was used for stirring. The FTIR of marble slurry was recorded on Bruker TENSOR 27.

2.2 Materials

Marble slurry was taken from Sukher industrial area surrounding Udaipur(Rajasthan). It was thoroughly washed many times with double distilled water to remove any soluble impurities. The washed sample was dried in an oven at 383 K for 24 hrs. to make it moisture free. Finally this treated adsorbent was used throughout the course of investigation. The particle size of marble slurry was sieved using sieve size of less than 200 μm. Marble slurry contained CaO 17.10%, SiO_2 28.50%, MgO 26.61% Al_2O_3 1.63% FeO_2 4.63% and loss on ignition 21.32%. Presence of carbonates in marble slurry was characterized through FTIR analysis. The observed peaks at about 711, 878, 1432, 1810 and 2500 cm^{-1} coincided with pure $CaCO_3$.

Stock solution of cobalt(4.77g/l)was prepared using cobaltsulphate(AR grade) in double distilled water. Further solutions were prepared by diluting the stock solution as per requirement.

2.3 Adsorption experiment

To study adsorption isotherm, experiments were conducted by varying amount of adsorbent from 200 mg/L to 2200 mg/L at constant concentration of adsorbate. In second experiment concentration of adsorbate was varied from 500 mg/L to 5000 mg/L at constant quantity of adsorbentat 1.2 g/L. The effect of time, pH and temperature were studied with Co(II) concentration of 1900 mg/L and quantity of adsorbent at 1.2 g/L. The solution was stirred for 30 min. using magnetic stirrer and this solution was filtered to a filtrate which had residual Co(II) ions not adsorbed by marble slurry. The residual concentrations were determined using atomic absorption spectrophotometer. The quantity of adsorbed Co(II) ions (mg/g) was calculated using the following formula[17].

$$q = [(C_i - C_r) /m] V \text{ ………. } (1)$$

where q = The quantity of adsorbate adsorbed from the solution. V = Volume of the suspension, C_i = the concentration before adsorption, C_r = the concentration after adsorption and m = the weight in gram of the adsorbent. The data was fitted into the following isotherms: Langmuir, Freundlich and Tempkin[18]. The removal efficiency was determined by computing the percentage adsorption using the formulae in Eq. (2)

$$\text{Adsorption (\%)} = Ci - C_r / C_i \times 100 \text{ ………. } (2)$$

2.4 Optimization of conditions for removal of Co(II)

All studies excluding temperature dependence were done at room temperature that is 298 ± 1K. Initial concentration of marble slurry was assessed form 100 to 2000 mg/L of marble slurry taken for 1900 mg/L of Co(II) solution at pH 7.

Different concentration of Co(II) in the range of 500 to 5000 mg/L have been taken to optimize the best concentration at which adsorbent adsorbed ≈ 100% Co(II). Stirring time has also been studied ranging from 2 to 50 min. at 250 rpm of magnetic stirrer. Effect of temperature on adsorption of Co(II) onto marble slurry was examined in the range 298 to 358 K. Effect of pH on adsorption of Co(II) onto marble slurry was examined in the range 2 to 10. Thus entire studies have been done to optimize different parameters, which were 0.12gm marble slurry, 30min. stirring time at an optimum temperature of 298±1K.

3. RESULT AND DISCUSSION

3.1 Adsorption isotherms of Co(II) ionsonto marble slurry

The equilibrium adsorption of the Co(II) ions were carried out by adding 0.12 g. of the marble slurry with 100 ml of different concentrations of Co(II) from 500 mg/L – 5000 mg/L in a 250 ml beaker with stirring for 50 minutes on the magnetic stirrer. The mixture was filtered and the filtrate was analyzed for metal ions concentration using AAS. The adsorption data obtained were verified for purpose of mechanistic understanding by fitting into Langmuir, Freundlich and Temkin adsorption isotherm.

3.2 Langmuir isotherm

The Langmuir isotherm[19] describes quantitatively the formation of a monolayer adsorbate on the outer surface of the adsorbent, and after that no further adsorption takes place. This adsorption occurs on a homogeneous surface by monolayer adsorption without interaction between adsorbed molecules. The Langmuir isotherm is written as;

$C_e/q_e = C_e/q_m + 1/q_m b$ ………. (3)

Where $C_e$is equilibrium concentration of solute (mg/L), $q_m$is adsorption capacity (mg/g), 1/b is free energy of adsorption, and q_e is amount of Co(II) adsorbed at equilibrium time (mg/g). When Langmuir equation is plotted (C_e/q_e verses C_e) a linear slope is obtained (fig-1), straight line shows the applicability of Langmuir equation, b and q_m were calculated by intercept and slope which were 0.0163 ml/g and 322.58 mg/g respectively. This model also suggested that monolayer coverage of Co(II) ions occur onto the outer surface of marble slurry. The separation factor R_L is calculated from the following equation.4

$R_L = 1/1+bC_0$ ……….(4)

If $R_L > 1$, the adsorption was unfavorable if $0<R_L<1$, the adsorption is favorable. Value of separation factor 0.031 is indicating that the equilibrium sorption was favorable. This has been shown in figure 1.

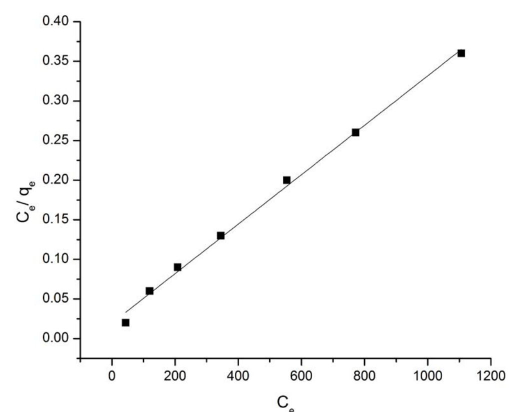

Fig-1. Langmuir adsorption isotherm

3.3 Freundlich isotherm

The Freundlich isotherm is based on multilayer adsorption with interaction between adsorbed molecules. The model is applied to adsorption characteristics for the heterogeneous surfaces[20]. The Freundlich equation may be written in linear form as

$\log q_e = \log K_f + 1/n \log C_e$ ………. (4)

Where q_e (mg/g) amount of Co(II) ions adsorbed, K_f is the indicator of adsorption capacity, 1/n is intensity of the adsorption and C_e is equilibrium concentration of Co(II) mg/L. When graph was plotted between log q_e and log Ce a straight line was obtained. Parameter n and logK_f were calculated from slope and intercept which were found to be 4.65 L/gm and 3.052 respectively with correlation coefficient of 0.9985. Favorable adsorption of Co(II) ion onto marble slurry was suggested by the fact that the value of n is greater than unity[21-22]. The graph has been shown as figure 2.

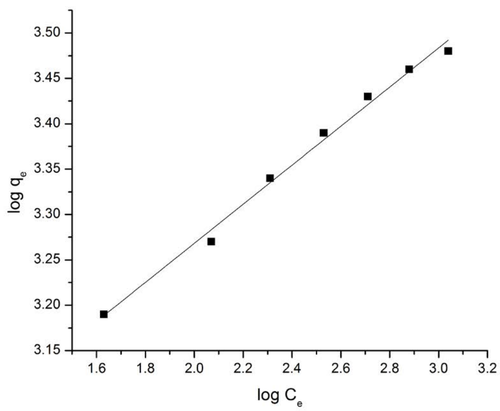

Fig-2. Freundlich adsorption isotherm

3.4 Tempkin isotherm

The Tempkin isotherm model[23] correlates adsorbent-adsorbate interactions of Co(II) onto marble slurry. Tempkin isotherm may be written in linear form as;

$q_e = RT/b_T \ln(A_T) + (RT/b_T) \ln(C_e)$ ………. (5)

q_e and C_e were defined above, R is universal gas constant and T is absolute temperature. A_T is the equilibrium binding constant corresponding to the maximum binding energy, and b_T is related to the heat of adsorption. A_T and b_T were calculated by intercept and slope found to be 0.483 L/g and 5.07 respectively. The equation with correlation coefficient of 0.988 shows linearity of the relationship indicating strong binding of Co(II) onto adsorbent, as shown in figure 3.

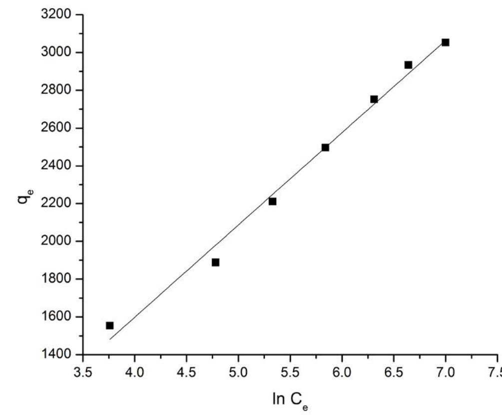

Fig-3. Tempkin adsorption isotherm

3.5 Effect of various other ions

The effect of other ions like Pb(II) and Cu(II) ions at equal concentrations are studied for the removal of Co(II). The results indicate that the percentage of Co(II) removal is slightly decreesedby the presence of these ions in aqueous solutions. This may be due to a competition between these cations and Co(II) ions for adsorption onto marble slurry.

3.6 Adsorption mechanism

As far as mechanism is indicated it seems most probable that cations are removed by ion exchange mechanism, complexation and precipitation. The main components of marble slurry are calcite ($CaCO_3$) and some amount of quartz (SiO_2). Though calcite is sparingly soluble in water and when it is suspended in water some ions like HCO_3^-, $Ca(HCO_3)$, Ca^{2+} and $CaOH^-$ were formed which affect the pH of solution. OH^-, H^+ and HCO_3^- were also potential ions with Ca^{2+} and $CaCO_3$. Silica present in marble slurry on chemisorption of water induces the hydroxide surface for further adsorption of metal i.e. Co(II). These results were confirmed by stirring of marble slurry with distilled water for 50 minutes which showed the change in pH from 5.8 to 8.3. This might be due to the adsorption of H^+ ions from water or desorption of OH^- ion from marble slurry surface. Thus it was confirmed that the marble slurry has a negatively charged surface[24].

According to pH study it was confirmed that pH range 6 to 8 is suitable for maximum adsorption for Co(II)ion onto marble slurry. Below pH 6 the adsorption is less than 100% because of the partial dissolution of marble slurry and repulsion between positive charge surface and Co(II) ion. It may be proposed by the possible ion exchange mechanism between Co^{2+} ion and marble slurry[25]. This was confirmed by measuring the Ca^{2+} ion concentration before and after the adsorption. In between pH 6 to 8 adsorption increases gradually and reaches ~ 100%, but above pH 8 adsorption percentage does not increase which may be due to precipitation of $Co(OH)_2$. Maximum adsorption occurs between pH range 6 to 8 which may be due to electrostatic forces between negatively charged surface of marble slurry and predominant species $Co(OH)^+$. Above pH 8 adsorption may also take place through precipitation of insoluble $CoCO_3$ and $Co(OH)_2$. It is confirmed by shifting in IR spectra of marble slurry after adsorption. Above pH 9, Co(II) forms negative speciesi.e. $Co(OH)_3^-$ and $Co(OH)_4^{-2}$. At this range adsorption is decreased, which may be attributed to the incapability of adsorption of negative species of Co(II) onto the negative surface of marble slurry.

4. CONCLUSIONS

Marble slurry has been found to be a cheap and effective inorganic adsorbent for the removal of Co(II) ions from water. This process was successfully applied for the removal of Co(II) ion from polluted drinking water, and can be commercially exploited if the detailed feasibility studies are done. Further, the method has advantage of removing multipleions such as Cu(II) and Pb(II) from the effluent which increasesthe applicability of this method.

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