Study Of Using Bentonite – Poly Ethylene Glycol Composite for Metal Removal from Water

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Abstract: - Direct polymerization of polyethylene glycol (PEG) in suspensions of Bentonite (Ben) was used for preparation of Ben-PEG composite. The prepared composite was characterized using field-effect scanning electron microscopy, surface area measurements, and X-ray diffraction. In the XRD pattern there is a change in peak intensity. But New peaks appeared. This may be due to high dispersion of particles of polymer in the Ben matrix or low concentration of the modifying agent. The crystallinity absence after loading the sorbent with cadmium and lead ions in the SEM measurement indicates that there was no crystalline phase after sorption. The optimal conditions for adsorption of Cd^{2+} and Pb^{2+} ions were found to be a PEG content of 0.2 % and a contact time of 150 min. The sorption experiments were performed under different operating variables, including, pH, adsorbent dose and initial concentration of metals. For both Cd^{2+} and Pb^{2+}, Adsorption parameters were determined using both Langmuir and Freundlich isotherms, but the experimental data were better fitted to the Langmuir equation than to Freundlich equation. The adsorption equilibrium was described by the Langmuir model, which confirmed the presence of saturated mono-layer of adsorbent molecules on the adsorbent surface, that the energy of adsorption is constant. The potential of Ben-PEG composite for the removal of cadmium and lead from aqueous solution was substantiated.

Key words: Polymerization; Poly Ethylene Glycol; Bentonite; Cadmium and Lead Ions.

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1 Introduction

The amount of toxic pollutants increased as a result of industrialization as well as the increase in human activities. Among them, heavy metals, dyes, and phenolic compounds [1]. In recent years, the adsorption process has attracted much attention because of its easy control, reduced operating costs and outstanding performance [2-3]. Heavy metal ion contamination exists in aqueous waste streams from different industries such as, batteries, metal plating manufacturing besides agricultural sources where fungal sprays and fertilizers are seriously utilized [4]. The heavy metal ions released into the environment represents a risk to the ecosystem, human health and particularly to people due to its toxicity for living organisms [5-6]. Clay and bentonite are adsorbents and have received great attention due to their environmental suitability, high mechanical and chemical stability, low cost, and natural abundance. These materials are characterized by high surface area and high cation exchange capacity and are used as adsorbents for various separation purposes [7-10]. The improvement of the adsorption ability of natural adsorbents such as clay and bentonite is essential [11].

Many clay adsorbents in the natural state do not have a high capacity for adsorption, so they are often modified to improve the properties of adsorption, thermal activation, catalysts and various complexing agents such as organic materials and polymers used to activate natural adsorbents with different methods [12]. The novelty of research work is preparation of adsorbent with low cost and is applicable to be used for removal of heavy metal pollutants with high removal efficiency.

The aim of this work was to study the characteristics of modified bentonite sorbent and study the removal of lead and cadmium ions. In this work, the Ben clay was modified with poly ethylene glycol (PEG) which is an available reagent and non- toxic, miscible in water and interacts at the molecular level. Batch adsorption experiments are carried out and the adsorption kinetics and isotherm were contemplated.

2 Experimental Setup

2.1. Materials

Bentonite (Ben) (95% purity), purchased from the local company (Egypt); Poly ethylene glycol (PEG) produced by Sigma-Aldrich with molecular weight of 4000 g mol−1; $Pb(NO_3)_2$ and $CdCl_2 \cdot 2H_2O$ produced by Alpha chemicals.

2.2 Preparation of Adsorbents

The Ben clay was treated with different concentrations of PEG. For this purpose, 25 gm natural Ben was mixed with 200 ml of 0.2, 0.5, 1.0, 1.5, 2 and 4 % aqueous solutions of PEG, using continuous stirring at 25℃ for 2 h and left for 36 h at ambient temperature. Then the suspension of the adsorbent was separated from the solution by filtration. Then washed thoroughly with distilled water and dried at 130℃ for 5 h. Finally, the sorbents obtained were ground to a powder of 80 µm in size using a porcelain mortar.

2.3 Batch Experimental System

Batch adsorption experiments were conducted using Ben/PEG composite by varying the dose (0.5, 1, 1.5, 2, 2.5 and 3 g/L), and contact time (0, 30, 60, 90, 120, 150 and 180 min. agitated with 0.5 g). All experiments were conducted in a jar test at 150 rpm at room temperature. After equilibrium, the concentration of samples was measured by Atomic Absorption Spectrophotometer, (ICE3000, Thermo scientific Limited, UK.). The percentage of removal efficiency (R %), has been calculated from equation (1)

Absorption (%) = (Co-Ce) / Co *100 (1)

where R % is the removal efficiency, Co is the initial metal concentration in solution (mg/L), Ce is metal concentration after adsorption in solution (mg/L).

The capacity of absorption qe (mg/g) at equilibrium has been calculated using equation (2)

Qe (mg/l) = (Co-Ce) * V/m (2)

Where Qe is the adsorption capacity at equilibrium, mg/g.
V is the aqueous solution volume, L.
m is the adsorbent weight, g.

2.4. Sorbent Characterization

XRD model X Pert Pro Philips MPP PW 3050/60 X-Ray diffractometer used for detailed mineralogical composition of the sorbent material. On the other hand, Scanning Electron Microscopy (SEM) was used to determine microstructure and morphological features of the prepared sorbent by using SEM Model Quanta 250 FEG (field emission gun) with accelerating voltage 30 KV, (FEI Company, Netherlands).

2.5 Adsorption Study Pattern

2.5.1 pH Effect

About 0.5 gm of Ben-PEG composite was added to 30 mg/l of lead nitrate and cadmium chloride solutions separately at temperature 27 C $\pm$ 2 ℃ and the stirring of the solution was mixed at 150 rpm. The pH effect on adsorption of metal ions onto raw Ben was studied earlier [13]. The pH was adjusted using NaOH for alkaline medium and HCL for acidic medium.

2.5.2 Contact Time Effect

A dosage of 0.5 gm of Ben-PEG composite with different contact times ranging (30-180 minutes) added to 30 mg/l of cadmium chloride and lead nitrate solutions separately, ambient temperature 27 $\pm$ 2 ℃ and the solution stirring rate was fixed at 150 rpm.

2.5.3 adsorbent Doses Effect

Different adsorbent doses (0.5-3 gm) of Ben-PEG composite were added to 30 mg/L of lead nitrate and cadmium chloride solutions separately for 120 minutes at temperature 27 $\pm$ 2℃ and pH 7.

2.5.4 Initial Metal Ion Concentration Effect

A dosage of 0.5 gm of Ben-PEG composite was mixed in solutions with initial metal ion concentrations ranging from (5-30 mg/L) at temperature 27 $\pm$ 2℃ and pH 7.

3. Results & Discussion

3.1 Characterization of Adsorbents

The obtained Ben–PEG sorbent was thoroughly characterized by EDX, FE-SEM and XRD Analysis. Physico-chemical and textural characterization of the Ben and modified Ben sorbent is summarized in table 1. Ben in its dry state has a moisture content of around 8.1% and ash content of 6.1%. Moreover, the data show that the initial Ben clay modification leads to a reduction in the total pore volume of acetone (from 28.2 to 18.12%), which indicates a reduction in the mesopores number. In addition, the increase in iodine adsorption (from 28.60 to 39.00%) indicates microporous structure improvement. Water sorption measurements indicated that the pore volume decreased by polymer modification. Hence, we observed that the modification of Ben by PEG leads to a predominance of meso and micro-pores in the structure of the sorbent, which significantly enhance the adsorption of heavy metal ions.

Table (1) Textural characterization of Ben and Ben-PEG

Characterization	Ben	Ben-PEG
Ash Content, %	6.1	21
Moisture, %	8.1	4.6
Adsorption activity on iodine, %	28.6	39
The total pore volume of acetone, %	28.2	18.12
The total pore volume of water, cm^3g^{-1}	0.01	0.008

Figure 1A,1B shows typical FE-SEM images of natural Ben and modified Ben–PEG. natural Ben (Fig. 1A) has a uniform texture provided by micropores which have a diameter in the range of 2–5μm. Needle-shaped appendages of the polymer are shown in this image (Fig. 1B), which indicates the PEG impregnation. The crystallinity is absent after loading the sorbent with Cd^{2+} and Pb^{2+} ions (Fig. 1C and 1D) indicates that there was no crystalline phase after sorption.

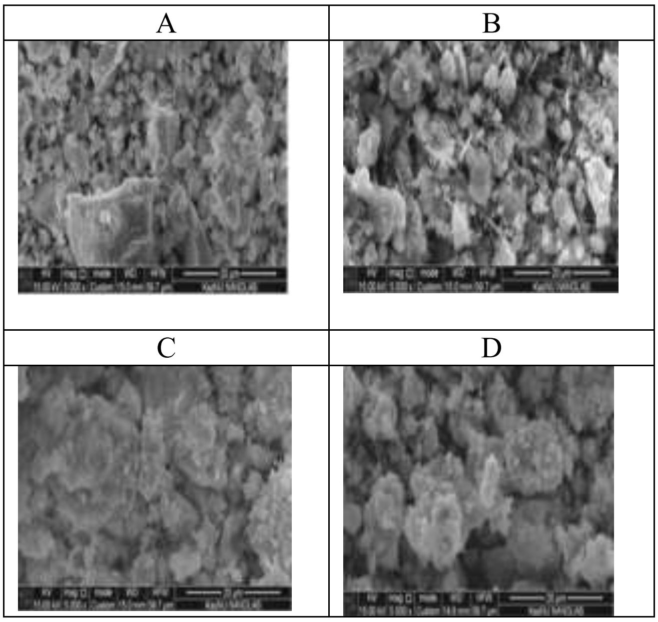

Fig1: SEM images of sorbents: (A) Ben, (B) Ben–PEG, (C) Ben–PEG-Cd and (D) Ben–PEG-Pb.

The main mineral of Ben is the Montmorillonite, it has a 2:1 layer structure, containing octahedral alumina sheet between tetrahedral silica sheets [14]. The bond between the silica sheets is very weak, allowing exchangeable ions and water to enter. Adsorption of PEG can occur on both interlayer spaces and external surfaces. So, the adsorption happens according to the ion-exchange mechanism.

The XRD patterns of raw Ben (A) and modified Ben (B) are shown in Figure (2), the raw Ben contains diffraction patterns of Montmorillonite, that located at 2θ = 20.3, 32.3, and 62.4 and quartz, where the characteristic peaks located at 2θ= 37.2, 39.1 and 50.65, respectively. The other peaks for impurities due to illite, field spar and cristobalite [15]. However, as can be observed in the diffraction pattern of Ben-PEG as shown in Fig. (2), there is a change in peak intensity. No new peaks appeared. This may be due to high dispersion of particles of polymer in the Ben matrix or low concentration of the modifying agent.

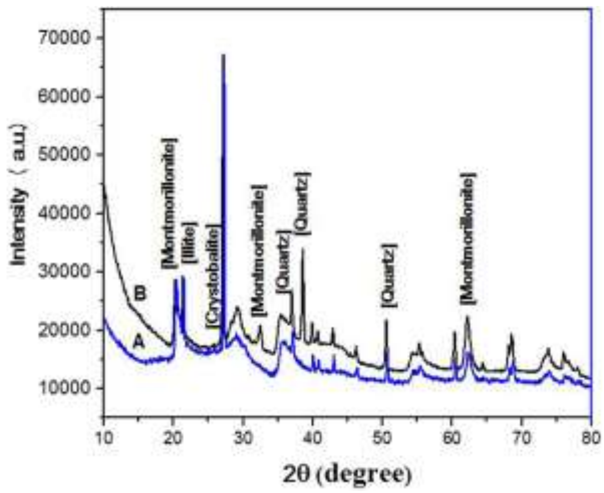

Fig. 2. XRD patterns of: (A) Raw Ben and (B) Ben–PEG.

3.2. Effect of pH

The effect of variation in pH on the removal of Cadmium and Lead ions has also been studied using Ben-PEG composite in the range from 3 to 11 using 0.1 % HCl and 0.1 % NaoH solutions that gave the maximum value of pH for our investigations for cadmium and lead ions removal. It is apparent from Fig. (3) that the lead removal shows maxima at pH 7 solution and then decreases with further increase in pH and the cadmium removal shows maxima at pH 9 solution and then decreases with further increase in pH.

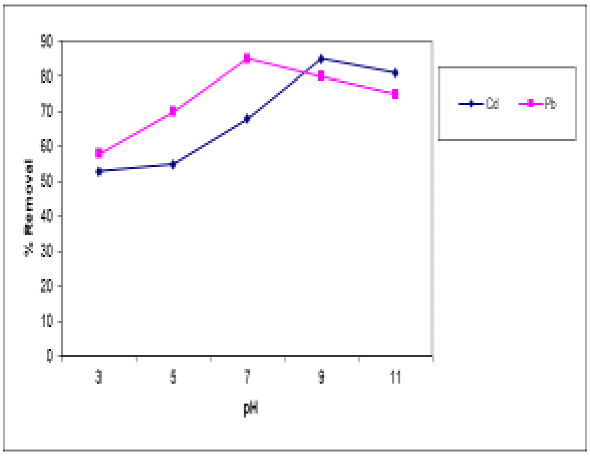

Fig. 3: Effect of variation in pH on adsorption of cadmium and lead ions on Ben-PEG Composite

3.3. Effect of contact time

The effect of stirring time on the removal of cadmium and lead ions using Ben-PEG composite was studied by varying the time of stirring from 30 to 180 minutes for the optimum equilibrating time, pH adjusted at 7 and stirring rate 150 rpm. Results in Fig. (4) show that the equilibrium in adsorption of cadmium ions is attained at 150 minutes of stirring time and lead ions are attained at about 150 minutes of stirring time. Therefore, the optimum stirring time of 150 minutes has been chosen for all investigations throughout the study.

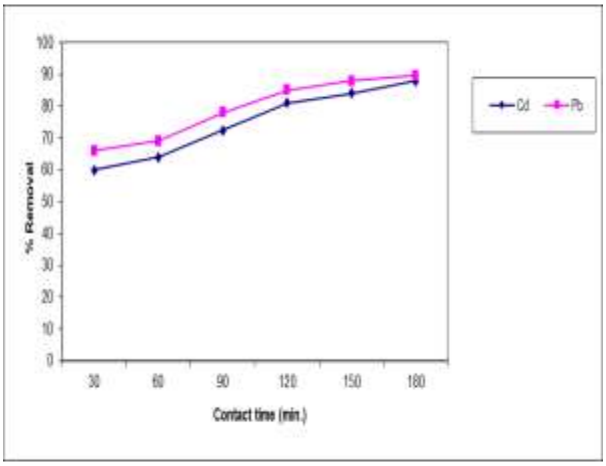

Fig. 4: Effect of contact time on adsorption of cadmium and lead ions on Ben-PEG

3.4. Effect of adsorbent dose

The effect of adsorbent dose of Ben-PEG composite on the removal of cadmium and lead ions was studied by varying adsorbent dose from 0.5 to 3 gm at 27 $\pm$ 2°C. The pH of solution adjusted at 7 and time 150 minutes. It is observed that the maximum adsorption obtained at 2.5 gm for cadmium and lead ions removal as shown in Fig. (5).

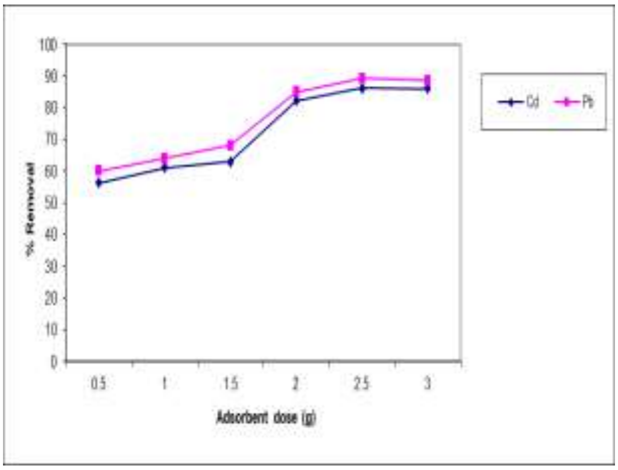

Fig. 5: Effect of adsorbent dose of Ben-PEG composite on adsorption of cadmium and lead ions

3.5. Effect of initial metal concentration

Adsorption studies were carried out on a fixed weight of Ben-PEG Composite 2 g with varying lead concentrations from 5 to 30 mg/L. It is observed from our studies that the cadmium and lead removal efficiency increase with increasing lead concentrations and rises to maxima up to around 25 mg/L as shown in Fig. (6). In a previous study result [16] have shown that such behavior is anticipated due to the buffering properties of lead compounds.

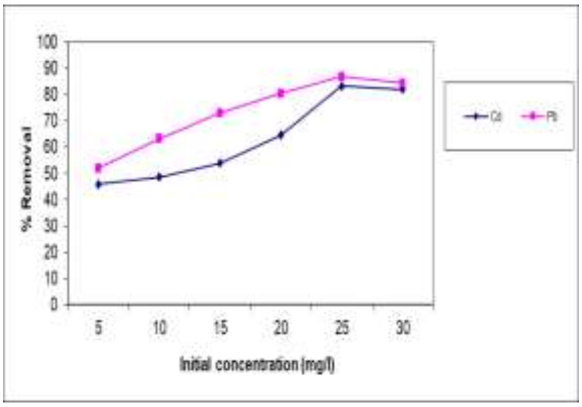

Fig. 6: Effect of initial concentration of metals on adsorption of cadmium and lead ions on Ben-PEG Composite

3.6. Adsorption models

3.6.1. Adsorption isotherm

An adsorption isotherm equation is an expression of the relation between the amount of solute adsorbed and the concentration of the solute in the fluid phase since the adsorption isotherms are important to describe how adsorbates will interact with the adsorbents which are important for design purposes; therefore, the correlation for equilibrium data using an equation is essential for practical adsorption operation [17]. Two isotherm equations were adopted in this study as follows:

3.6.1.1. Langmuir isotherm equation

The Langmuir equation is based on the assumptions that maximum adsorption corresponds to a mono-layer of adsorbent molecules on the surface of adsorbent, so the energy of adsorption is almost constant [18] The Langmuir equation is defined as:

$Q_e = (b.Q_m.C_e)(1+bC_e)$ (3)

And in linearized form is:

$Ce/Qe = (Ce/Q_m) + (1/(bQ_m))$ (4)

Where "Q_m" is Langmuir constant related to the adsorption capacity and "b" is Langmuir constant related to sorption energy. "C_e" is the equilibrium concentration in mg/l, and "Q_e" is the amount of adsorbate adsorbed per unit weight of adsorbent (mg/g). The plots C_e/Q_e against C_e are shown in Fig. (7) and Fig. (8). The adsorption of cadmium and lead ions on Ben-PEG composite give a straight line. It is clear that the linear fit is fairly good and enables the applicability of the Langmuir model.

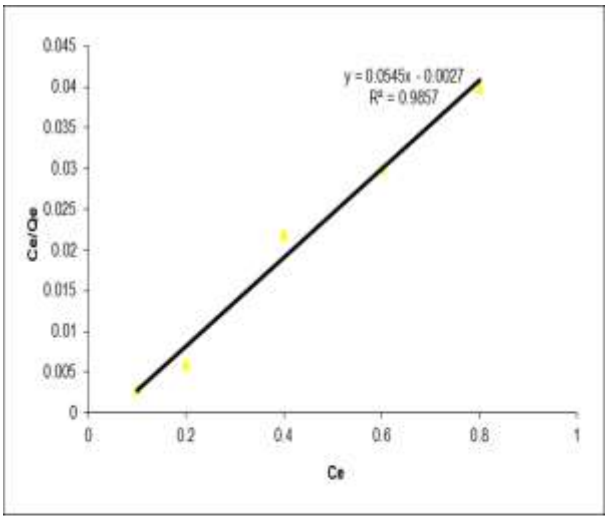

Fig. 7: Langmuir isotherm plot for adsorption of cadmium ions on Ben-PEG composite

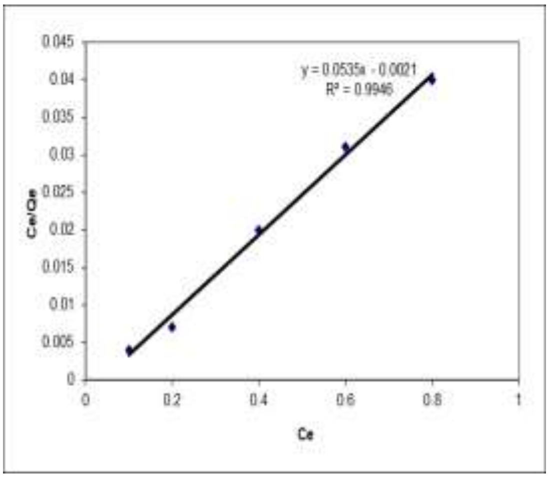

Fig. 8: Langmuir isotherm plot for adsorption of lead ions on Ben-PEG composite

Table 2: Langmuir constants from Langmuir isotherm

	R^2	Q_m	b
Cadmium removal	0.9857	14.42	246.2
Lead removal	0.9946	12.92	210.9

3.6.1.2. Freundlich isotherm equation

The Freundlich sorption isotherm, one of the frequently used mathematical descriptions, gives an expression including the surface heterogeneity and the exponential distribution of active sites and their energies.

$Q_e = k. C_e^{1/n}$ (5)

and in linearized form is :

$\text{Log } Q_e = \log k + (1/n) \log C_e$ (6)

Where" C_e" is the concentration at equilibrium in mg/l, "Q_e" amount of adsorbate per unit weight of adsorbent (mg/g), "k" is a parameter according to temperature and "n" is a characteristic constant for the adsorption system under study. The plots of log Q_e against log C_e are shown in Fig. (9) and Fig. (10), the adsorption of cadmium and lead ions onto Ben-PEG composite give a straight line; values of "n" between 2 and 10 show good adsorption [18].

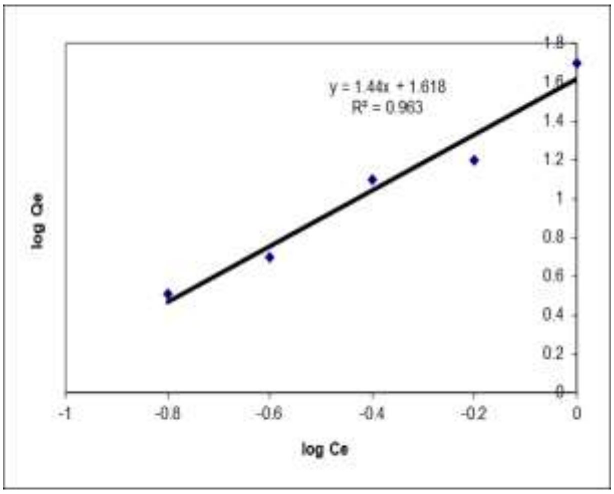

Fig. 9: Freundlich isotherm plot for adsorption of cadmium ions on Ben-PEG composite

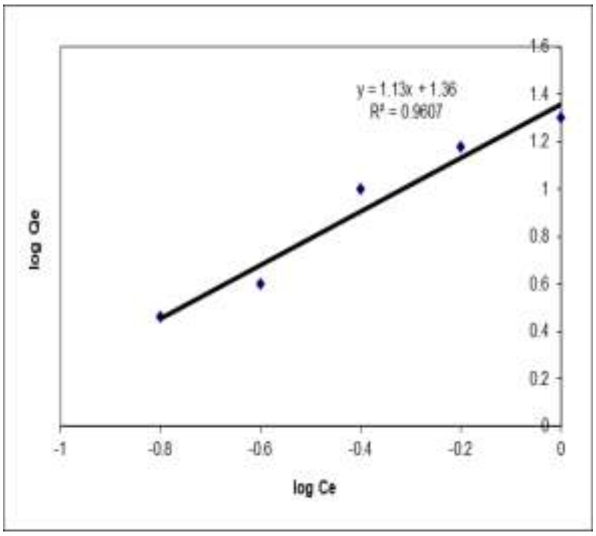

Fig.10: Freundlich isotherm plot for adsorption of lead ions on Ben-PEG composite

Table 3: Freundlich constants from Freundlich isotherm

	R^2	k	n
Cadmium removal	0.963	0.012	0.54
Lead removal	0.9607	0.01	0.53

4. Conclusions

The Ben-PEG composite was successfully prepared by direct polymerization and used as an adsorbent for removing Cd^{2+} and Pb^{2+} from aqueous solutions. SEM and XRD analysis indicate intercalation of the PEG polymer into the initial structure of the Ben. The adsorption of Cd^{2+} and Pb^{2+} was found to be dependent on pH, adsorbent dose and the metal ion concentration. The optimal conditions for adsorption of Cd^{2+} and Pb^{2+} ions were found to be a PEG content of 0.2 %, contact time of 150 min., adsorbent dose 2.5 gm, and initial concentration of metal ions 25 mg/l. The adsorption equilibrium for both Pb^{2+} and Cd^{2+} can be described by both the Langmuir model and the Freundlich model, but best fitted to the Langmuir model and therefore it is more suitable for the analysis of kinetics. The results show that the Ben–PEG composite is an effective sorbent for the extraction of cadmium and lead ions using modified, low-cost sorbent, which can be used for purification of wastewater at the industrial level. In future research the bentonite clay can be treated and used for removal of dyes from water.

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Contribution of Individual Authors to the Creation of a Scientific Article (Ghostwriting Policy)

The author contributed in the present research, at all stages from the formulation of the problem to the final findings and solution.

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Conflict of Interest

The author has no conflict of interest to declare that is relevant to the content of this article.