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Removal of zinc ion from industrial effluents by hydrotalcite-like compound

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ABSTRACT

Hydrotalcite and similar compounds are found to be a potential adsorbent for removal of different metal ions. In present work we have synthesized a low-cost hydrotalcite-like compound, takovite, using the co-precipitation method. Further, part of the synthesized material was calcined at 773 K. Both normal and calcined takovite were characterized by XRD. Using this hydrotalcite-like compound the adsorption of Zn was studied in industrial effluents in a batch system by keeping different agitation times (15–1020 min), varying pH in the range 2–6 and varying the temperature in the range 283–313 K. In the controlled conditions, the percentage adsorption of Zn was found to be 76% and 93% for normal and calcined takovite respectively. The equilibrium isotherm data were analysed using Freundlich isotherm model. The values of log a and $1/b$ were found to be 0.778 and 0.083 for normal and 0.88 and 1.44 for calcined takovite, respectively, and the correlation coefficient (r^2) was 0.9849 and 0.9945 for normal and calcined takovite, respectively.

Keywords: Hydrotalcite-like compound; Takovite; Calcined takovite; Co-precipitation; Adsorption; Freundlich isotherm

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1. Introduction

Industrial wastes are one of the most prevalent sources of water pollution. In 1997 in Poland alone their output was 8542.8 Hm^3; 227.1 Hm^3 of it were washed away down drains, whereas the rest found its way to receivers and contributed to pollutions of primary and secondary character [1]. Considering data as well as protection of the environment, it is really necessary to treat sewage on the spot. The exact determination of its content is, among others, a guarantee that the procedure has been properly carried out. It is noteworthy that wastes coming from different branches of industry differ considerably from one another and are difficult to characterize. The constituents commonly found in industrial wastes include such synthetic organic substances as oils, fats, resins, dyes, phenols, tars, detergents, heterocyclic compounds, chlorine derivatives of organic compounds, hydrocarbons and their derivatives as well as such inorganic substances as acids, bases, heavy metals in different chemical forms, phosphates, chlorides, sulphides, sulphates, ammonium compounds and nitrates [2] . Considering these factors, wastewater treatment is necessary and if possible, the water can be reused. The removal of heavy metal ions for water purification has drawn attention to search for such materials which are not only good adsorbents of metals but can be regenerated for further use.

Hydrotalcite-like compounds ($HTlC_S$), often identified as anionic clays, are layered double hydroxides (LDH_S) constituted by stacking of positively charged sheets (brucite-like layers) separated by internal layers space

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containing solvated anions. The charge of the brucite-like layers is generated by the substitution of part of the divalent metal cations by trivalent ones. The general formula of these materials is

$$[M(II)_{1-X}\,M\,(III)_X\,(OH)_2]^{X+}\,A^{n-}{}_{X/n}\cdot\,mH_2O$$

where M(II) is a divalent cation [Mg(II) and/or Ni(II), Zn(II), Co(II), Mn(II)], M(III) is a trivalent cation [Al(III) and/or Fe(III), Ga(III), Cr(III), V(III)] and A^{n-} is an anion with charge *n* (OH^-, CO_3^{2-}, NO_3^-, Cl^-, SO_4^{2-}) [3–6]. They can be synthesized using different methods [5], the most common being the co-precipitation at constant pH of dilute solutions containing M(II) and M(III) cations with solutions containing carbonate and hydroxide ions [7–9]. The most important characteristic of the structural properties of the hydrotalcite-like compounds is the distance between the neighbouring cationic layers, also known as basal spacing. This parameter depends to a large extent on the nature of the anions in the internal layers. Hydrotalcite-like compounds have many industrial applications, particularly in the calcined form. The calcination of hydrotalcite-like compounds induces dehydration, dehydroxilation and loss of compensation anions, forming the mixed oxides with basic properties and a poorly crystallized structure [7,10–12]. The major share of the total world production of zinc is used up in industrial application such as zinc coating to protect iron and steel by hot-dip galvanizing, electro galvanizing, spraying and painting. If the effluents from these industries are not properly treated, they are a significant source of water pollution and cause fever, depression, malaise, cough, vomiting, salivation and headache [13]. Maximum permissible concentrations of zinc in drinking water is 5–15 mg L^{-1}. The permissible level of zinc for industrial wastewater to be discharged into inland surface water is 5 mg L^{-1} and into marine coastal area is 15 mg L^{-1} [13]. The study reveals that industrial effluents are the biggest sources of zinc pollution [14]. The search for low-cost adsorbents for removal of various pollutants continues [15–19]. A number of methods have been put forward for removal of heavy metal ions including zinc from industrial wastewater [20–23]. In the present study an attempt has been made for the removal of zinc from industrial effluents using synthesized hydrotalcite-like compound, takovite.

2. Experimental studies

2.1. Reagents

The following reagents were used: nickle nitrate (Loba Chemie), aluminium nitrate (B.D.H.), sodium hydroxide (Loba Chemie), sodium carbonate (Loba Chemie).

2.2. Preparation of adsorbent

Miyata [24] has suggested conditions for preparation of hydrotalcite-like compounds, which have followed for the preparation of takovite. 40 mL of an aqueous solution containing nickel nitrate and aluminium nitrate (3:1), were added in 200 mL of water under stirring (Soln. 1). 16 g of NaOH and 2.86 g of Na_2CO_3 dissolved in 1 L of water solution (Soln. 2), Then solution 1 was added drop by drop into solution 2, under vigorous stirring on a magnetic stirrer. The pH was maintained between 11.5 and 12 by addition of NaOH and HCl and was monitored with the help of a pH meter (Century CP 901). The maintenance of pH is critical because if the pH exceeds 12, then dissolution of Al(III) ions can occur, and if the value goes below 11.5, a more complex pathway for the precipitation exists, and thus the process is not always complete. The mixed suspension was centrifuged to recover green precipitate, the solid washed with deionized water and then the precipitate dried in an oven for 24 h at 373 K. Out of total mass obtained, half was kept as normal and another half was calcined in a crucibile in an oven. Initially the temperature was maintained at 323 K, and then it was raised to 773 K and this temperature was maintained for 10 h. Afterwards the temperature was lowered to 353 K at a rate of 276 K/min. Both calcined and normal takovite were ground to fine powder using a pestle and mortar.

2.3. Characterization of adsorbent

X-ray diffraction is the most common technique used for the characterization of minerals [25]. The technique is based on the reflection of X-rays by characteristic atomic lattice planes within the mineral crystals [26]. The prepared hydrotalcite-like compounds were characterized by X-ray diffraction (XRD). XRD was performed on Rigaku D/max-2200 PC diffractometer operated at 40 kV/20 mA, using CuKα_1 radiation with a wavelength of 1.54 Å in the wide angle region from 20° to 80° on 2 θ scale.

2.4. Batch adsorption experiments

Untreated industrial effluents were collected from fertilizer industry, Indian Farmers Fertilizers Coop Ltd. (IIFCO), Phoolpur, Allahabad. The adsorption capacity of takovite was determined from the contact of 100 mL of effluents in conical flask with 0.6 g of takovite. The mixture was shaken in an orbital shaker (Shivam, IS0 900/2000) at 120 rpm followed by filtration. The filtrate containing the residual concentration of metal was determined by atomic absorption spectrophotometer (ECIL AAS Model No. 4141). The percent adsorption [23] was calculated using the following equation:

$$\%\text{ adsorption} = \left[\left(C_i - C_f\right)/C_i\right]\cdot 100 \qquad (1)$$

where C_i and C_f are respectively the initial and final concentrations of the metal ions in the solution. Adsorption is influenced by many physicochemical factors, including agitation time, pH, adsorbent dose and temperature.

3. Results and discussion

3.1. Characterisation of adsorbent

Fig. 1 shows the XRD patterns of the normal and calcined takovite synthesized by the co-precipitation method. XRD spectra of normal takovite show peaks at the positions of 11.51°, 29.10°, 33.83°, 34.99°, 36.80°, 39.49°, 44.50°, 51.41°,61.06° and 62.52°, which are in good agreement with the JCPDS file for takovite (JCPDS 15–0087, a = 3.025 Å, b = c = 22.59 Å) and can be indexed as the hexagonal rhomb-centered structure of takovite having a space group R3m (166). All available reflections of the present XRD peaks (i.e., Scherrer's broadening) attributes the formation of takovite. The particle sizes, d of takovite were estimated by Debye–Scherrer's equation:

$$d = \frac{0.9\lambda}{B\cos\theta} \tag{2}$$

where d is the particle size, λ is the wavelength of radiation used, θ is the Bragg angle and B is full width at half maxima (FWHM) on 2 θ scale.

For normal compound, the XRD spectra showed small kink-type peaks, and the average particle size was found to be ~40 nm. Furthermore, it was also observed that after calcination these small kink-type XRD peaks were removed and became narrow and very intense, indicating the enhancement in crystallinity as compared to normal compound. Surprisingly, the crystal size of this calcined compound, was decreased from ~40 nm to ~30 nm after calcination.

3.2. Effect of agitation time

The effect of agitation time on adsorption of Zn(II) by the adsorbent is shown in Fig. 2. It can be seen that the percentage of metal ion adsorption increased with increasing the time of equilibration. Other parameters, such as adsorbent dose 0.5 g, pH 5.0 of solution were kept constant, while the temperature was kept at 313 K. It can be seen that the removal of 200 mg L^{-1} Zn (II) increased with time to obtain almost equilibrium at about 120 min. After that, the contact time had no significant effect on metal removal percentage. Very high adsorption rates were observed at the beginning because of the great number of sites available for adsorption, and equilibrium was then gradually achieved. It was found that 90% of metal ions was removed within 2 h.

3.3. Effect of pH

pH is an important parameter in adsorption of metal ions from aqueous solution because it affects solubility of metal ions, concentration of counter ions in the functional groups of the adsorbents and the degree of ionization of the adsorbate during a reaction. To examine the effect of pH on Zn(II) removal efficiency, the pH was varied from 2 to 6. As shown in Fig. 3, the uptake of Zn(II) depends on

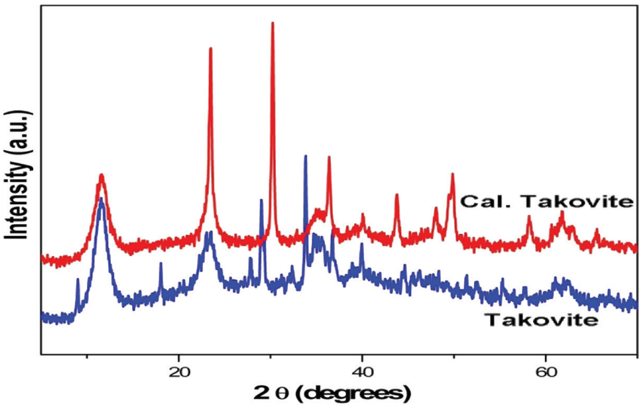

Fig. 1. XRD of synthesized normal and calcined takovite.

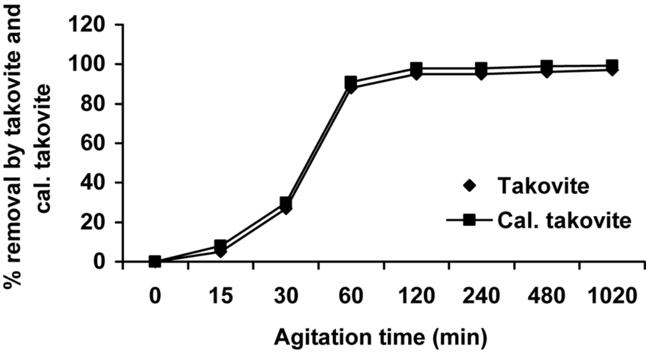

Fig. 2. Effect of agitation time on adsorption of Zn(II) on normal and calcined takovite: pH = 5; initial metal ion concentration (C_i) = 200 mg L^{-1}; adsorbent dose (m) = 0.5g; temperature (T) = 313 K; stirring speed = 120 rpm.

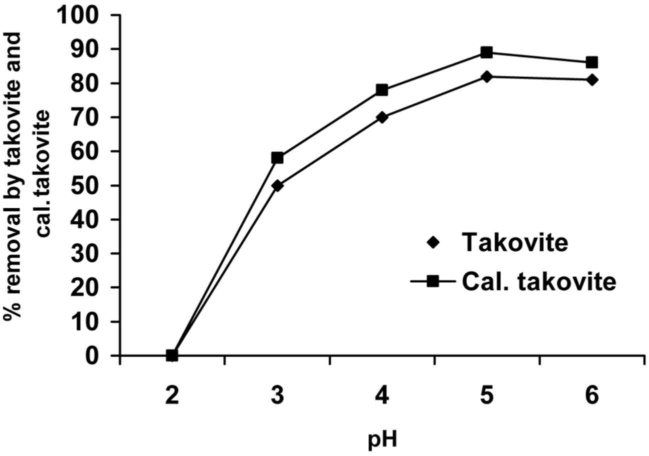

Fig. 3. Effect of pH on the adsorption of Zn(II) on normal and calcined takovite: initial metal ion concentration (C_i) = 200 mg L^{-1}; adsorbent dose (m) = 0.5 g; temperature (T) = 313 K; stirring speed = 120 rpm.

pH, where adsorption increases with the increase in pH and optimal metal removal efficiency occurs at pH 5 for both normal and calcined compounds. The H^+ concentration affects both the surface charge of the adsorbent and the hydrolysis of metal ions [27]. As has been mentioned above, the optimum pH, where the adsorption is optimal, gives the extent of removal of Zn(II), which is maximum at this pH for both normal and calcined takovite. This may be attributed to the competition between H^+ and Zn(II) for the sorption sites at low pH values. At pH values higher than 6, hydrolysis of Zn(II) is appreciable and $Zn(OH)_2$ starts precipitating, and therefore no attempt was made to study the effect of pH beyond 6.0.

3.4. Effect of adsorbent dose

The dependence of Zn(II) adsorption on the dose was studied by varying the amount of adsorbents from 0.1 to 0.6 g/100 mL, while keeping other parameters (pH 5.0, agitation time 120 min, and temperature 313 K) constant. From Fig. 4 it can be observed that the removal efficiency of the adsorbent generally improved with increasing the dose. This is expected due to the fact that the higher is the dose of the adsorbent in the solution, the greater availability of exchangeable sites for ions. All of them showed no further increase in adsorption after a certain amount of the adsorbent was added (0.1–0.6 g/100 mL). At 200 mg L^{-1} concentration of Zn(II), the maximum Zn(II) removal efficiency was about 76% for normal compound and 93% for calcined compound.

3.5. Effect of temperature

Adsorption of Zn(II) was carried out at four different temperatures 283, 293, 303 and 313 K using takovite as an adsorbent. It was observed (Fig. 5) that between 283–293 K there is a sharp increase in adsorption. Thereafter the adsorption continues to rise with the temperature but the rise is slow. While studying the removal of Zn(II) and other heavy metals from industrial wastewater using hydrogen peroxide, Badmus et al. [22] noted a similar rise in adsorption with temperature, and maximum removal occurred at 303 K. This trend was also observed for removal of phenol from aqueous solutions by sorption on low-cost clay by Nayak and Singh [17] and for removal of Cu(II) by newspaper pulp [19]. These results indicate that adsorption is an endothermic process, and hence the removal by adsorption increases with temperature.

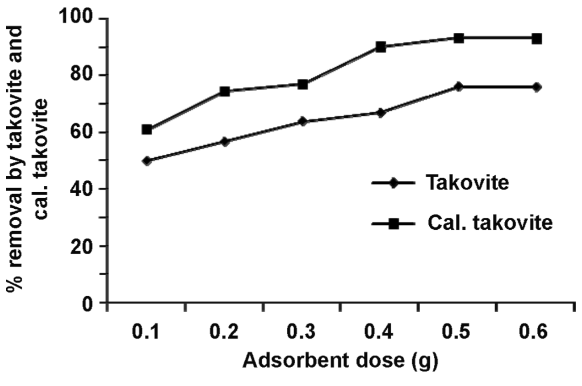

Fig. 4. Effect of adsorbent dose on the adsorption of Zn(II) on normal and calcined takovite: pH = 5; initial metal ion concentration (C_i) = 200 mg L^{-1}; temperature (T) = 313 K; stirring speed = 120 rpm.

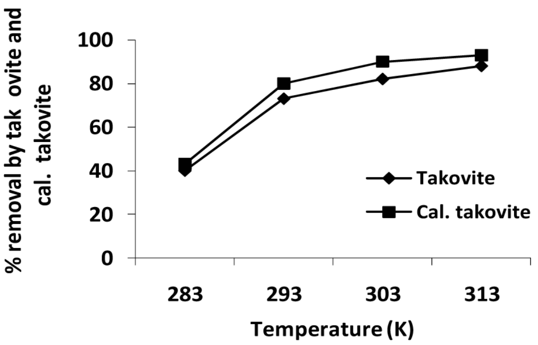

Fig. 5. Effect of temperature on adsorption of Zn(II) on normal and calcined takovite: pH = 5; initial metal ion concentration (C_i) = 200 mg L^{-1}; adsorbent dose (m)= 0.5 g; stirring speed = 120 rpm.

3.6. Adsorption isotherm

Adsorption of Zn(II) on hydrotalcite-like compound was studied in the concentration range of 10–200 mg L^{-1} with 0.5 g of adsorbent. The uptake of Zn(II) by takovite and calcined takovite was evaluated in accordance with the linearized form of Freundlich isotherm equation [28]. The Freundlich equation is an empirical equation based on adsorption on a heterogeneous surface and the possibility of multilayer adsorption. The equation is commonly represented by:

$$q_e = aC_e^b \tag{3}$$

where a and b are the Freundlich constant characteristics of the system, indicating the adsorption capacity and the adsorption intensity, respectively. To simplify the derivation of a and b, the above equation can be linearized as

$$\log qe = \log a + \frac{1}{b}\log Ce \tag{4}$$

Therefore, a plot of log q_e vs. log C_e enables the constant a and exponent b to be determined. C_e is the equilibrium concentration (mg L^{-1}), q_e is the amount of metal ion adsorbed per unit mass of adsorbent (mg g^{-1}), a and b are the constants. q_e can be calculated by the equation:

$$q_e = C_i V - C_f V / m \tag{5}$$

where C_i is the initial concentration of metal ions in the

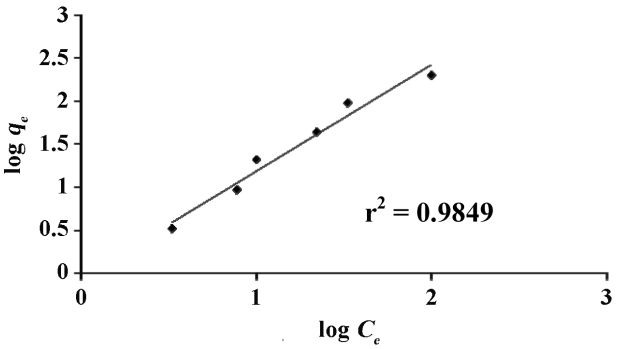

Fig. 6. Freundlich isotherm for adsorption of Zn(II) on normal takovite.

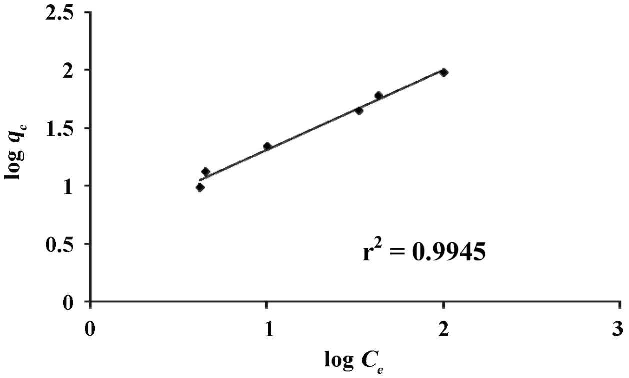

Fig. 7. Freundlich isotherm for adsorption of Zn(II) on calcinied takovite.

aqueous solution (mg L^{-1}), C_f is the final concentration of metal ions in the aqueous solution (mg L^{-1}), m is the mass of the adsorbent (g) and V is the volume of the solution.

The straight line nature of the curve in Figs. 6 and 7 indicates that the adsorption process follows the Freundlich type. The values of log a, $1/b$ and r^2 were found to be 0.778, 0.083 and 0.9849 for normal takovite and 0.88, 1.44 and 0.9945 for calcined takovite. Erdem et al. [29] studied the adsorption of Zn(II) by natural zeolite and calculated the Freundlich constant as log $a = 0.19$, $1/b = 0.43$ and $r^2 = 0.9417$. Comparing these values with our values of the Freundlich parameter, we observed that the value of r^2 is higher in our case and therefore our data fit better the Freundlich isotherm than the data of Erdem.

5. Conclusion

It was discovered that anionic clay hydrotalcite-like compound (takovite) adsorbed a significant amount of zinc ions from industrial effluents. From the experiments it can be concluded that calcined takovite adsorbs a greater amount of metal ions than normal takovite for the same concentration of species in the solution and mass of the adsorbent, and the percentage of zinc ion adsorption steadily increases with increasing the agitation time, pH, adsorbent dose and temperature.

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Symbols and abbreviations

a, b — Freundlich constants
A^{n-} — An anions with charge n
B — Full width at half maxima (FWHM)
C_e — Equilibrium concentration, mg L^{-1}
C_f — Final concentration of metal ion in solution, mg L^{-1}
C_i — Initial concentration of metal ion in solution, mg L^{-1}
d — Particle size
Hm — Hectare meter
HTlC_S — Hydrotalcite-like compounds
JCPDS — Joint Committee on Powder Diffraction Standards
LDH_S — Layered double hydroxides
m — Mass of adsorbent, g
M(II) — Divalent cations
M(III) — Trivalent cations
q_e — Amount of metal ion adsorbed per unit mass of adsorbent in equilibrium conditions, mg g^{-1}
r^2 — Correlation coefficient
V — Volume of the solution
XRD — X- ray diffraction
λ — Wavelength of radiation
θ — Bragg angle

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