Removal of strontium from aqueous solutions by adsorption Onto orange peel: isotherms, kinetics, and thermodynamic studies

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Abstract

The adsorption of Sr(II) from aqueous solution on orange peel (OP) and chemically modified ones with NaOH (NaOP) and KCl (KOP) was studied at varying pH, solid/liquid ratio, contact time, temperature range of (20-60ºC). Adsorption equilibrium were established in about 1h and the adsorption kinetics followed the pseudo-second order kinetics model. The equilibrium data was analyzed using Langmuir, Freundlich, Temkin and Dubinin-Radushkevich adsorption isotherms. Langmuir model provides the best correlation for the adsorption of Sr(II) by the three adsorbents (OP, NaOP and KOP), and the mono-layer adsorption capacity for Sr(II) removal are 12.5, 54.94 and 52.36 for OP, NaOP and KOP mg/g, respectively. Thermodynamic studies showed the spontaneous and exothermic nature of the adsorption of Sr(II) by OP, NaOP and KOP. Present investigation emphasized that the chemically treated orange peel exhibited a high potential for the removal of strontium from aqueous solution.

Keywords

Sr(II), adsorption, isotherm, orange peel

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1. Introduction

Heavy metal contamination of industrial wastewater is an important environmental problem. Many industries release various concentrations of strontium. The primary use of strontium is in the manufacture of X-ray absorbing glass for cathode ray tubes and it is also used for removing lead from solutions of zinc sulphate in the electrolytic zinc process, and for the production of strontium metal, electroceramics and oxide superconductors. Strontium has a variety of commercial and research uses. It has been used in certain optical materials, and it produces the red flame color of pyrotechnic devices such as fireworks and signal flares.

Strontium has also been used as oxygen eliminator in electron tubes and to produce glass for color television tubes. Beyond the four stable isotopes which are naturally present in soil, strontium-90 is also present in the surface soil around the world as a result of fallout from past atmospheric nuclear weapons tests. Strontium preferentially adheres to soil particles, and the amount in sandy soil is typically about 15 times higher than in interstitial water (water in the pore space between soil particles); concentration ratios are typically higher in clay. Strontium ion is slightly toxic, the toxicity of its compounds is thus closely associated with the anion of the compound concerned. Strontium ions removal from aqueous solutions has been traditionally carried out by chemical precipitation, ion exchange, membrane processes, which are expensive and inefficient, especially for low-strength wastewaters [1]. In the last few years, adsorption has been shown to be an economically feasible alternative method for removing trace metals from wastewaters and water supplies [2]. Various researchers have described the adsorption of Sr(II) ions from aqueous solutions onto various organic and inorganic adsorbents [1-7]. Many people tried hard to find efficient and low cost materials. Most agricultural wastes are considered to be low value products. Orange peel is one of the valuable agricultural wastes. However, using untreated agricultural by-products as adsorbents can also bring severe problems, such as low adsorption capacity, high chemical oxygen demand (COD) and biological chemical demand (BOD) as well as total organic carbon (TOC), due to the release of soluble organic compounds contained in the plant materials, such as lignin, tannin, pectin and cellulose, into the solutions [8]. The increase of the COD, BOD and TOC can cause depletion of oxygen content in water and then threaten the aquatic life. To release such problems, chemical treatment on solid adsorbents was used as a technique for improving their physical and chemical properties and increasing their adsorption capacity[8-10]. Orange peel (OP) is a material composed of several constituents. Among them pectin (galacturonic acid), hemicelluloses, cellulose and lignin acid bear various polar functional groups, including carboxylic and phenolic acid groups, that can be involved in metal ions complexion [8]. As the low cost, OP is an attractive and inexpensive alternative for the adsorption removal of dissolved metals. In the present work, it have been focused on the removal of strontium ion from aqueous solutions using raw orange peel and that chemically modified with sodium hydroxide and potassium chloride and investigate various parameters including pH, temperature, contact time and concentration of Sr(II) ions on the adsorption efficiency.

2. Materials and methods

2.1 Chemicals:

All chemicals used in the present work were of analytical purity. 0.1 N HCl and 0.1 N NaOH were used for pH value adjustment.

2.2 Preparation of Sr solution:

An accurately weighed quantity of the $SnCl.2H_2O$ (purchased from Merck company) was dissolved in deionized water to prepare a stock solution (1000 mg/L). Experimental solutions of the desired concentrations were obtained by successive dilutions (25, 50, 75, 125, 150, 175, 200 and 300 mg/L).

2.3 Adsorption experiments:

The sorption mixture was consisted of 0.1 g of adsorbent and 20 ml of strontium solution (100 mg/L) for 6h at 20°C. After equilibrium, the adsorbent solution passed through a filter paper whatman 40 and was analyzed for metal ion content using an atomic absorption (Varian, spectra-110-220/880 Australia Pty. Ltd.) equipped with a Zeeman atomizer. The amount of strontium adsorption at equilibrium q_e (mg/g) was calculated from the following equation:

$$q_e = (C_o - C_e)V / m \qquad (1)$$

where C_o and C_e represent the initial and equilibrium metal ion concentrations (mg/L), respectively; V is the volume of the metal ion solution (mL) and m is the amount of adsorbent (mg).

The adsorbent dosage was changed in the range of 0.04-0.2 g.

The strontium concentrations were varied from 25 to 300 ppm.

To study the effect of pH on sorption, the pH of the strontium solution was adjusted to values in the range 1.8 - 7.3 by the addition of 0.1 M HCl or 0.1 M NaOH prior to experiment. All pH measurements were performed with BOECO, BT 600, model pH meter.

Time dependent experiments were carried out by leaving the adsorption mixture at various predetermined intervals and analyzing the strontium content at the end of contact time. Each time, a different sample was used to ensure that the solid/liquid (S/L) ratio did not change after sampling. The amount of adsorption at time t, q_t (mg/g), was calculated by

$$q_t = (C_o - C_t)V/m \qquad (2)$$

The thermodynamic studies were investigated by carrying out batch study at the optimal conditions and at different temperatures. The temperatures chosen for study were 20°C, 30°C, 40°C, and 60°C. The temperature of the strontium solution was adjusted using a thermostatic water bath (Memmert WB29 Model).

2.4 Adsorbents preparation

2.4.1 Raw orange peel

Orange peel was washed with distilled water and dried in sun light for 4 days. The raw orange peel was excessively dried in an oven at 60°C for 24 h and then ground to a fine powder of particle size less than 355 µm here after, abbreviated as OP.

2.4.2 Treatment with alkali after washing with ethanol

About 15 g raw orange peel was mixed with 100 ml ethanol and 100 ml 1 N NaOH and left for 24 h. The alkali/peel slurry after repeated decantation was filtered and then washed with distilled water until pH was neutral. The filter residue was dried in an oven for 24 h at 60°C. Drying at 60°C was chosen because high drying temperature might cause a decrease of number of cellulose based OH-group [11]. Finally, about 8 g have been remained, hereafter abbreviated as NaOP. The alkali modified orange peel is crushed then milled and sieved to obtain an average particle size lower than 355 µm.

2.4.3 Treatment with KCl after saponification and washed with ethanol

About 15 g of raw orange peel is socked in about 100 ml ethanol, 100 ml 1N NaOH and 100 ml 1N KCl for 24h. The produced slurry is filtered and then washed with distilled water after repeated decantation till pH value of solution becomes neutral. The modified slurry was dried in an oven at 60°C for 24h, then crushed and milled and finally sieved to particles size lower than 355µm. The product is abbreviated as KOP.

2.5 Adsorbents characterization

The FTIR analysis of the adsorbents (OP, NaOP and KOP) were taken with a Fourier-transform infrared spectrophotometer (JASCO FT/IR-410, Japan). Pressed pellets were prepared by grinding the powder specimens with spectroscopic grade KBr for FTIR spectra test. The spectra were recorded from 4000 to 400cm−1.

3. Results and discussion

3.1. Characterization of the adsorbents

The FTIR spectra of OP, NaOP and KOP were carried out as a qualitative analysis to determine the main functional groups present in the adsorbent. The FTTR spectra details of the three adsorbents, OP, NaOP and KOP are given in Table 1. The broad band of 3397-3321 cm^{-1} is O-H stretching vibrations of cellulose, pectin, absorbed water, hemicellulose and liginin. The band 2924-2922 cm^{-1} indicates symmetric or asymmetric C-H stretching vibration of aliphatic acids. The peaks at 1095-1061 cm-1 assigned to vibration of C-O-C and O-H of polysaccharides. The peak at 1736 cm^{-1} in the OP spectrum indicates non ionic carboxy groups (-COOH, -COOCH3). Disappearing of such peak at NaOP and KOP spectra indicates that the methyl ester are hydrolyzed with NaOH and ester group is converted to carboxylate ions. The spectra of NaOP and KOP show two new peaks, the first one at 1624-1613 cm-1may be assigned to asymmetric vibrations of C=O while the second of 1423-1420 cm-1 may be attributed to symmetric vibration of C=O.

3.2. Effect of pH on Sr(II) removal

The experiment carried out at different pH of medium showed that there was a change in the removal percentage of strontium ions over the entire pH range shown in Fig. (1). It can be observed that NaOP and KOP showed higher adsorption ability for Sr(II) than OP and NaOP shows a little better adsorption ability for Sr(II) than KOP. As shown in Fig.(1) at low pH value 0f 1.8, the adsorption efficiency was 68.2% and 34.15% for NaOP and KOP, respectively, and for OP, the value was only 18.05. When solution pH raised from 1.8 to 7.3, the adsorption efficiency increased sharply first and increased less untill pH reached 6.6 and then decreased. The maximum strontium ion uptake was observed at the pH 6.6, and the adsorption efficiency reached about 98.37% for NaOP and 98.13% for KOP. The slight increase in adsorption efficiency of NaOP may be due to the more availability of free active sites on NaOP surface. At low pH, the concentration of proton is high, so strontium ions binding sites become positively charged and then metal cations and protons compete for binding sites of adsorbent powder which results in lower uptake of strontium ions. As pH increases in the range from 1.8 to 6.6, the concentration proton exist in the solution will be decreased and hence will not give the chance to compete with strontium ions on the adsorption sites of the adsorbent powder, thus facilitating greater strontium ions uptake. After pH 6.6 the removal efficiency decreases as pH increases, which is referred to insoluble strontium hydroxide starts precipitating from the solution. Therefore, at these pH values, both adsorption and precipitation are the effective mechanisms to remove the strontium in aqueous solution. The strontium cations in aqueous solution convert to different hydrolysis products [12].

3.3. Effect of solid to liquid (S/L) ratio

Solid to liquid ratio is another important parameter influencing the adsorption efficiency. Fig.2. shows the effect of S/L ratio on the Sr(II) adsorption by the three adsorbents under study, OP, NaOP and KOP. AS shown in Fig. 2. the uptake of strontium ions increased as the S/L ratio increased, but it increased less when S/L ratio surpassed 5.0 g/L. This trend is expected because as the adsorbent dose increases, the number of active sites for binding metal ions on the adsorbent increases and thus more strontium is attached to their surface. Thus it results in the increment of adsorption efficiency until saturation. However, considering the cost, the optimum ratio is 5.0 g/L was chosen in this study. As shown in Fig. 2. the uptake of strontium ion by NaOP is a slight better than that recorded for strontium uptake by KOP.

3.4. Adsorption isotherm

The instigation of the adsorption isotherm is fundamental, and plays an important role in the determination of the maximum capacity of adsorption. It also provides a panorama of the course taken by the system under study in a concise form, indicating how efficiently an adsorbent will adsorb and allows an estimate of the economic viability of the adsorbent commercial applications for the specified solute [12]. OP, NaOP and KOP were used as adsorbents for Sr(II) removal. Four isotherms equations have been tested in the present study to analyze the equilibrium data of the three adsorbents (OP, NaOP and KOP), namely, Langmuir [13], Freundlich [14], Temkin [15] and Dubinin-Radushkevich [16]. Langmuir model is the most widely used isotherm and its equation written as,

$$C_e/q_e = (1/q_L K_L) + (1/q_L)\, C_e \qquad (3)$$

where q_e is the mono-layer adsorption capacity of adsorbent (mg/g), K_L is the Langmuir adsorption constant (L/mg) and q_L is the mono-layer adsorption capacity of adsorbent (mg/g). Therefore, a plot of C_e/q_e versus C_e gives a straight line of slope $1/q_L$ and intercepts $1/(q_L K_L)$.

The Freundlish model can be expressed as:

$$\text{Log } q_e = \log K_F + (1/n) \log C_e \qquad (4)$$

where K_F and n are the Freundlich adsorption constants, which can be determined by the linear plot of log qe versus log Ce.

The Temkin isotherm equation is given as:

$$q_e = B \ln A + B \ln C_e \qquad (5)$$

where A and B are Temkin constants. A plot of q_e versus ln C_e can be used to determine the constants A and B.

The Dubinin-Radushkevich (D-R) isotherm was also used to fit with the experimental data, and it can be represented as,

$$\ln q_e = \ln q_m - ß\mathcal{E}^2 \qquad (6)$$

where ß is a coefficient related to the mean free energy of adsorption ($mmol^2/J^2$), qm is the maximum adsorption capacity and Ɛ is the Polanyi potential (J/mmol) that can be written as:

$$\varepsilon = RT\,(1+1/C_e) \quad (7)$$

where R is the gas constant and T is the absolute temperature.
The equilibrium adsorption isotherms were performed by plotting metal ions adsorbed (q_e) against the equilibrium concentration of strontium ions (C_e) in solution (Fig. 3). Apparently, the adsorption capacity of MgOP and KOP are much higher than that of OP, which indicates the effectiveness of chemical modification and NaOP shows a little better adsorption ability for strontium than KOP.

Correlation coefficients and parameter values for the four isotherms were presented in Table 2. Based on the correlation coefficients, the applicability of the isotherms was compared (Fig. 4.). The experimental results indicated that the sorption of strontium onto OP, NaOP and KOP followed Langmuir model. Sr(II) sorption capacity was 12.50, 54.59 and 52.36 for OP, NaOP and KOP, respectively.

To determine if adsorption process is favorable or unfavorable for Langmuir type adsorption process, Langmuir isotherm is then classified using a dimensionless constant separation factor (R_L), which can be defined as:

$$R_L = 1/(1+K_L\,C_{max}) \quad (8)$$

where C_{max} is the highest (initial) metal concentration in solution (mg/L). If the value of $R_L < 1$, it indicates a favorable adsorption and if $R_L > 1$ then, an unfavorable adsorption. The R_L values for the adsorption of Sr(II) onto OP, NaOP and KOP was in the range $0 < R_L < 1$, indicating that Langmuir adsorption is favorable.

3.5. Kinetics studies

The kinetics of strontium adsorption can be modeled by various equations. The pseudo-first-order Lagergren equation is given as [17],

$$\text{Log}\,(q_e-q_t) = \log q_e - (k_1/2.303)\,t \quad (9)$$

where q_t and q_e are the amounts of ion adsorbed at time t and at equilibrium (mg/g), respectively, and k_1 is the rate constant of pseudo-first-order adsorption process (h^{-1}). The slope and intercept of plots of $\log(q_e-q_t)$ versus t were used to determine the first-order rate constant k_1 and equilibrium adsorption capacity q_e. The pseudo-second-order kinetic model by Ho and McKay [18], with the linear form:

$$t/q_t=1/(k_2q_e^2)+(1/q_e)t \qquad (10)$$

where k_2 is the equilibrium rate constant of pseudo-second-order adsorption (g/mg.h). If the pseudo-second-order equation is applicable, the plot of t/q_t versus t gives a linear relationship, and then k_2 and qe can be calculated from the slope and intercept of the line.

The adsorption data may also be analyzed using the Elovich equation [19], which has the linear form:

$$Qt=1/ß \ln (\alpha ß) + (1/ß) \ln t \qquad (11)$$

where ß is the initial sorption rate constant (mg/g h), and the parameter ß is related to the extent of surface coverage and activation energy for chemisorptions (g/mg). The constant can be obtained from the slope and intercept of the plot of q_t versus ln t.

The intraparticle diffusion model was also tested. The initial rate constant for intraparticle diffusion is obtained using the equation [20]:

$$q_e=C + k_{int}\, t^{1/2} \qquad (12)$$

where k_{int} is the intraparticle rate constant ($mg/g.h^{1/2}$). Fig. 5 represents the effect of contact time on Sr(II) adsorption on OP, NaOP and KOP. As shown in Fig. 5. the strontium uptake increased sharply at time 0-1 h then became almost stable, which denoted attainment of equilibrium. The phenomenon may be due to the fact that, initially, all active sites on the adsorbents surface were vacant and the solution concentration was high. After that period, few surface active sites were available, so only a slight increase in the metal uptake was observed [21].

Table 3 represents the constants of kinetics models for strontium adsorption on OP, NaOP and KOP. The obtained data revealed that pseudo-second order equation provides the best correlation coefficient (Fig.6) with extreme high values (>0.99). In addition, the calculated q_e values also agree with the experimental data in the case of pseudo-second-order kinetics. The obtained data were 10.51, 19.30 and 19.19 for OP, NaOH and KOP respectively while the experimental data were 11.9, 19.67 and 19.63 for the same order. These suggest that the adsorption data are well represented by pseudo-second-order kinetics and it supports the assumption that the chemical adsorption is the rate-limiting. The reaction mechanism may be partly a result of the ion exchange between strontium and the hydroxyl and carboxylic groups on the orange peel surface [19].

3.6. Thermodynamic studies

Thermodynamic considerations of an adsorption process are necessary to conclude whether the process is spontaneous or not. The Gibbs free energy change, ΔG°, is an indication of spontaneity of a chemical reaction and therefore is an important criterion for spontaneity. Both energy and entropy factors must be considered in order to determine the Gibbs free energy of the process. Reactions occur spontaneously at a given temperature if ΔG° is a negative quantity. The free energy of an adsorption, considering the adsorption equilibrium constant K_C is given by the following equation:

$$\Delta G^\circ = - RT \ln K_C \tag{13}$$

where ΔG° is the standard free energy change (J/mol), R the gas constant (8.314 J/mol K), and T is the absolute temperature (K). Considering the relationship between ΔG° and K_C change in equilibrium constant with temperature can be obtained in the differential form as follows [39]:

$$K_C = C_\partial / C_e \tag{14}$$

where C_∂ is mg of adsorbate adsorbed per liter and C_e is the equilibrium concentration of solution, mg/L. According to thermodynamics, the Gibb's free energy is also related to the enthalpy change (ΔH°) and entropy change (ΔS°) at constant temperature by the van't Hoff equation:

$$\ln K_C = - \Delta G^\circ/RT = - (\Delta H^\circ/RT) + (\Delta S^\circ/R) \tag{15}$$

Using the equation (15), the values of entropy change (ΔS°) and enthalpy change (ΔH°) can be calculated from the intercept and slope of the plot of ln Kc vs. 1/T. The results of the thermodynamic studies of the strontium adsorption process are presented in Tables 4 and in Fig. 7.

For the three adsorbents under the studies, the negative ΔG° value obtained from the equation (18) confirmed that the feasibility of the adsorption process and the spontaneous nature of the adsorption. Sr(II) gave negative values for ΔH° and ΔS°. A negative enthalpy (ΔH°) indicates that the adsorption process is exothermic. The magnitude of ΔH° may give an idea about the type of sorption. Two main types of adsorption are physical and chemical. Basically, the heat evolved during physical adsorption is of the same order of magnitude as the heats of condensation, i.e., 2.1-20.9 kJ/mol, while the heats of chemisorption generally falls into a range of 80-200 kJ/mol [19]. From Table 4, the absolute values of ΔH° for NaOP and KOP are 30.3 and 42.24 kJ/mol, respectively, which therefore indicate that Sr(II) adsorption by NaOP and KOP would be attributed to a physico-chemical adsorption process rather than a pure physical or chemical adsorption process. On other hand, the absolute value of ΔH° for OP is only 7.51 kJ/mol, which means the Sr(II) adsorption process onto OP surface is a pure physical process. Negative values of ΔS° indicate a decrease in randomness at the solid/solution interface during the adsorption process while low value of ΔS° indicates that no remarkable change on entropy occurs. For all adsorbents, OP, NaOP and KOP, the magnitude of ΔG° decreases as the temperature increases. The decrease in adsorption with rise in temperature may be due to weakening of adsorptive forces between the active sites of adsorbent and adsorbate species and also between the adjacent molecules of the adsorbed phase or because the mobility of metal ions in the solution increases with increase in temperature [19]. However, the magnitude of ΔG° for both NaOP and KOP is higher than values recorded for OP which reflects the effectiveness of treatment.

4. Conclusion

From this study it can be concluded that modification of orange peel (OP) with NaOH and KCl can effectively remove strontium from aqueous solution. The adsorbent which modified with NaOH (NaOP) shows a little better adsorption ability for Sr(II) than those modified with KCl (KOP). PH study revealed that maximum Sr(II) removal could be achieved at pH 6.6. The experimental data perfectly fitted the Langmuir isotherm model with regression coefficient $R^2 > 0.99$ for all adsorbents (OP, NaOP and KOP). Moreover, the experimental data was found to be fit better with the pseudo-second order kinetic model. The negative value of ΔG°,ΔH° confirms that Sr(II) adsorption is a spontaneous and an exothermic process. The negative value of ΔS° indicates a decrease in randomness at the solid/solution interface during the adsorption.

References:

[1] S. Chegrouche, A. Mellah, M. Barkat, Removal of strontium from aqueous solutions by adsorption onto activated carbon: kinetic and thermodynamic studies, Desalination 235 (2009) 306–318.

[2] A. Ahmadpoura, M. Zabihia, M. Tahmasbib, T. Rohani Bastamib, Effect of adsorbents and chemical treatments on the removal of strontium from aqueous solutions, Journal of Hazardous Materials 182 (2010) 552–556.

[3] M. Hafizi, H. Abdolghasemi, M. Moradi, Strontium adsorption from sulfuric acid solution by Dowex 50W-X Resins, Chin. J. Chem. Eng. 19 (2011) 267-272.

[4] A. Ghaemi, M. torab-Mostaedi, M. G. Maragheh, Characterization of strontium (II) and barium (II) adsorption from aqueous solution using dolomite powder, J. Hazard. Mater. 190 (2011) 916-921.

[5] L. Quan, L. Haining, L. Tengym, G. Min, Q. Binju, Y. Xiuhen, W. Zhijian, Strontium and calcium ion adsorption by molecularly imprinted hybrid gel, Chem. Eng. J. 157 (2010) 401-407.

[6] Y. Park, Y. Lee, W. S. Shin, S. Choi, Removal of cobalt, strontium and cesium from radioactive laundry wastewater by ammonium molybdophosphate polyacrylonitrite (AMP-PAN), Chem. Eng. J. 162 (2010) 685-695.

[7] J. Maresova, M. Pipiska, M. Rozloznik, M. Hornik, L. Remenarova, J. Augustin, Cobalt and strontium sorption by moss biosorbent: Modeling of single and binary metal systems, Desalination 266 (2011) 134–141.

[8] N. Feng, X. Guo, S. Liang, Enhanced Cu(II) adsorption by orange peel modified with sodium hydroxide, Trans. Nonferrous Met. Soc. China 20 (2010) s146-s152.

[9] N. Feng, X. Guo, S. Liang, Kinetic and thermodynamic studies of the biosorption of Cu(II) by chemically modified orange peel, J. Trans. Nonferrous Met. Soc. China 19 (2009) 1365-1370.

[10] S. Liang, X. Guo, N. Feng, Q. Tian, Application of orange peel xanthate for the adsorption of Pb^{2+} from aqueous solutions, J. Hazard. Mater 170 (2009) 170: 425-429.

[11] F. Gode, E. D. Ataly, E. Phlivan, 2008, Removal of Cr VI from aqueous solutions using modified red pine saw dust, Journal of Hazardous Materials, 152 (2008) 1201-1207.

[12] P. S. Kumar, R. Gayathri, R. P. Arunkumar, Adsorption of Fe (III) ions from aqueous solution by Bengal gram husk powder: equilibrium, isotherms and kinetic approach, EJEAFChe 9 (6) (2009) 1047-1058.

[13] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361‑1403.

[14] H. M. F. Freundlich, Uber die adsorption in Losungen, Z. Phys. Chem. 57 (1906) 385‑470.

[15] M.I. Temkin, V. Pyzhev, Kinetics of ammonia synthesis on promoted iron catalysts, Acta Physicochim. USSR 12 (1940) 217‑222.

[16] M. M. Dubinin, L.V. Radushkevich, Proc. Acad. Sci. Phys. Chem. Sect. USSR 55 (1947) 331‑333.

[17] S. Lagergern, About the theory of so-called adsorption of soluble substances, K. Sven. Vetenskapsakad. Handl. 24 (4) (1898) 1‑39.

[18] Y. S. Ho, G. Mckay, The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat, Can. J. Chem. Eng. 76 (1998) 822‑827.

[19] S. Liang, X. Guo, N. Feng, Q. Tian, Isotherms, kinetics and thermodynamic studies of adsorption of Cu2+ from aqueous solutions by Mg2+/K+ type orange peel adsorbents Journal of Hazardous Materials 174 (2010) 756–762.

[20] G. Annadurai, R.S. Juang, D.J. Lee, Use of cellulose-based wastes for adsorption of dyes from aqueous solutions, J. Hazard. Mater. 92 (2002) 263‑274.

[21] Y. Liu, Y.J. Liu, Biosorption isotherms, kinetics and thermodynamics, Sep. Purif. Technol. 61 (2008) 229‑242.

Table 1. Comparison of infrared bands in 4 000 - 400 cm^{-1} spectral region.

Functional group of adsorbent	Wavenumber/cm-1		
	OP	NaOP	KOP
O-H stretching vibration	3321	3321	3397
symmetric and asymmetric C-H stretching vibration	2924	2924	2922
Non-ionic carboxyl groups (-COOH, -COOCH3)	1736	-	-
Asymmetric vibrations of C=O	-	1623	1613
symmetric vibrations of C=O	-	1423	1420
Stretching vibration of C-O-C	1084	1095	1061

Table 2. Values of parameters of each isotherm model used.

Isotherm Model	Adsorbents	Parameter	R^2
Langmuir	OP	q_L=12.500 K_L=0.343	0.998
	NaOP	q_L=54.59 K_L=0.308	0.997
	KOP	q_L=52.36 K_L=0.186	0.992
Freundlich	OP	K_F=4.995 n=4.824	0.828
	NaOP	K_F=13.119 n=2.182	0.893
	KOP	K_F=10.132 n=0.994	0.852
Temkin	OP	A=19.290 B=1.708	0.867
	NaOP	A=5.122 B=9.599	o.974
	KOP	A=1.186 B=9.155	0.988
Dubinin-Radushkevich	OP	q_m=24.27 ß=1×10^{-7}	0.951
	NaOP	q_m= 31.27 ß=1×10^{-8}	0.733
	KOP	q_m= 46.10 ß=6×10^{-8}	0.902

Table 3. Values of parameters of each kinetic model used.

kinetic Model	Adsorbents	Parameter	R^2
Pseudo-first-order	OP	q_e=2.897 k_1=0.109	0.310
	NaOP	q_e =3.190 k_1=0.237	0.793
	KOP	q_e = 5.835 k_1=0.256	0.766
Pseudo-second-order	OP	q_e =10.515 k_2=0.743	0.997
	NaOP	q_e =19.305 k_2=0.454	o.9996
	KOP	q_e =19.193 k_2=0.447	0.9995
Elovich	OP	$\alpha=8.7\times10^3$ ß=1.02	0.548
	NaOP	$\alpha=2.1\times10^6$ ß=0.842	o.819
	KOP	$\alpha=5.8\times10^5$ ß=10.02	0.836
Intraparticle-diffusion	OP	k_{int}=7.755	0.416
	NaOP	k_{int} = 15.513	0.713
	KOP	k_{int} = 15.133	0.724

Table 4. Values of thermodynamic parameters for the adsorption of Sr(II) by OP, NaOP and KOP.

Adsorbent	T(K)	Kc	ΔG°(kJ/mol)	ΔH°(kJ/mol)	ΔS°(J/mol K)
OP	293	1.50	-0.99	-7.51	-22.48
	303	1.32	-0.70		
	313	1.14	-0.34		
	333	1.04	-0.11		
NaOP	293	60.35	-9.99	-30.30	-70.79
	303	32.33	-8.76		
	313	16.73	-7.33		
	333	13.58	-7.22		
KOP	293	67.03	-10.24	-42.24	-112.36
	303	19.58	-7.49		
	313	10.42	-6.10		
	333	7.52	-5.59		

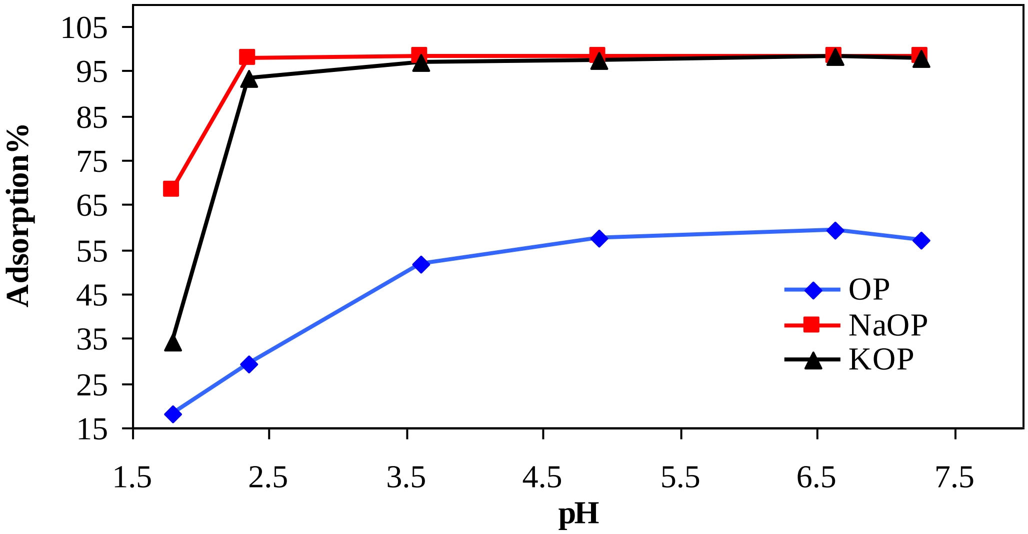

Fig. 1. Effect of pH on adsorption of Sr(II) by OP, NaOP, KOP. Initial Sr(II) concentrations 100 mg/L, S/L 5.0 g/L, contact time 6h, temperature 293K.

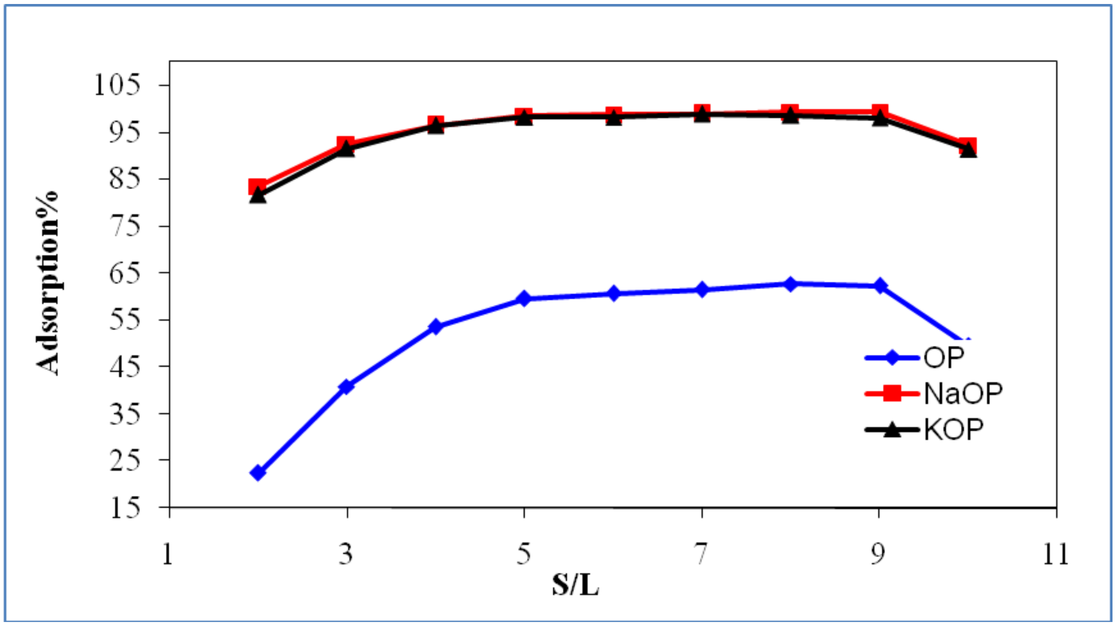

Fig. 2. Effect of solid/liquid (S/L) ratio on adsorption of Sr(II) by OP, NaOP and KOP. Initial Sr(II) concentration 100mg/L. pH 6.6, contact time 6h, temperature 293K.

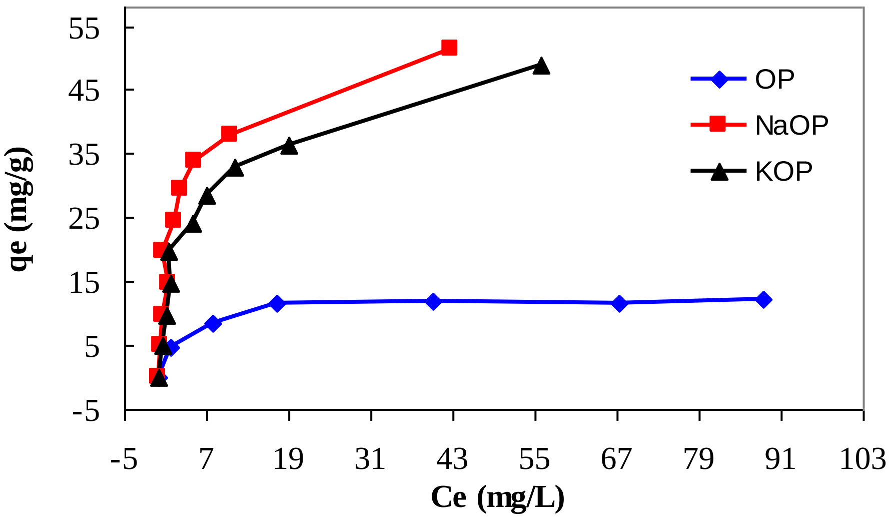

Fig. 3. Adsorption isotherms of Sr(II) by OP, NaOP and KOP. S/L 5.0 g/L, pH 6.6, contact time 6h, temperature 293K.

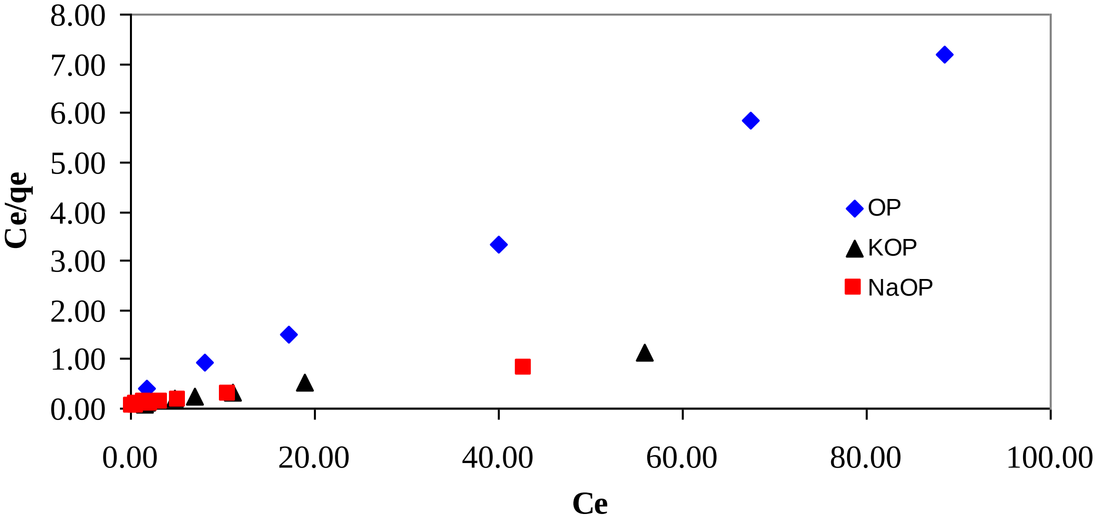

Fig. 4. Plot of C_e vs. C_e/q_e for estimation of correlation coefficient R^2 of Langmuir model.

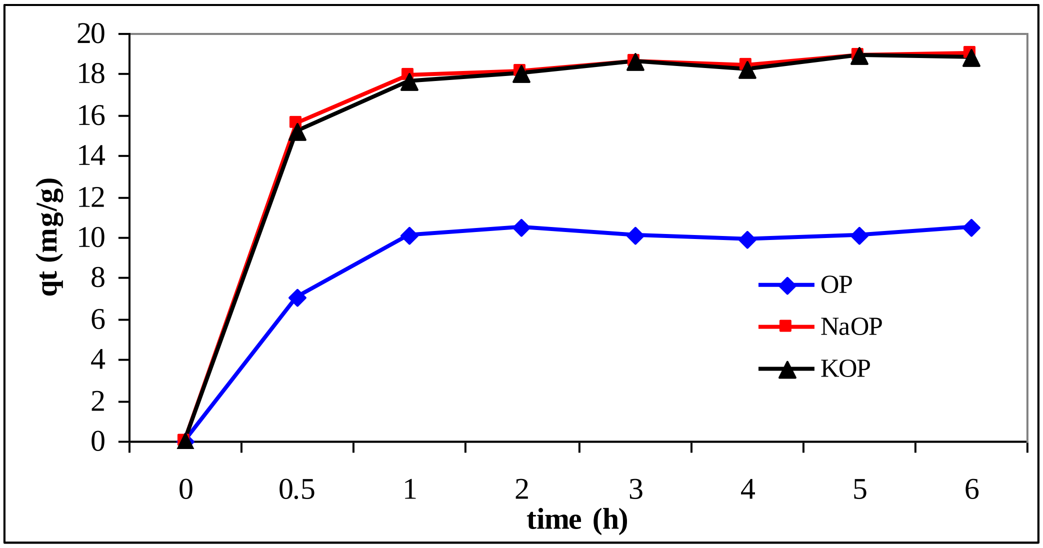

Fig. 5. Effect of time on Sr(II) adsorption by OP, NaOP and KOP. Initial concentration 100 mg/L, S/L 5.0 g/L, pH 6.6, and temperature 293K.

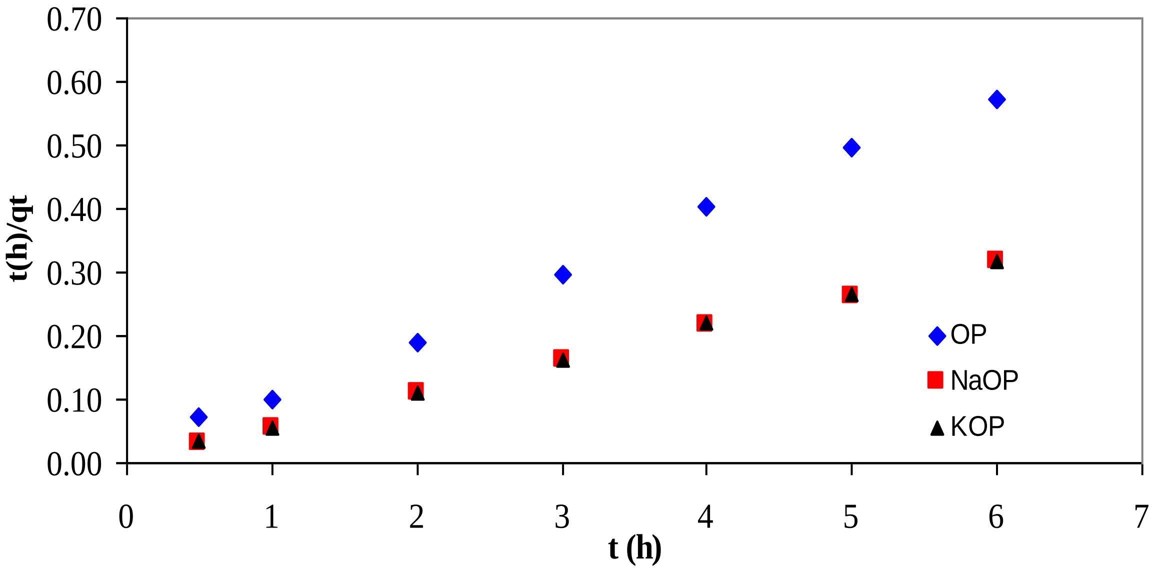

Fig. 6. Plot of t (h) vs. t/q_e of pseudo-second order graph.

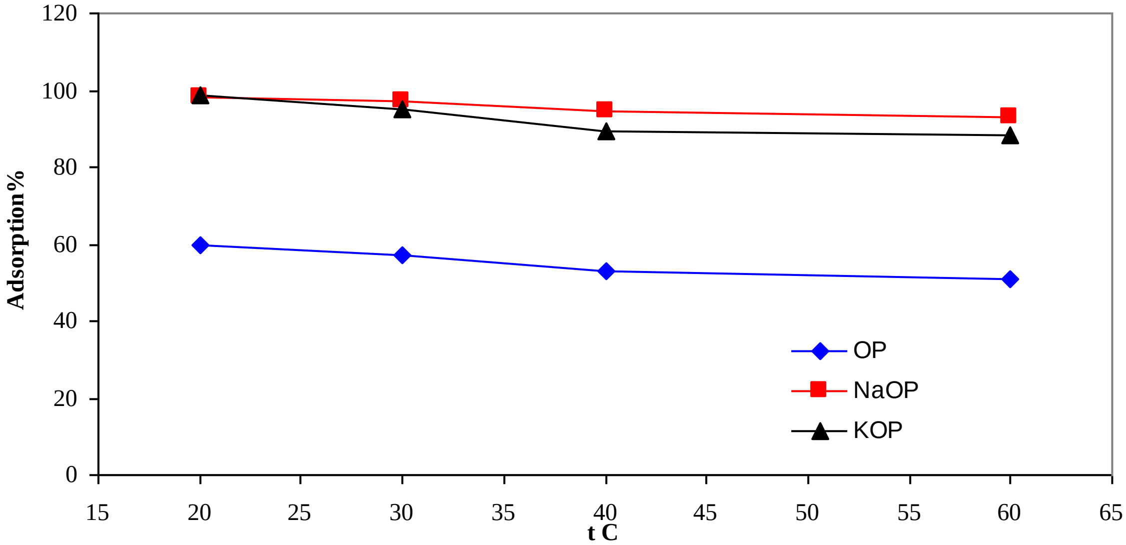

Fig. 7. Effect of temperature on adsorption of Sr(II) by OP, NaOP and KOP. Initial concentration 100 mg/L, S/L 5 g/L, pH 6.6, contact time 6h.