TPM Vol. 32, No. S2, 2025
ISSN: 1972-6325
https://www.tpmap.org/

A SPECIFIC SPONTANEOUS MODIFIED CLAY EXHIBITS URANIUM ION ADSORPTION CHARACTERISTICS

RANU SINGH*[A], JAYATI CHATTERJEE MITRA[A], SANTOSH KUMAR SAR[B], SHASHI KANT JAISWAL[B], PANKAJ TAMRAKAR[C]

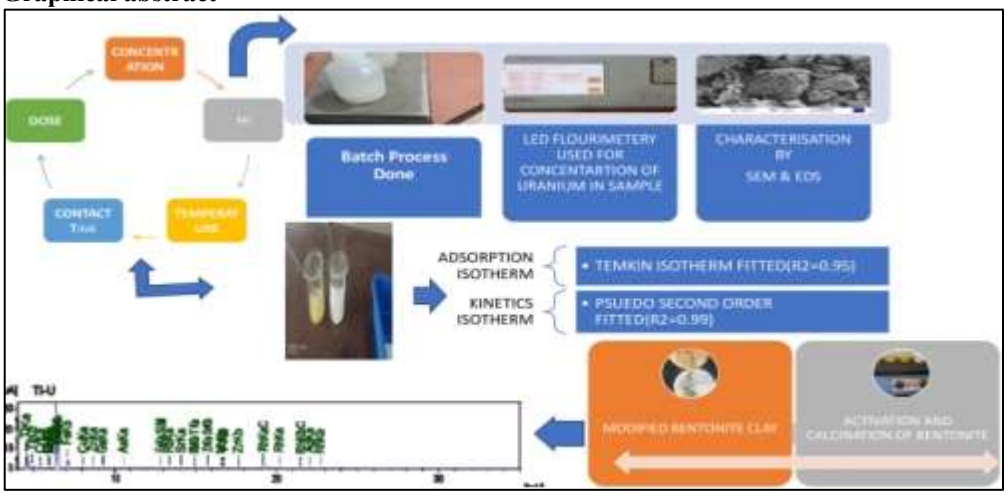
[A,] DEPARTMENT OF CHEMISTRY; CV RAMAN UNIVERSITY, KOTA, BILASPUR (C.G.), INDIA
[B] DEPARTMENT OF APPLIED CHEMISTRY BHILAI INSTITTE OF TECHNOLOGY, DURG (C.G.), INDIA
[B] DEPARTMENT OF APPLIED CHEMISTRY BHILAI INSTITUTE OF TECHNOLOGY, DURG (C.G.), INDIA
[C] SENIOR SCIENTIFIC OFFICER, REGIONAL FORENSIC SCIENCE LABORATORY, DURG(C.G.), INDIA

EMAIL ID: ranu17.singh@gmail.com[A], jayatimitra@cvru.ac.in[A], Santosh.sar@bitdurg.ac.in[B], Sk.jaishwal@bitdurg.ac.in[B], ashuneily@gmail.com[C]

Abstract

Modified low-cost adsorbents, specifically Bentonite clay mineral, have been studied and analysed for their efficacy in removing uranium from soil and rock. It was determined that Temkin was the most appropriate representation for adsorption isotherms, with $R^2 = 0.95$. On the other hand, the kinetic analysis was characterized by pseudo second order ($R^2 = 0.99$). The adsorption capacity of modified Bentonite is 24.75 µg/l. XRF, SEM, and EDS investigations were performed to characterize the adsorption characteristics of the modified clay Bentonite surface area. Bentonite at a dosage of 0.1 g per 50 ml of adsorbent effectively eliminated 95% of U(VI) from a metal ion solution with a concentration of 50 µg/l at 308 K within 40 minutes. The equilibrium adsorption is documented at pH =7. Various thermodynamic characteristics have been evaluated, including Gibbs free energy, entropy, and enthalpy. To validate the findings of the modified clay (Bentonite) laboratory study referenced above, we conducted uranium adsorption tests with natural soil and rock samples contaminated with naturally occurring uranium and succeeded in removing 87% and 85% of the rock and soil samples.

Graphical abstract



Keywords: Uranium, Adsorption, Bentonite, Removal

INTRODUCTION

Uranium is an element characterized by its inherent instability, wherein it spontaneously emits alpha particles a helium-4 nucleus of two protons and two neutrons from its atomic nucleus. These particles have a half-life of 4.468 billion years. Uranium has been proven to pose radiation and chemical hazards. The main sources of contamination for soils and groundwater are uranium ore, processed uranium, and the waste generated during mining [Evseeva et. al.(1947) and Perel'man(1996)] . Entry of uranium into groundwater and subsequent flow into rivers and lakes poses a particularly dangerous risk to human health. Hence, the intentional fixing of uranium in soil is a topic of great interest to ecologists. This characterizes its responsiveness to environmental redox conditions. Uranyl develops highly mobile molecules under oxidative circumstances [Perel'man (1999)]. For reducing circumstances, U(IV) undergoes oxidation to form the stable uranyl oxide UO_2. This phenomenon governs the diverse behaviour of uranium in soils. An extensive variety of robust materials has been utilized as

adsorbents for heavy metals, toxic chemicals, and radioactive substances. Clays such as kaolinite, bentonite, and montmorillonite have been the primary focus of significant research in this area. Atomic absorption spectroscopy (AAS), inductively coupled plasma-optical emission spectroscopy (ICP-OES), and inductively coupled plasma mass spectrometry (ICP-MS) are among the analytical techniques employed in the field of uranium measurements. This study has chosen the LED Fluorimeter LF-2a methodology. Previous research has demonstrated that the adsorption of uranium ions onto Kaolinite is enhanced through the processes of calcination and acid activation of Kaolinite, particularly within the concentration range of 5–35 ppm [Wang et.al. (2010)]. Solvent extraction is one of the best advanced chemical processes intended for uranium separation and removal adsorption as well as other studies [Ali et.al. (2018),Youssef et.al. (2020) ,Hagag et.al.(2023)].The ion exchange resin study, and the Inclusion membrane, as well as, liquid emulsion electroplating and membrane [Amoli et.al.(2006),. Kulkarni et.al. (2018)] among other methods. Solvent extraction and adsorption methods are commonly employed. Highly concentrated uranium (>1000 mgL^{-1}) solvent extraction is preferred for economic use and is applicable at low acidic pH levels [Ali et.al. (2018)]. In contrast, the adsorption of lower uranium concentrations (<1000 mgL^{-1}) primarily occurs at elevated acidic pH (3–6) or neutral pH levels [Hagag et.al. (2023)]. The adsorption capacity of clay minerals can be enhanced by exchanging the naturally exchangeable cations with organic cations, which makes the clay surface more hydrophobic [Cadena et.al.(1990),Malakul et.al.(1998)]. Adsorption, interaction, and cation exchange capability allow clay minerals to interact with a broad range of cations and organic molecules. These minerals may function as economical sorbents for removal.

The chemical formula of the most common and well-known silicate clay mineral, Kaolinite & Bentonite are $Al_2Si_2O_5(OH)_4$, ($Al_2O_3{\cdot}4SiO_2{\cdot}nH_2O$,) and it is present on every continent [Kadir et.al. (2017)],Ceramics [Zeballos et.al. (2016)]cosmetics, painting [Hradli et.al.(2016)], and cement are just a few of the many industrial fields that predominantly utilize kaolinite. Indeed, adsorption investigations were the primary scientific applications of kaolinite & bentonite. Numerous studies have documented the adsorption of kaolinite, such as the low-cost adsorbent kaolinite [Mustapha et.al. (2020)], protein-fragment on mineral surfaces [Awad et.al.(2020)], PbCl2/CdCl2, pharmaceutical residues [Hounfodji et.al.(2020)] and composites doxycycline and Congo red [Olusegun et.al.(2021)]. Adsorption, a physio-chemical process in the solid/liquid phase, is increasingly recognized as an effective method for absorbing heavy metals, pollutants and essential elements. Consequently, the accessibility of resources, affordability, practical applications, and ease of preparation methods attract significant attention from both the scientific community and industry. It is important to highlight that wastes, ores, resins, zeolites, biomass, and composites serve as the foundational materials for adsorbents. At present, the ores that are predominantly utilized as adsorbents comprise Phosphate, Kaolinite, Bentonite, and granite. During the course of this research, modified clay samples of Bentonite were put through a series of tests to determine their ability to absorb uranium. A process known as acid activation was utilized in order to modify clay samples[Christidis et.al.(1997)]. This study focused on assessing the uranium adsorption properties of modified clay samples that include Bentonite. The primary factors influencing the effectiveness of uranium removal from clay samples include uranium concentrations, contact time, and pH, all of which were thoroughly examined.

MATERIAL AND METHODOLOGY

Bentonites, which are mostly composed of clay minerals belonging to the smectite group, are utilized in a substantial number of industrial applications. A distinctive characteristic of this mineral group is the replacement of Si^{4+} with Al^{3+}. the crystal structure by a cation of reduced valency. The loosely-held "exchangeable" cations Na^+, Ca^{2+}, Mg^{2+}, and H^+, which are mostly found on the interlayer crystal surface, balance the remaining negative charges. A number of distinctive properties of smectite, such as a large chemically active surface area, a high cation exchange capacity, an interlayer surface with unusual hydration characteristics, and occasionally the capacity to significantly alter the flow behaviour of liquid, are caused by its structure, chemical composition, exchangeable ion type, and small crystal size**.** The exchangeable cations in bentonite are readily replaceable, with Na^+ being rapidly substituted by Ca^{2+} and Mg^{2+} under leaching conditions**[**Odom (1984) **].**

1.Identifying the Modified Clay Samples that were studied (adsorbents)

The present work investigated the potential of Bentonite as raw materials for the adsorption of uranium. Bentonite was purchased from Bio Organic (Gems of Organic), batch number and F/1396, and neutral code HP/86/2002.Clay minerals natural exchangeable cations with organic cations, resulting in a more hydrophobic clay surface**[**Cadena et. al.(1990),Malakul et.al. (1998)**].**

XRF ANALYSIS

The XRF analysis of bentonite indicates that this type of clay primarily comprises aluminium silicate, with sodium and calcium serving as exchangeable cations. Therefore, it is classified as an intermediate bentonite with a moderate swelling capacity[Mekhemera et.al. (2008)]. The chemical composition of the modified clay is presented in Tables 1 and 2, while the XRF pattern is depicted in Figures 1a, 1b, 2a, 2b, and 3a, 3b.This XRF study pattern displays various peak lists before and after the activation of Bentonite. This investigation demonstrates that activation enhances surface area, facilitating the exchange of cations and anions in modified clay.

Table-1Chemical composition of Bentonite clay before and after activation

Element	Before	After

Si	46.135%	71.911 %
Fe	24.734%	12.809 %
Al	16.548%	5.449 %
K	4.584%	3.781 %
Ti	2.868%	4.772 %
Cl	1.811%	0.630 %
Ca	1.467%	0.135 %
S	1.022%	0.302 %
Mn	0.262%	0.062 %

2. Adsorption Experiment

To eliminate any potential influence, all glassware was rinse with a diluted solution of nitric acid (HNO_3) and then rinsed with deionized water (DDW).Quantitative sorption experiments were carried out in 50ml Erlenmeyer flasks to explore the influence of pH (2-10), quantity (0.05-2g/50 ml), initial uranium concentration (1-50 µg/l), contact time (5-40 min), and temperature (25-45 °C) on the optimal removal of U(VI).The pH of the solution medium was modified by adding 0.1 M solutions of sodium hydroxide (NaOH) and hydrogen nitrate (HNO_3). Control experiments were conducted in conjunction with each experiment. The polypropylene was systematically stirred at a speed of 400 rpm in a spinning shaker for a predetermined duration.During the process of determining the quantity of uranium that was present in the filtrate, the flasks were subjected to a moderate agitation, and samples that were taken at various time intervals were centrifuged. The concentration of uranium in the filtrate was determined by employing an LED fluorimeter, which is widely recognized as the most accurate and reliable instrument for quantifying uranium in aqueous solutions, even at a low concentration of 0.1 µg L^{-1} [Sahu et.al.(2014)]. A comparison of the concentration of uranium in the solution before and after adsorption was used to calculate the amount of uranium that was adsorbed onto the biosorbent

According to [Aytas et.al. (2009)]adsorption capacity (qe) and removal efficiency (%) are found using Eqs. (1) and (2), respectively:

$$\textit{Adsorption quantity } qe\ (\mu g/g) = (Ci - Ce) * V/m \quad (1)$$

$$\textit{Removal efficiency } (\%) = [(Ci - Ce)/Ci] * 100 \quad (2)$$

The concentration of Uranium (VI) adsorbed on modified clays at equilibrium was represented as qe. Initial concentration of the U (VI) solution was labeled as Ci, whereas the concentration at equilibrium was referred to as Ce. The volume of the U (VI) solution is represented as V, while the weight of the modified clay is indicated as m. The difference between the initial and final concentrations has been determined using the removal efficiency (%) equation in order to determine the adsorption percentage (removal efficiency from U(VI) solutions).

3. **Initial preparation of the clay samples under investigation**

A series of pretreatments [Christidis et.al.(1997)] were carried out in order to improve the removal efficiency of Bentonite clay samples. Acid activation of clay samples is one of the required pretreatments. This is accomplished by treating 0.5 grams of clay with 25 milliliters of 1.5 N hydrochloric acid at a temperature of 70 degrees Celsius in a water bath for eight hours. The clay was calcinated by first exposing samples to a temperature of 400 degrees Celsius for one hour, and then agitating the samples with 25 milliliters of 1.5 N hydrochloric acid for the same amount of time. In the end, the mixture was then subjected to filtration, after which the solid fraction was washed with deionized water, and finally, it was dried at room temperature. A meticulous examination of the impact of each pretreatment was conducted.

4.CHEMICAL, REGENTS, APPARTUS

To prepare uranium solutions at different concentrations, 100 mg/L of ICP-66 N-0.01X-1 Uranium was used as a stock solution. HNO_3, $Na_4P_2O_7$, H_3PO_4, and NaOH were some of the analytical grade (AR) chemicals that were utilized in the research. A Quantalase LED fluorometer, which was manufactured in India, was utilized in order to ascertain the fluorescence intensity of the sample solution in aqueous medium. The Hanna Multiparameter equipment (HI 5521 and HI 5522) was utilized in order to ascertain the salinity, conductivity, TDS, and pH .

5. QA and QC

The device and the calibration process were conducted using standard uranium stock solution (ICPMS-66 N-0.01X-1 Uranium) at a dosage of 100 mg/L. The LED Fluorometer LF-2a has a range of 0.5 ppb to 1000 ppb. Standard laboratory tools including analytical balances and micropipettes were used to prepare uranium solutions with varying amounts. A conventional addition technique was used to offset the matrix effect. Each measurement was calculated as the average of four measurements. Acceptable results fell within a standard deviation of ±10%. Three different tests were conducted for each measurement. Uranium concentration has been measured in a temperature-controlled, dust-free environment.

6.Characterization of adsorbent

The clay samples were analysed via scanning electron microscopy (SEM) utilizing a Zeiss Gemini SEM500 and energy-dispersive X-ray spectroscopy (EDS) at the IIT Bhilai facilities, both prior to and after to the altering. X-ray Fluorescence(XRF) analysis at Regional Forensic Science Laboratory,Durg.

7.Batch experiment

The sorption investigations were performed solely with the modified clay. In an Erlenmeyer flask with the 7 pH, 0.1 grams of modified clay were dissolved in 50 ml of U(VI) solution. The flasks were stirred at varying

temperatures for specific durations to attain optimal mixing.The LED Fluorometer LF-2a approach was used to measure the amount of residual U(VI) ions in an aqueous solution.

RESULT AND DISCUSSION

Results of Uranium adsorption study

1. Influence of pH

Batch analyses were performed at different pH levels (2–10) to determine the optimum pH level for the adsorptive effectiveness of the modified clay. Figure-4 illustrates that % elimination of uranium(VI) as a function of pH.Initially, the percentage of removal was found to rise with the solution's pH until it reached pH 7. After that, the percentage of removal progressively decreased, reaching its maximum at pH 7, which was 98%. The fact that the uranium adsorption process is highly dependent on the pH of the solution is an important point to identify. At a pH level that is lower than 5, the quantity of H_3O^+ ions is greater than that of the UO^{2+} ions by a significant margin. Moreover, the surface is expected to be filled with H_3O+ ions, thereby reducing the availability of binding sites for the adsorption of UO_2^{2+}. As the pH exceeds 5, an increased quantity of H_3O^+ ions departs from the clay mineral surface, thereby facilitating cation exchange with UO_2^+ ions at the available sites. This initiates hydrolysis precipitation, resulting from the formation of complexes in the aqueous solution. The complexes identified are $UO_2(OH)^+$, $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_3(OH)_5$, and $(UO_2)(OH)_2$; these complexes enhance the adsorption of uranium(VI)[Vivero-Escoto et.al.(2013),Ivanova et.al. (2014)]. At pH levels exceeding 7.0, carbonate uranyl ions [UO_2CO_3, $(UO_2)(CO_3)_2^{2-}$$(UO_2)(CO_3)_3^{4-}$] predominate. When pH exceeds 7, the charge of U(VI) species transitions from positive to negative [Ajimal et.al. (2006)].

2.Impact of initial ion concentration

The impact of initial ion concentration was determined through batch experiments that were conducted at a range of initial ion concentrations (2-50 μgL^{-1}). Fig. 5 illustrates the experimental data, which indicates that the percentage removal increases as the initial ion concentration increases until 50 μgL^{-1}. As the concentration of the adsorbate increases, the adsorption efficiency is subsequently reduced. This behavior appears to be the consequence of the active sites of the adsorbent being saturated. However, the secondary axis data in Fig. 6 indicates that the adsorbent's absorption capacity increases as the initial ion concentration increases. This is a result of the increasing promoting force, which surpasses the mass transfer resistance between the solid and liquid phases.

Impact of contact Duration

To investigate the effects of contact duration, approximately 0.1 g of modified clay was introduced to 50 mL of a 50 $\mu g\ L^{-1}$ U(VI) solution at pH 7 and a temperature of 25 °C, with contact time ranging from 5 to 40 minutes. Figure 7 illustrates the process of U (VI) adsorption onto modified clay Bentonite. At the outset, the removal efficiency percentage rose from 66.4% to 98.32% as the duration extended to 40 minutes. Upon attaining its maximum, it subsequently exhibits a stable value for a defined duration, specifically ranging from 5 to 40 minutes.

Impact of adsorbent dose

A series of adsorption experiments were conducted to examine the impact of modified clay dosage amount under controlled conditions. The experiments involved uranium with an initial concentration of 50 µg/L, maintained at room temperature (approximately 25°C) and a pH of 7, with a contact time of 40 minutes. The analysed ratios range from 0.05 to 2g. The results illustrated in Figure 8 and 9 indicate that the uranium adsorption efficiency onto Bentonite decreased as the weight of the adsorbent increased, decreasing from 92% to 49%. The decrease in the quantity adsorbed with an increase in mass is attributable to the increased interactions among the particles of the materials. Overcrowding of adsorbent particles may cause the adsorption sites to overlap, which would reduce the adsorption capacity **[**Garg et.al. (2003), **Ndongo et.al. (2015)].**

Impactof Temperature

Temperature effects on uranium (VI) adsorption were studied at temperatures ranging from 283 K to 333 K. Figure 10 shows a graph based on experimental data. This demonstrates that the percentage elimination rises with temperature and stabilizes at 303 K, or almost at room temperature. Subsequently, it exhibited a consistent removal efficiency upon attaining the maxima. The experiment was performed at 303 Kelvin.

TPM Vol. 32, No. S2, 2025
ISSN: 1972-6325
https://www.tpmap.org/

Open Access

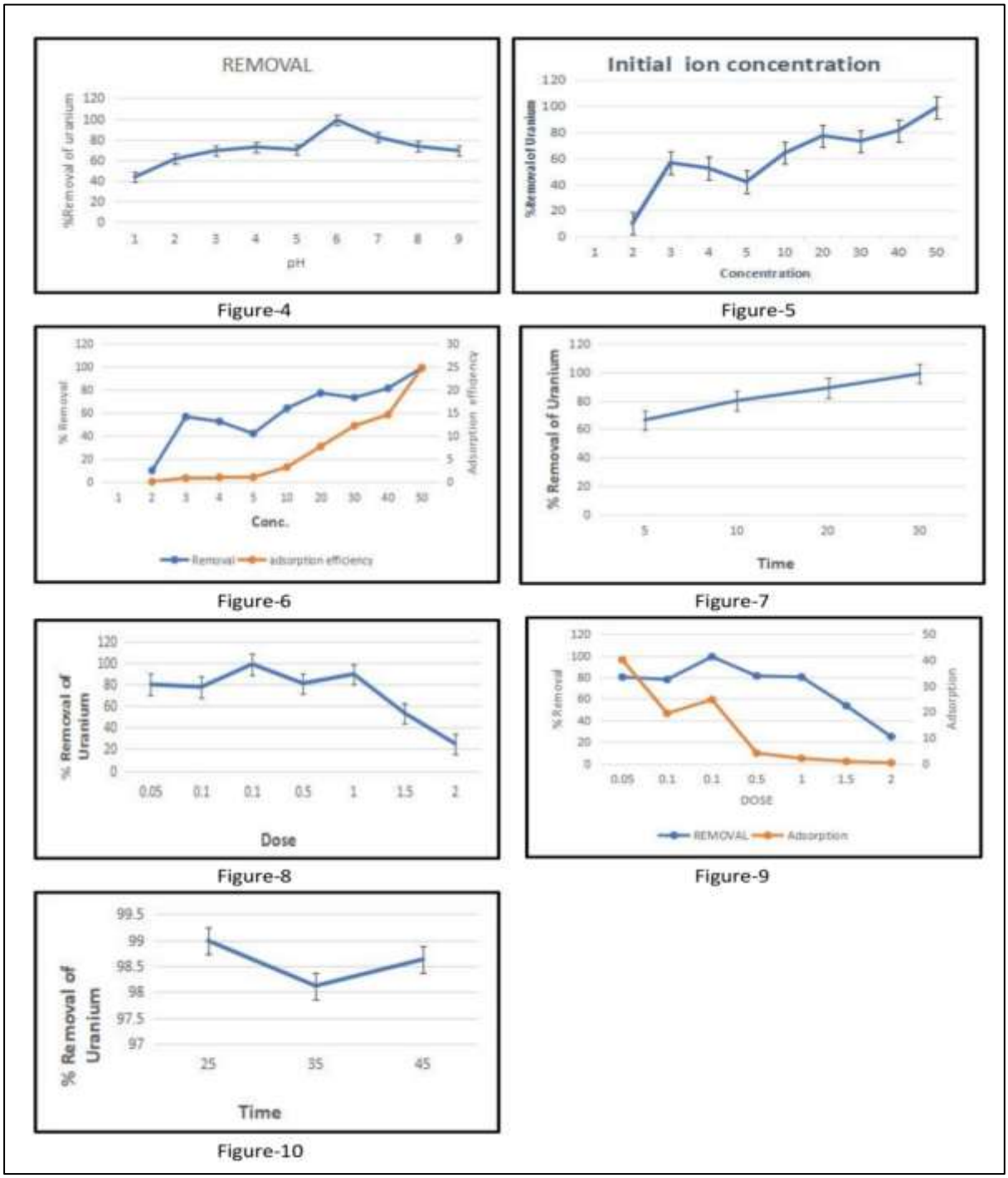


Figure-4 Figure-5

Figure-6 Figure-7

Figure-8 Figure-9

Figure-10

Fig-11 Impact of pH,concentration,time,dose and contact of time& adsorption effiency on concentration and doses.

Adsorption Isotherms

The equilibrium investigation is an effective method for analysing the behaviour of the adsorbent surface. One of the primary focuses of isotherm models is the interaction between adsorbate and adsorbent isotherms. The Langmuir Temkin and Freundlich isotherms, which have been shown in Table 3, are examples of this interaction. The Langmuir isotherm describes homogeneous monolayer adsorption on a surface, whereas the Freundlich isotherm applies to heterogeneous surfaces [Kaur et.al. (2003)]. Equations (3) and (5) denote the linear representations of the Langmuir and Freundlich adsorption isotherms.

$$\frac{C_e}{q_e} = \frac{1}{K_{Lqm}} + \frac{C_e}{q_m} \quad \textbf{(3}$$

In this context, q_m represents the maximum monolayer adsorption capacity measured (µg/g). K_L denotes the Langmuir constant (L/µg). Additionally, qe indicates the adsorption capacity in micrograms per gram (µg/g), while Ce refers to the equilibrium concentration in micrograms per litre (µg/L). Plotting Ce/qe against Ce (Equation (3)) yields a linear relationship characterized by a slope of 1/qm and an intercept of $1/K_L\ q_m$**.** The

Langmuir isotherm is characterized by a dimensionless constant known as the separation factor RL [Patil et.al.(2016)] expressed as

$$R_L = \frac{1}{1 + K_L\ C_0} \qquad (4)$$

The adsorption process is irreversible when $R_L = 0$ and favourable when $0 < R < 1$. However, when $R_L > 1$, the isotherm is in an unfavourable state.

The Freundlich isotherm model pertains to heterogeneous surface energy systems and is employed to characterize multilayer adsorption, including the interactions among adsorbed molecules. The Freundlich isotherm is expressed by Equation (4).

$$\ln(q_e) = \ln(K_F) + \frac{1}{n} \ln C_e \qquad (5)$$

Absorption intensity (1/n) and sorption capacity (K_F) are two parameters associated with the Freundlich isotherm model. Additionally, the exponent (1/n) functions as an indicator of the effectiveness and capability of the adsorbent/adsorbate system. Plotting ln qe against ln Ce as described in Equation (5) results in a linear relationship defined by a slope of 1/n and an intercept of ln K_F.

According to the Temkin isotherm model, the adsorption heat of all molecules decreases linearly with the increase in coverage of the adsorbent surface. Additionally, the Temkin isotherm model assumes that adsorption is characterized by a uniform distribution of binding energies, up to a maximum binding energy. Equation (6) can be used to describe the Temkin isotherm.

$$q_e = \frac{RT}{b} \ln K_T + \frac{RT}{b} \ln C_e \qquad (6)$$

where K_T is the equilibrium binding constant (l/mol) corresponding to the maximum binding energy, b is related to the adsorption heat, R is the universal gas constant (8.314 J K/Mol) and T is the temperature (K). Plotting qe versus ln(Ce) (Equation (6) results in a straight line of slope RT/b and intercept (RT ln K_T)/b.

The Temkin adsorption isotherm model demonstrates better fitting, evidenced by its greater correlation coefficient for Bentonite ($R^2 = 0.95$) in contrast to the Freundlich isotherm model ($R^2 = 0.91$) and the Langmuir adsorption isotherm model ($R^2 = 0.62$). Table 3 provides a comparison of the reported maximum adsorption capacities with other recorded values. All of the adsorption isotherm models for modified clay Bentonite are explained in the above fig;11

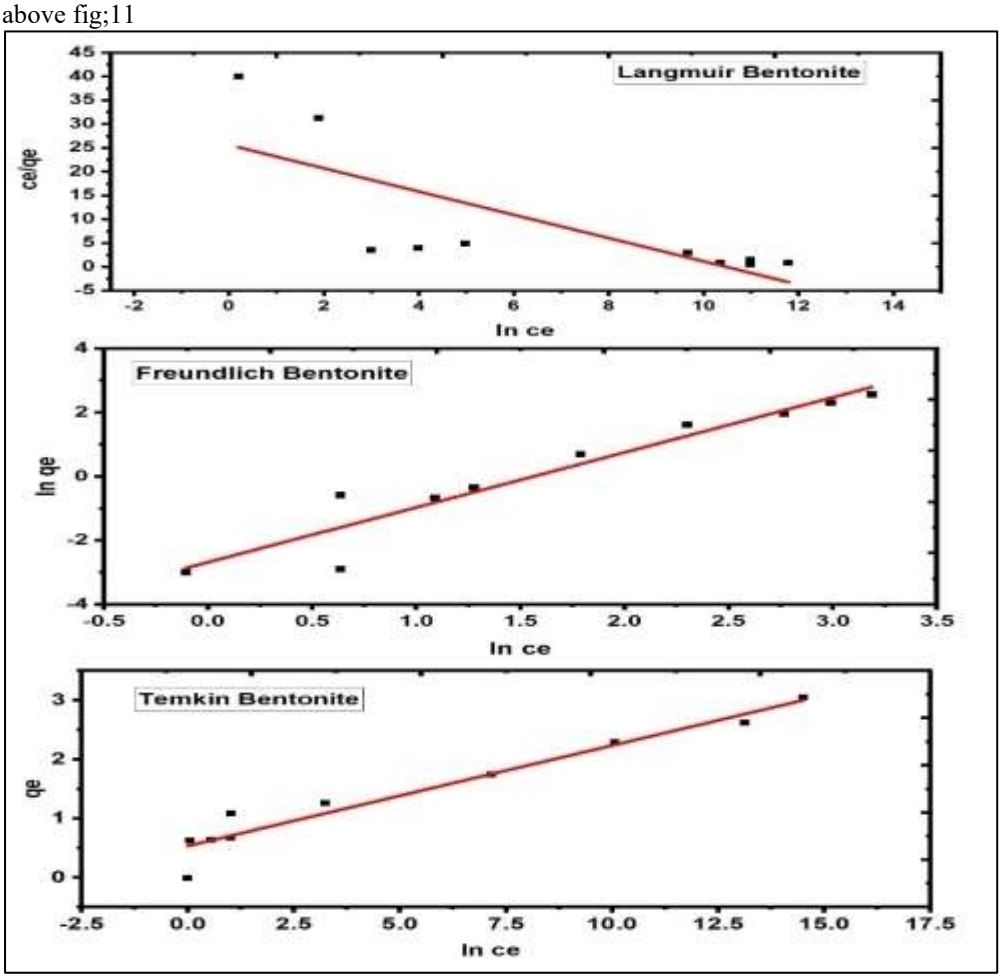


Figure-12 Modified clay (Bentonite) showing Adsorption Isotherm Models

TPM Vol. 32, No. S2, 2025
ISSN: 1972-6325
https://www.tpmap.org/

Open Access

Table-2 Langmuir, Freundlich and Temkin isotherms models

Langmuir parameters			Freundlich parameters			Temkin parameters		
Q_{max}(µg g^{-1})	K_L(L μg^{-1})	R^2	K_F (µg g^{-1})	1/n	R^2	A (µg g^{-1})	B	R^2
0.0605	0.937	0.62	0.582	0.372	0.91	1.37	4794	0.95

Adsorption Kinetics

Data from experiments were analyzed using both pseudo-first-order and pseudo-second-order kinetic models to determine the kinetics of uranium (VI) adsorption onto the modified clay (Bentonite) adsorbent. The adsorption kinetics of U(VI) ions onto modified clay Bentonite were verified using the pseudo-second order model. At three different temperatures (298 K, 308 K, and 318 K), the kinetics of uranium (VI) adsorption by adsorbent were investigated while keeping the initial concentration of metal ions constant at 50 µg/L. The first equation according to the pseudo-order is as follows:

$$log(q_e - q_t) = logq_e - \frac{K_1}{2.303}t \quad (6)$$

q_e and q_t (µg/g) denote the adsorption capacities of U(VI) ions at equilibrium and at time t, respectively, while K1 signifies the first-order constant (min−1). Figure 12 demonstrates that the values of qe and K1 may be obtained from the intercept and slope.

The following is the pseudo-second order equation.

$$\frac{t}{q_t} = \frac{1}{K_{2q_e2}} + \frac{t}{q_e} \quad (7)$$

K_2 represents the pseudo second order constant, (g/µg min^{-1}). The values of qe and k_2, as determinedby the slope and intercept [Diwan et.a. (2020)] are presented in Fig12, Table -4 presents the data. The pseudo-second-order model demonstrates superior fitting, evidenced by a higher correlation coefficient (R^2=0.99) in comparison to the pseudo first-order kinetics (R^2=0.87).

The calculated value of q_e from the pseudo-second-order equation was 28.26 µg/g for bentonite which closely aligns with the experimental values of q_e (24.73 µg/g). In contrast, the values estimated through the pseudo-first-order kinetics were lower, at 9.57 µg/g for Bentonite. The results indicated that pseudo-second order kinetics was observed in the adsorption of uranium (VI) by modified clay (Bentonite).

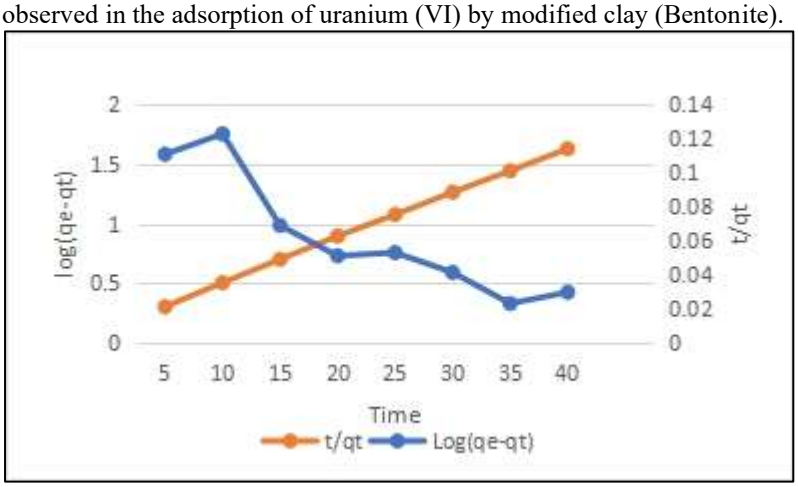


Fig. 13 Pseudo first-order and Pseudo second-order kinetics for the adsorption of U(VI) onto modified clay

Table 3 Kinetics value of adsorption of Uranium (VI)

Pseudo first order kinetics			Pseudo second order kinetics		
K_1	Q_e	R^2	K2	Q_e	R^2
0.039	9.57	0.87	0.038	28.26	0.99

ADSORPTION THERMODYNAMICS

Investigations based on thermodynamics provide reliable insights into the structural changes that occur in adsorbents after they have been processed by adsorption. A comprehensive understanding of thermodynamic properties, such as the changes in free energy (ΔG), enthalpy (ΔH), and entropy (ΔS), can be derived from the changes in the thermodynamic equilibrium constant. At three different temperatures—298 K, 303 K, and 313 K—the sorption capacity of modified clay is evaluated. Equation (9) was utilized to get the thermodynamic parameter [Yu et.al.(2016)].

$$lnK_d = \left(\frac{\Delta S}{R}\right) - \left(\frac{\Delta H}{RT}\right) \quad (8)$$

The distribution coefficient (Kd) signifies the ΔH, ΔS, and T, which correspond to enthalpy, entropy, and temperature (Kelvin), respectively; R represents the gas constant. ΔG (Gibbs free energy) has been calculated from equation (9).

$$\Delta G = \Delta H - T\Delta S \quad (9)$$

The thermodynamic parameter values for the sorption of uranyl ions on modified clay are presented in Table-5. The positive enthalpy change ΔH signifies that the adsorption process is endothermic. The entropy change ΔS is also positive in this manner, suggesting that the process is irreversible and favours the stability of sorption with greater randomness. The adsorption reaction becomes more favourable as ΔG^0 decreases with rising temperature [Adeogun et.al.(2019)]. The negative value of ΔG^0 indicates that adsorption occurs spontaneously.

Table 4 Thermodynamic parameters for uranium removal onto modified clay

Temperature(K)	ΔG^0 (kJ mol^{-1})	ΔH^0 (kJ mol^{-1})	ΔS^0 (J mol^{-1} K^{-1})
298 K	-2.82	22.5	3897.1
308K	-3.03		
318K	-3.27		

Mechanism of uranyl ion adsorption on modified clay

The presence of heavy metals depends on the retention capacity of the adsorbents interacting with the metals. The availability of metals is affected by sorption-desorption processes, particularly concerning clay surfaces. The mechanism of uranium adsorption by modified bentonite can be clarified through the research conducted by Mohamed (2016) and Youssef (2017). Activation of Bentonite clays through acid treatment and subsequent calcination, as shown by the researchers, results in changes to the clays' physical and chemical properties yet retains the clays' layered structure. The adsorption of Uranium(VI) on the clay mineral Bentonite is due to the enhanced availability of aluminon sites.

EDS

According to the data presented in Figure 13, the EDS spectra of the modified clay adsorbent exhibit noticeable changes in the peaks both before and after the adsorption of uranyl ions. The peaks of sodium, chloride, and calcium show variations both before and after the adsorption of uranyl ions. Consequently, this offers information regarding the adsorption of uranyl ion[Zang et.al.(2016)].

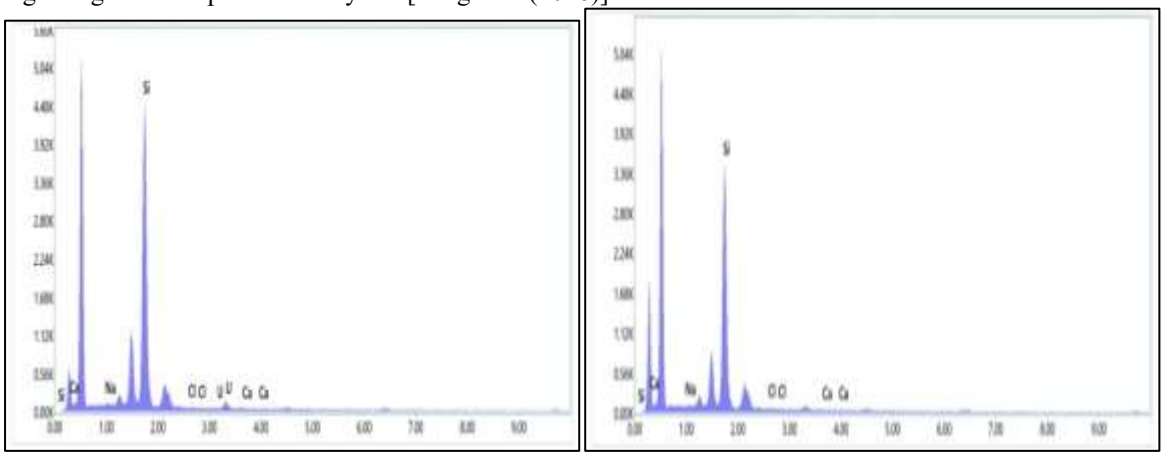


Fig-14 EDS Analysis of modified clay(Bentonite) after and before adsorption

SEM ANANLYSIS

As shown in Fig. 14, the size distribution and morphological structure of the modified claysample (adsorbent) were investigated using scanning electron microscopy (SEM). Before adsorption, the surface of the modified clay adsorbent displayed cavities that were later occupied by the deposition of metal ions onto the modified clay. The SEM images of the modified clay sample, both prior to and following adsorption, clearly depict the features of adsorption.

The appearance is heterogeneous, rough, and glossy before to adsorption, contrasting with the post-adsorption state characterized by brightened surfaces exhibiting spherical or almost round forms [Simamora et.al.(2018)]. The particle can establish bonds with another particle, commonly referred to as agglomeration.

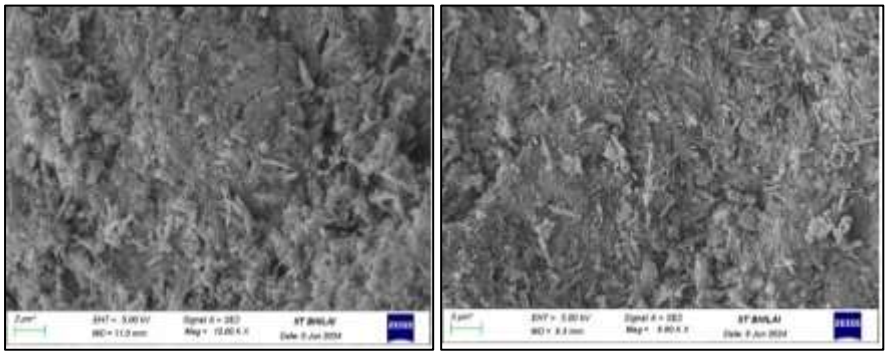


Fig-15 SEM Analysis showing morphology of modified clay (Bentonite) after and before adsorption

Verification along with application of the Bentonite modified clay

The approach that was proposed was utilized on samples of natural uranium contamination that were found in soil and rock. Samples were gathered in Chhattisgarh's Durg district (Auri village). Samples of soil and rock were taken from latitude 20.9277 and longitude 81.44045. Standard procedures for sampling and analysis were used. The LED fluorometer LF-2a is utilized in order to conduct the analysis of the uranium content in accordance with the standard protocols. To verify the results of the modified clay (Bentonite) laboratory study mentioned above, we performed uranium adsorption tests using natural soil and rock samples contaminated with naturally occurring uranium. Approximately 0.1 g of modified clay (Bentonite) was added to 50 mL of a 50 μg L^{-1} uranium solution at pH 7, at a temperature of 25 °C, with a contact time of 40 minutes. Uranium removal in both samples (rock and soil) achieved 85% & 87% .The suggested method for removing uranium from natural samples is supported by a strong correlation between the results from synthetic and natural samples.

Table-5 Table showing the application of modified Bentonite clay on real samples consisting of soil and rock

Area	Sample	Conc. of U	After Removal	Removal%
Durg(Auri)	soil	2.8302	0.126	87%
	Rock	4.2567	0.179	85%

CONCLUSION

This work concluded a thorough examination of the adsorption characteristics of modified Bentonite clay. Adsorption mechanisms, kinetics, thermodynamics, and optimal ranges of different parameters are presented, along with other adsorption features. At pH 7, the modified clay Bentonite has been demonstrated to be a highly efficient adsorbent for removing uranium from rock, soil, and aqueous solutions. When using 0.1g amount of modified clay, the best removal can be achieved in 30 minutes. Experimental data demonstrated strong concordance with the Temkin adsorption isotherm (R^2=0.957).

The Temkin isotherm model indicates that the adsorption heat of all molecules exhibits a linear decrease as the level of coverage of the adsorbent surface increases.This was demonstrated with Bentonite-modified clay. The Temkin adsorption isotherm indicated a maximum adsorption capacity of 24.75 μg of U(VI) per gram of modified clay. The adsorption process is both spontaneous and endothermic, as indicated by the negative Gibbs free energy (−2.82 kJ mol−1) at the ideal temperature of 303K and the positive enthalpy (ΔH = 22.5 kJ mol−1). A strong applicability of the adsorption dynamics was demonstrated by the pseudo-second-order kinetic model, which exhibited a good correlation coefficient(R^2=0.99). The characterization was conducted using scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS)and. X-ray Fluorescence (XRF), demonstrating that bentonite clay serves as a more effective adsorbent. It was noted that in both samples, (rock and soil)uranium removal exceeded 87%. This demonstrates that the modified clay is effective in treating natural samples as well, as demonstrated by the fact that it was successfully applied to particular naturally uranium-contaminated samples that weretaken from the village of Auri in the state of Chhattisgarh.

Author contribution

All authors contributed to the final outcome. All authors reviewed and approved the final manuscript.

Funding

There is no funding for this study.

Declaration of Competing Interest

The authors declare no competing interests.

Acknowledgements

The authors extend their gratitude to the Chemistry Department at Dr. C.V. Raman University for providing access to their laboratory facilities. The authors wish to acknowledge the Department of Applied Chemistry at Bhilai Institute of Technology, Durg, for their assistance in facilitating laboratory work and supplying essential chemicals. The authors wish to extend their appreciation to Central instrument facilities IIT Bhilai .

Ethics approval and consent to participate

Not applicable

REFERENCES

1. Odom I.E. (1984) Smectite clay minerals: Properties and uses. Phil Trans R Soc Lond 311: 391-409.
2. Cadena ,F.,Rizvi ,R.,Peters R.W (1990) Feasibility Studies for the Removal of Heavy Metals from Solution Using Tailored Bentonite. Hazardous and Industrial Waste Conference, Dexel University, pp: 77-94
3.Malakul,P., Srinivasan,KR., Wang,HY (1998) Metal adsorption and desorptioncharacteristics of surfactant-modified clay complexes. Indian Eng Chem Res 37: 4296-4301.
4. Mekhemera,W.K., Hefneb,JA ,Alandisa,N.M , Aldayel,O.A., Raddadi ,A.S (2008) Thermodynamics and kinetics of Co (II) adsorption onto natural and treated bentonite. Journal of Chemistry 3: 409-423.
5. Sahu,S.K., Maity,S., Bhangare,R,C.,Pandit,G.G., Sharma ,D.N(2014) Determination of uranium in ground water using different analytical technique, vol 34., Bhabha Atomic Research Centre, Mumbai.
6. Aytas,S.,Yurt, M., & Donat,R.,(2009) Adsorption characteristic of U(VI) ion onto thermally activated bentonite, Journal of Hazardous Material, 172 667-674, doi: 10.1016/j.jhazmat.2009.07.049
7.Vivero-Escoto JL, Carboni M, Abney CW, De Kraft KE, Lin W (2013) Organo-functionalized mesoporous silicas for efficient uranium extraction. Microporous Mesoporous Mater 180:22–31. https://doi.org/10.1016/j.micromeso.2013.05.030
8. Garg,VK, Gupta,R., Yadav,AB , Kumar,R (2003) Dye removal from aqueous solution by adsorption on treated sawdust. Bioresource Technology 89: 121-124
9. Ndongo,K.G., Ndi,N.J, Belibi,BDP, Kouotou,D.,Tagne ,GM (2015) Adsorption of Zinc(II) ions from aqueous solution onto Kaolinite and Meta kaolinite. Der Pharma Chemica 7: 51-58 .
10.Adeogun,A., Akande,J., Idowu,M., & Kareem,S., (2019) Magnetic tuned sorghum Husk bio adsorbent for effective removal of cationic dyes from aqueous solution isotherm kinetics, thermodynamics and optimization studies applied water science 9, 1 to 17
11. Ajimal,M.R , Rao,A.K , Ahmed,J., Ahmad,R.,(2006) Adsorption of Zinc(II) ions from aqueous solution onto Kaolinite and Metakaolinite. Journal of Environmental Science and Engineering 48: 221-224
12. Ali H., and Khan. E., (2018) Bioaccumulation of Non-Essential Hazardous Heavy Metals and Metalloids in Freshwater Fish. Risk to Human Health. Environmental Chemistry Letters, 903-917.https://doi.org/10.1007/s10311-018-0734-7
13. Amoli,S., Barker,H. J. & Flowers, A.(2006) Electrodeposition and determination of nano-scale uranium and plutonium using alpha-spectroscopy. *J Radioanalytical Nuclear Chem***268**, 497–501 . Https://doi.org/10.1007/s10967-006-0197-3.
14.Awad,M.E., Sanchez,A.B., Roa,E.E., Laguna,A.H,& Diaz,C.I.S(2020) Modelling of the adsorption of a protein-fragment on kaolinite with potential antiviral activity, App.Clay Science ,199: 105865, doi: 10.1016/j.clay.2020.105865
15. Cadena F, Rizvi R, Peters RW (1990) Feasibility Studies for the Removal of Heavy Metals from Solution Using Tailored Bentonite. Hazardous and Industrial Waste Conference, Dexel University, pp: 77-94.
16.Christidis,G.E., Scott ,P.W., and Dunham, A.C. ,(1997), Acid activation and bleaching capacity of bentonites from the islands of Milos and Chios, Aegean, Greece. Applied Clay Sci., 12, 329-347.
17. Diwan,V., Sar,S.K., Biswas,S.,& Lalwani,R.,(2020) Adsorptive extraction of uranium(VI) from aqueous phase by dolomite,vol-11, Groundwater for Sustainable Development, https://doi.org/10.1016/j.gsd.2020.100424.
18. Evseeva, L. S., Perel'man, A. I. And Ivanov, K. E. ,(1947) *Uranium Geochemistry in the Hypergenesis Zone* (Atomizdat, Moscow, 1974) [in Russian]
19. Hagag, M.S., Esmaeel, Sh. M. A., Salem,F., Ali ,A.H. & Zaki,S.A.(2023) Thermal activation of kaolinite titanium hydroxide composite for uranium adsorption from aqueous solutions Volume 20, pages 9041–9052, International Journal of Environmental Science and Technology, https://doi.org/10.1007/s13762-022-04533
20.Hounfodji,J.W., Kanhounon,W.G., Kpotin,G., Atohoun,G.S.,Laine,J., foucaudy., &Badauri,M.,(2021) Molecular insights on the adsorption of some pharmaceutical residues from wastewater on kaolinite surfaces, Chemical engineering journal(,vol-407, https://doi.org/10.1016/j.cej.2020.127176
21.Hradli ,D.,Hradilova,J.,& Bezdicka,P.,(2020)Clay Minerals in European Painting of the Mediaeval and Baroque Periods, *Minerals10*(3), 255; **https://doi.org/10.3390/min10030255**
22. Ivanova,B.& M.Spiteller.M., (2014) Adsorption of uranium composites onto salt rockoxides—experimental and theoretical study. J Environ Radio act 135:7583. Https://doi.org/10.1016/j.jenvr ad.2014.03.019 .
23. Kadir,S., Lah1 ,T.KU., Nalgil , N.O.,Erkoyun,H., & Elliott,W.C ,(2017) Mineralogy, Geochemistry, And Genesis Of Bentonites In Miocene Volcanic-Sedimentary Units Of The Ankara-C¸ Ankiri Basin, Central Anatolia, Turkey, , Clays and Clay Minerals, Vol. 65, No. 2, 64–91,
24.Kaur,R., singhj., Khare,R., Singh,S., Ali,A, 2003. Batch sorption dynamics, kinetics and equilibrium studies of Cr (VI), Ni (II) and Cu (II) from aqueous phase using agricultural residues. Appl Water Sci 3, 207–218
25. Kulkarni Vinay,S., Juvekar,A., Mukhopadhyay ,S.,(2018) Intensification of emulsion liquid membrane extraction of uranium(VI) by replacing nitric acid with sodium nitrate solution, Chemical Engineering and Processing-processintensification,vol-125,page-18-26, https://doi.org/10.1016/j.cep.2017.12.021
26.Malakul P, Srinivasan KR, Wang HY (1998) Metal adsorption and desorption characteristics of surfactant-modified clay complexes. Indian Eng Chem Res 37: 4296-4301

27. Mustapha,S., Tijani,J.O, Ndamitso,M.M.,(2020) The role of kaolin and kaolin/zno Nano adsorbents in adsorption studies for tannery wastewater treatment. *Sci Rep***10**, 13068 , https://doi.org/10.1038/s41598-020-69808-z
28.Olusegun,J.S, & Mohallem,D.S.,(2021) Comparative adsorption mechanism of doxycycline and Congo red using synthesized kaolinite supported $cofe_2o_4$ nanoparticles, Environmental Pollution,vol-260, https://doi.org/10.1016/j.envpol.2020.114019.
29. Patil,RN., Raisoni,G.H , Nagarnaik,P.B., Agrawal,D.K 2016. Removal of fluoride from ground water by using treated bark of *phyllanthus emblica* (amla) tree. Int. J. Civ.Eng.Technol.7,11-20.
30.Perel'man,A.I., and Kasimov,N.S.,(1999) *Landscape Geochemistry* (Astreya 2000, Moscow, 1999) [in Russian]
31. Perel'man,A.I.,(1996) "Landscape Geochemistry and Scientific Problems of Atomic Industry," Vestn.Mosk.Univ., Ser. 5: Geogr., 22–27
32.Simamora,P., M.J Manullang,M.J J. Munthe, Rajaukguk. J,(2018) The structural and morphology property of Fe3O4/ppy nanocomposite. Phys. Conf. 1-16
33. Wang, G., Chai,X., Liu,J., Deng, N., (2010)Adsorption of uranium (VI) from aqueous solution on calcined and acid-activated kaolin Appl. Clay Sci., 47 (3 -4) , pp. 448-451, 10.1016/j.clay.2009.11.003
34. Youssef,W.M., Sheikh,A.S.E., Ahmed S.H., Morsy,A.,(2020) Polyacrylic acid/polyaniline composite as efficient adsorbent for uranium extraction from nuclear industrial effluent, Journal of Radioanalytical and Nuclear Chemistry https://doi.org/10.1007/s10967-020-07060-5.
35.Yu.,A., Wang,J., Jiang,Y., (2016a) Removal of uranium from aqueous solution by alginate beads. Jing Nuclear Engineering and Technology 49, 534–540.
36.Zang,Y., Luo,Z.S., Huang,S.,Wang,J., Zong,Y., Zhou,J., Ou,M., (2016) Absorbent of expanded Rice Husk Powder for removal of urinal ion from aqueous solution, Rare me T. 34, 425- 432.
37Zeballos,A, Weihed,P, BlancoM., &Machaca,V., Geological, (2016) mineralogical and chemical characterization of Devonian Kaolinite bearing sediments for further application in the ceramic(tile) industry in La Paz Bolivia, Environmental Earth Sciences, 75:1-15 DOI 10.1007/s12665-015-5212-y