

Kienetic study of adsorptions cations of Ni⁺², Co⁺² and Fe⁺³ on the surfaces of amorphous Titanium phosphate

دراسة حركية لامتزاز كاتيونات النيكل والكوبلت والحديد على سطح فوسفات التيتانيوم

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Abstract:

Systematic study of kinetic of adsorption of the aqueous solutions of Ni⁺², Co⁺², Fe⁺³ and Fe cations the surfaces of prepared amorphous titanium phosphate using the first and second order model from the lagrengren equation. Interparticl diffusions was fitted to show the effect of porosity on the rate of adsorption .

الخلاصة:

دراسة نظامية حركية لامتزاز ايونات النيكل, الكوبلت, والحديد على سطح فوسفات التيتانيوم المحضرة مختبريا لاختبار موديل الرتبة الاولى الكاذبة والثانية الكاذبة من معادلة لآكرنكرن ان الموديل للرتبة الثانية الكاذبة هو اكثر انطباقا من الرتبة الاولى الكاذبة اعتمادا على الحصول على الخط المستقيم , كذلك درس تنافذ الجزيئات خلال المسامية الجزيئية لفوسفات التيتانيوم وتأثيرها على سرعة الامتزاز.

Introductions:

Kinetic study is important in any adsorption process and helps in identifying the type of adsorption, reaction pathway, capacity of adsorbent and reaction rate of the system. The kinetic data are essential for scaling up of sorption processes for industrial preparation. Kinetic studies on the adsorption of contaminants using different biomaterials have been reported previously [1-7]. In recent times, the use of agro wastes in a pure or chemically modified form for the remediation of contaminants in aqueous solution and industrial effluents has continued to attract considerable attention, with studies published by [8, 9, 10]. In a relatively recent study in a pure and chemically modified form has proved to have great potential as an adsorbent for metal ions in aqueous solutions.

The paucity of such information has led to this study. Therefore, this paper describes the adsorption kinetics of the cations (Ni²⁺, Co²⁺ and Fe³⁺) in aqueous solution using amorphous titanium phosphate.

Materials and method:

Titanium phosphate prepared as amorphous compound the method described in [11], its thermogramme was studied using TG/DTG carried with a setram TG-DSC-11 and FTIR spectra were recorded by using a parkin-Elmer1750X spectrophotometer in the range of (400-4000 cm⁻¹). Adsorption experiments were carried out by agitating 100 mg of Titanium Phosphate with 25 ml of aqueous solutions at desired concentrations between (10-50ppm) prepared from a mother solutions of 1000ppm of Ni(NO₃)₂.6 H₂O, Co(NO₃)₂.6 H₂O and Fe(NO₃)₃.9 H₂O were prepared by using distil water and pH=5, at 303 K ° using a thermostated shaker Bath,GFL(D-3006).Germany. Cations concentration

were estimated using spectrophotometrically by monitoring the absorbance at using UV–VIS spectrophotometer (Schimadzu 1700, Tokyo, Japan), at λ_{\max} for each cation. The pH was measured using pH meter (Hanna, 112, Romania). The cations solutions were separated from the adsorbent by centrifuging the mixture of the adsorbent from the cations solution at 3500 rpm for 30 min and its absorbance was measured applying pier-lambert law of absorbance. Effect of adsorbent dosage was studied with different adsorbent doses (100–500 mg/l) in 250 ml of each cations solutions after stirring for a fixed time. Effect of pH was studied by adjusting the pH of each cations by dropping a drops from solutions of dilute HNO_3 .

Results and Discussions:

FTIR:

From the spectrum FTIR was see that the broad band show at 3439 cm^{-1} was attributed to the vibrations of OH groups belong to different energetic types like water adsorbed on the surfaces of the Titanium Phosphates, the bands situated at 2368, 1751, 1649 cm^{-1} respectively. The vibrations at 660 and 573 cm^{-1} were attributed to the bending of the O-P-O, O-Ti-O respectively, two bands had detected at 1236 and 1017 cm^{-1} . Fig(1)

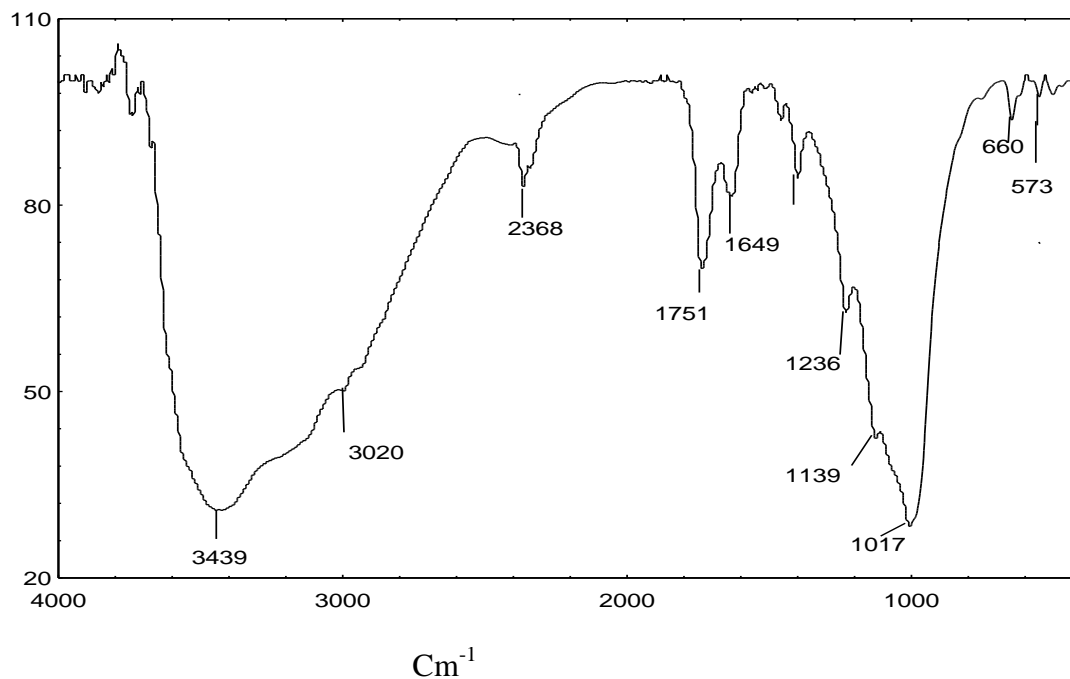
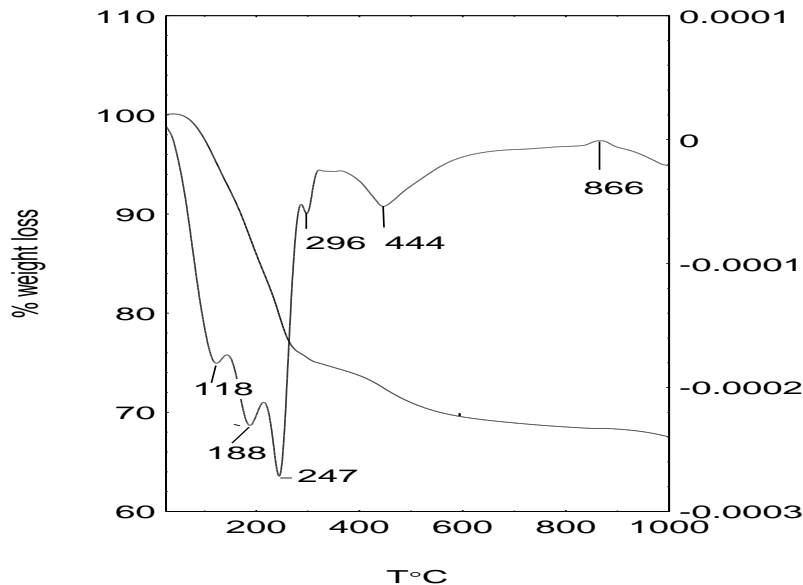


Fig.(1) FTIR of Titanium phosphate

TG/DTG

Three endothermic peaks were appear between 100-247 °C belong to evaporations of physically adsorbed water , water attached with hydrogen bonding to the surface of Titanium Phosphat and the peaks at 247°C and 296°C belong to the removal of hydroxides groups from Ti-OH and P-OH respectively. The peak at 444 °C was attributed to the dehydroxylations of H₂PO₄ . The last peak endothermic at 866°C due to the removal of last traces of structures hydroxides. Fig(2).



Fig(2) TG/DTG thermogram of Titanium phosphate.

Kienetic study:

The first-order and second-order kinetic models from lagrengren equation was applied to determine the rate constant of adsorption. $\ln(q_e - q_t) = \ln q_e - k_1 t$ is the form of first-order rate expression. The values at different concentration were calculated from the slopes and intercepts of plot of $-\log(q_e - q_t)$ versus t , this form was found less applicable in this case of adsorption depending on the r^2 value which is less than 0.5 for all cations adsorptions steps . So that The second-order kinetic model were applied to the present study according to calculated correlations were closer to unity for second-order kinetics model nearly unity fitted with the form $(t/q_e + 1/k_2 q_e^2 = \frac{t}{q_t})$. The initial adsorption rate, the equilibrium adsorption capacity, and the second-order constants were determined experimentally from the slope and intercept of plot of t/q versus t Fig.(3)

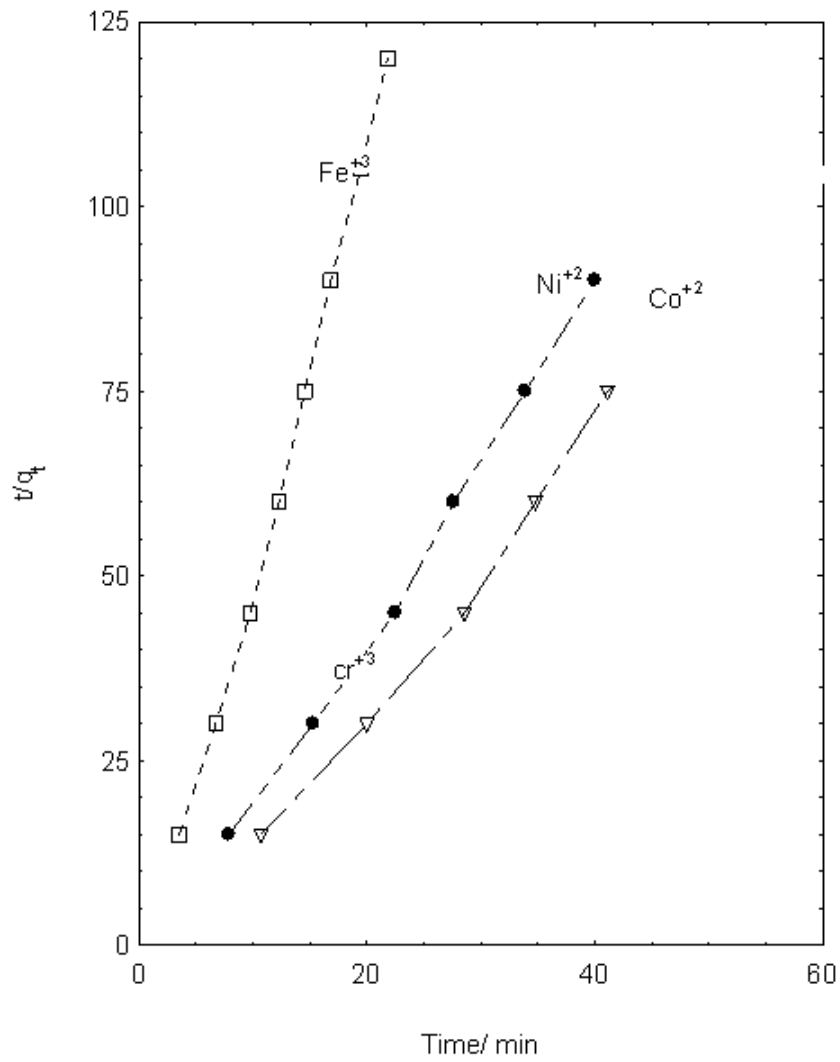


Fig.(3) Second order models of adsorption of Ni⁺², Co⁺² and Fe⁺³ cations on the surfaces of Titanium Phosphates.

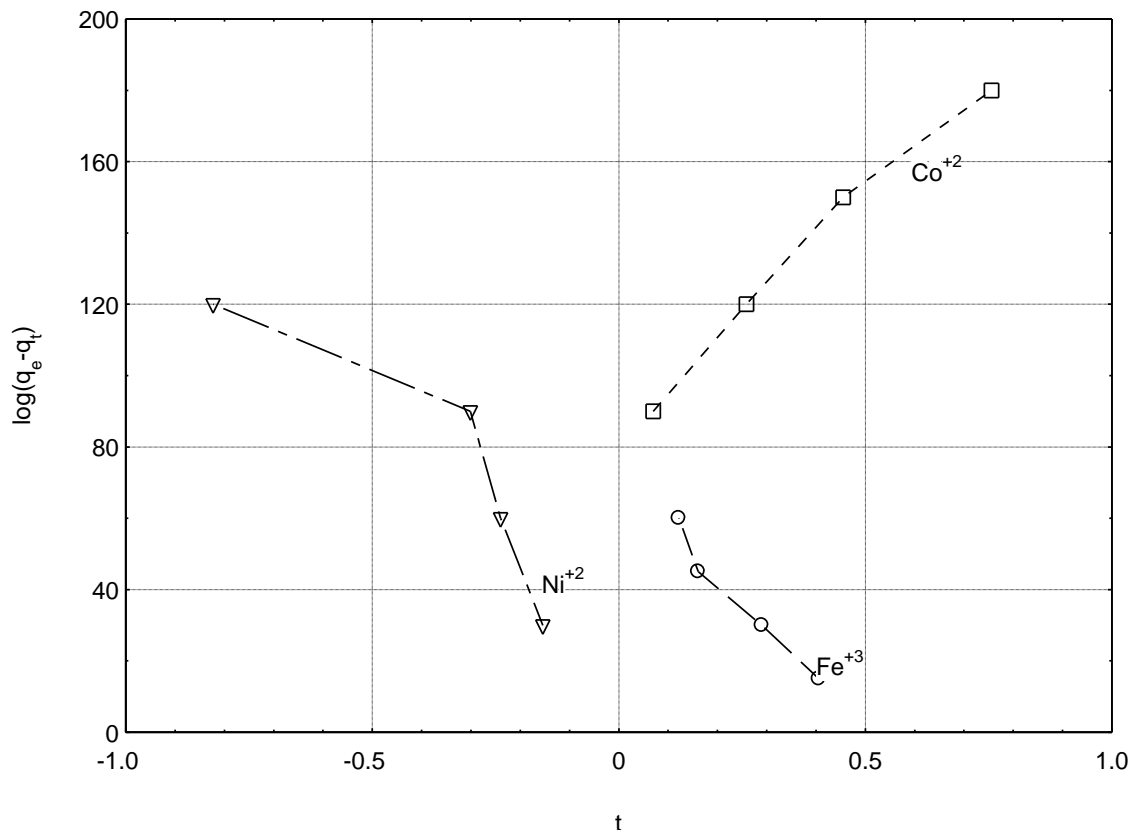


Fig.(4) first order model of lagrengren equation for the adsorptions of Ni²⁺, Co²⁺, Fe³⁺ cations on the surfaces of Titanium Phosphates.

Therefore, the adsorption kinetics could well be approximated more favorably by second-order kinetic model. Similar phenomena have been observed in the adsorption of 2,4-dichlorophenol on coir pith carbon [12].

Intra-particle diffusion study

An empirically found functional relationship, common to the most adsorption processes, is that the uptake varies almost proportionally with $t^{1/2}$, the Weber–Morris plot, rather than with the contact time t [13]. According to the equation of inter particle diffusion ($q_{t=kt^{1/2}}$) a plot of qt versus $t^{1/2}$ should be a straight line with a slope k_{id} and intercept C when adsorption mechanism follows the intra-particle diffusion process. Values of intercept give an idea about the thickness of boundary layer, i.e. larger the intercept with greater is the boundary layer effect [14,15]. The case of $Ni^{+2} > Co^{+2} > Fe^{+3}$ as shows in Fig. (5), qt versus $t^{1/2}$ is presented for cations. The linear plots are attributed to the macropore diffusion, which is the accessible site of adsorption. This is attributed to the instantaneous utilization of the most readily available adsorbing sites on the adsorbent surface. The values of (k_{id}) as obtained from the slope of straight lines are 9.68, 7.64, 5.07 and 2.6 for Ni²⁺, Co²⁺, Fe³⁺ and Fe respectively.

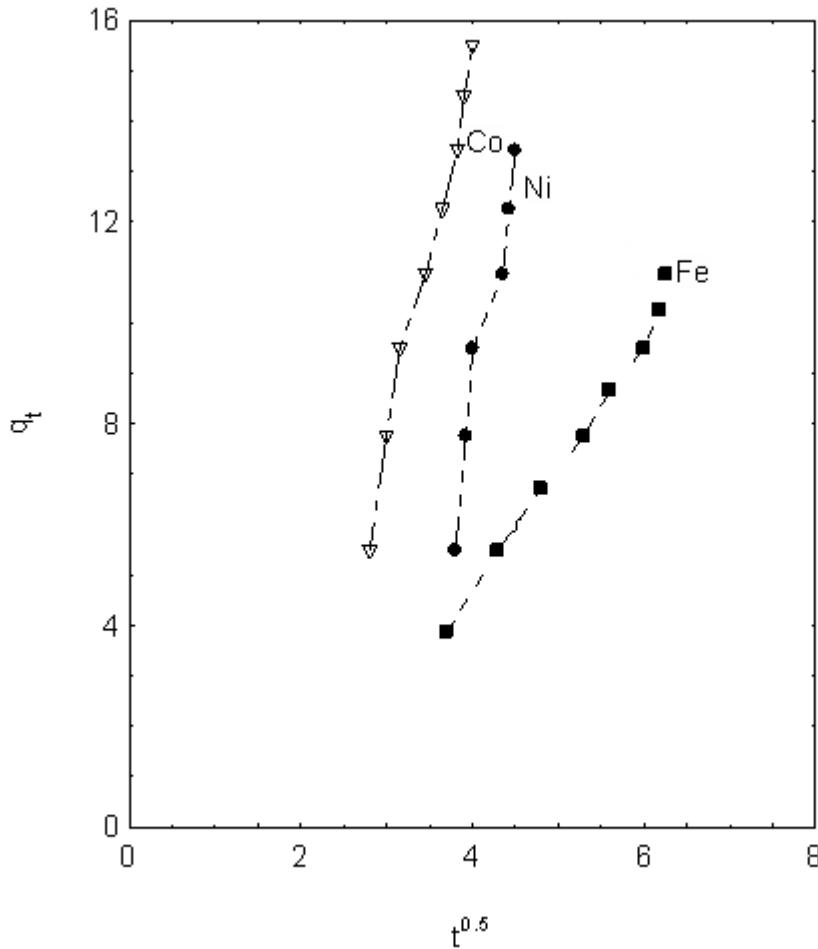


Fig (5) inter particles diffusions model of adsorptions of the cation Ni^{+2} , Co^{+2} , Fe^{+3}

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