Study of the Synthesis and Characterization of Poly(acrylic acid-co-acrylamide)-kaolinite Composite Reference to Adsorption of Cd and Pb from Aqueous Solutions

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Summary: A novel poly(acrylic acid-co-acrylamide)/ kaolinite composite was produced by copolymerization of partially neutralized acrylic acid and acrylamide with sawdust for crosslinking applying Bis-acrylamide having linear formulae $(C_7H_{10}N_2O_2.)$, $(H_2C=CHCONH)$ $2CH_2$, potassium persulfate, $K_2S_2O_8$ as initiator and sodium sulphite used as accelerator to reduce the polymerization time. Physiognomy of the composite was performed by techniques viz., Fourier Transform Infrared Spectroscopy, X-Radiation Diffractometry (Crystallography), Structural-Equation-Modeling, Energy-Dispersal X-Radiation-Analysis and Brunauer-Emmett-Teller methods. Divalent cadmium and lead electrolytes (adsorbate) adsorption on the adsorbent (composite) in aqueous solution was studied in batch experiments optimizing reaction parameters like "IA" of equilibrium amount, "CT" (wet time), neutrality (alkalinity and acidity) and calefaction (thermal reading). The quasi 2nd order kinetic archetypal ensued by AK. Adsorption isotherrms were applied to the empirical statistics which fitted well with a) Irving-Langmuir-isotherm and b) Freundlich adsorption isotherm. The supreme adsorption dimensions, q_m (from Irving-Langmuir isotherm) at *25°C*, were *28.57 mg g^{-1}* and *32.25 mg g^{-1}* for divalent cadmium and lead electrolytes, respectively. Data of activation energy (12.148 kJ mol^{-1} and *7.165 kJ mol^{-1}* for divalent cadmium and lead electrolytes respectively) indicated physio-absorption. Results of thermodynamic parameters like ΔG^o, ΔH^o and ΔS^o for both divalent cadmium and lead electrolytes suggested the phenomenon of the endothermic and spontaneity nature of the process. The newly synthesized composite attributed to its cost effective and environment friendly nature of the synthesis which will be deemed as a capable substance for the exclusion of adsorbent divalent cadmium and lead electrolytes from aqueous suspensions.

Introduction

Heavy metals environmental pollution is serious issue at world level due to rapid growth in industrialization. They are generally persistent, non-biodegradable and poisonous in nature [1]. They cause serious detrimental effects on biotic as well abiotic lives on each including health hazards in human and plants [2]. These metals include Pb, Cd, Cr, As etc. [3]. Metal plating, lead acid batteries, printing, glass and ceramic industries, lead mining, phosphate fertilizers, forest fire, electronics, automobile emission, paint are the major sources of Pb pollution [4]. Lead has been reported with problems like brain and kidney dysfunction, miscarriage, under developed fetus, disruption of nervous system and infertility [5]. In severe cases, still births, neonatal deaths, sterility and abortion causes [6]. The WHO drinking water standard for Pb is 0.01 mg/L [7]. Cd is highly toxic pollutant similar to Pb and another sources of pollutant is industries which can alloying electroplating, photography, metallurgical, phosphate fertilizers, textile print, pigments, Cd and Ni batteries. [8]. Intoxications due to cadmium develops malignancies in various organs, chondro-sarcoma, Ewing's sarcoma, hypertonia,

spasticity, pulmonary anomalies and itai-itai by ō (tubular dysfunctioning, GI anomalies) [9]. Attributed to its highly toxic nature, WHO has crammed the standard in water of drinking is to 0.02 mg L^{-1} [10]. Due its lethal and injurious impacts on biotic creatures and surroundings exclusion of adsorbent divalent cadmium and lead electrolytes from aq suspensions has been a major centre of research for scientists.

For enumeration of heavy metal a number of methods have been used which includes evaporation [11], electrodialysis [12], ion exchange [13], reverse osmosis [14], chemical oxidation / reduction [15], electrochemical treatments [16] and chemical precipitation [17]. These techniques usually require high maintenance cost and expensive facilities. On the contrary, researchers are always craving a low cost, simple in operation, effective and environment friendly method as alternative approach to the aforementioned techniques. In this regard, adsorption using a suitable adsorbent is considered an economical, effective, simple and widely applied method [18]. Rice husk [19], corncorb [20], tea waste

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[21], bagasse fly ash [22], sawdust (*Pinus halepensis*) [23], meranti tree sawdust [24], coconut shells [25], apricot stone [26], rice husk ash [27], walnut sawdust [28], olive cake [29] and sawdust (*Pinus* sylvestris) [30-34] referenced to adsorption of Cd & Pb from aqueous solutions. This research work will be base line data on poly (acrylic acid-co-acrylamide)/ kaolinite composite for the adsorption of cadmium & lead. Other very important reports about using polymer deposits for removal of heavy metals and other pollutants are found elsewhere [35-43].

Thus, this study aims to synthesize kaolinite composite by the combination of kaolinite and poly(acrylic acid-co-acrylamide) for adsorbent exclusion of adsorbent divalent cadmium and lead electrolytes from aqueous suspensions. Reaction parameters were optimized and the obtained data from the research work will be applied to various scientific models for better understanding of the reaction pathway.

Experimental

Materials

All the components used were of methodical evaluation and applied devoid of additional refinements. Acrylamide (98%) and acrylic acid (99%) monomers were attained by DAEJUNG's substances and elements. From Riedel-deHaen the Na_2S up to 95% monobasic were applied as instigator and catalyst. Merck provided sodium hydroxide (99%) and UNI-Chem® provided methylenebisacrylamide (MBA, 98.5%). Kaolinite was obtained from Cherat cement company PVT, limited Nowshera with mesh size of 300mμ. The whole experimental work was carried out by doubled distilled water for the getting of the accurate results.

Synthesis of poly(acrylic acid-co-acrylamide)/ Kaolinite composite

Samples for investigations were prepared by adding the Kaolinite at different concentrations. Briefly, nitrogen lines were equipped in *250 mL* flask and then processed by the mechanical stirrer for *30 min* to make homogenous mixture and then thermometer was inserted into the flask for checking the pH of the sample. Afterwards, given concentration of clay was disintegrating in DW and then poured in the container and kept in water bath at *45⁰C* for *15 min* for stirring. Then AA solution partially neutralizes with N, N-methylenebisacrylamide and *1.5%* NaOH was added to them. Then sodium sulfite, potassium KPS

solution and AM monomer was poured slowly in the container and vigorously stirred up to*15 min*. For removal of DO in the solution, N_2 was sustained during the chemical response span. And finally, till the weight became constant, the solution was kept in oven at 60⁰C after washing and filtering to obtain the final product [44].

Characterization

The spectra of P(AA-AM)-Kaolinite composite were recorded using SEM spectrometer (Model 1760x). The composite crystallinity and structure was recognized by X-Radiation Diffractometry (Crystallographic Model-JDX-3532). FTIR spectra of the kaolinite composites were recorded on a FT-IR (Thermo Nicolet Avatar 320 spectrophotometer USA) using ATR technique. The percentage of the total synthetic polymer formed and grafted to clay is called the grafting ratio , determined by using FT-IR technique. Elemental analysis was performed with Energy-Dispersal X-Radiation-Analysis (Version JSM_5910). Composite physiognomy was determined using Structural-Equation-Modeling (Version JSM_5910, J.E.O.L; Japan). The composite superficial extent was measured via superficial extent assay parser (Version:NOVA-2200e) by the technique of Brunauer-Emmett-Teller (BET) [45].

Adsorption Experiments

Separate aqueous solutions of divalent cadmium and lead electrolytes (*100 ppm* each) were used to conduct surface-assimilation experiments. In a typical run, *40 mL* of adsorbate and *0.3 g* of PAA-kaolinite were mixed in a conical flask and shaken in water shaker at *150 rpm* and *25ºC* for *3 h*. After shaking, suspensions were strained through Whatman-125 mm filter paper and analyzed for divalent cadmium and lead electrolytes concentration by applying Atomic adsorption spectrometer (AAS) using equation (1).

$$q = \frac{(C_o - C_e)}{m} \times V \qquad (1)$$

where q represents the coefficient of ionized adsorbent metalloids content on the composite (*mg.g⁻¹*), C_o and C_e are the amount of electrolytes of metalloids in the preliminary suspensions and equilibrium concentration, respectively (*mg mL⁻¹*), V is the volume of the aqueous phase (*mL*), and m is the mass of P(AA-AM)-Kaolinite composite (g). pH of mixtures was adjusted HCl or NaOH combinations.

Results and Discussion

Acryliamide and Acrylic-acid/ Acrylic polymer (IUPAC: propenoic acid) were grafted instantaneously towards Kaolinite in a monolithic identical standard applying Na_2S and FAS-KPS & *N,N'*-methylene-bis-acrylamide as pH sensitivity reporter under inert atmosphere. Two important variables (monomer ratios and cross-linker concentration) have impacts on composite organic molecules adsorption capacity were examined. The chemically reactive A-AM and AA mechanism of copolymerization onto Kaolinite in MBA presence is illustrated in Scheme 1.

Disintegration of Instigator

For generation of sulfate anion radical, the $S_2O^{2-}_8$ inciter disintegrates when exposed to thermal processing. Then substrate -OH group of Thar clay from radical abstracts hydrogen for constructing dynamic radixes on the substratum. So, this $S_2O^{2-}_8$ dynamic redox-system ensued in radically initiation of A-A-m and A-A polymerization in active centers on the substrate which headed to polymerizate implantation. Subsequently methylene-bis-acrylamide, interconnection mediator existing, the polymerizate includes a cross-linked edifice.

Assessment by FTIR Spectroscopy

The assessment by FTIR spectroscopy of sodium poly-acrylate is displayed in Fig. 1 (a). The result of the analysis indicates that semblance of absorbent bending at 3335, 1655 and 1115 cm^{-1} gives indication for chemically reactive force between the AM and AA.

The Fourier transform infrared spectroscopy spectrum of Kaolinite and consistent superabsorbent complexes integrated with altered Kaolinite are displayed in Fig. 1 (b, c). In Fig. 1(b) the coefficients of adsorption in the array of *3683–3510.6 cm^{-1}* are accredited to the extending of –OH groups of Kaolinite and the distinctive summit at *1110* cm^{-1} was because of the non-plane Si–O (*1000-1100 cm^{-1}* (strong & broad) extending genre of Kaolinite. The ensemble at 997 cm^{-1} was ascribed to radially Si–O (*1000-1100* (str.&brd.)) extending genre for laminated silicates (SiO_4^{2-}), whereas the bands at *910 cm^{-1}*, *522 cm^{-1}* and *472 cm^{-1}* correlated to –OH (stretch) & Al–O–Si (Silane) bending and M–O-M designates Si or additional metallic electrolytes occurred in Kaolinite [46].

Fourier transform infrared spectroscopy spectral array of the AA/AM implanted on Kaolinite is explained in Fig. 1 (c). It can be understood by looking at Fig. 1, that innovative absorption bands turned up at *3336 cm^{-1}*, *1656 cm^{-1}*, *1547.9 cm^{-1}*, *1402 cm^{-1}* and *1385 cm^{-1}* specified the C-O-N-H_2-stretch-amide unite, C-N stretching and N–H bending for amide group (N-H (1°-amines), 2 bands N-H (2°-amines). The solider well-resolved band at *1652 cm^{-1}* accredited to the extending throb (banding trembling) of C=O (2 bands) and at *1547.9 cm^{-1}* correlated to–CO_2.

Centered on the overhead confab it's proposed, the implant polymerizes at amid –OH clusters on Kaolinite and electrolytes take place all through the chemical processes.
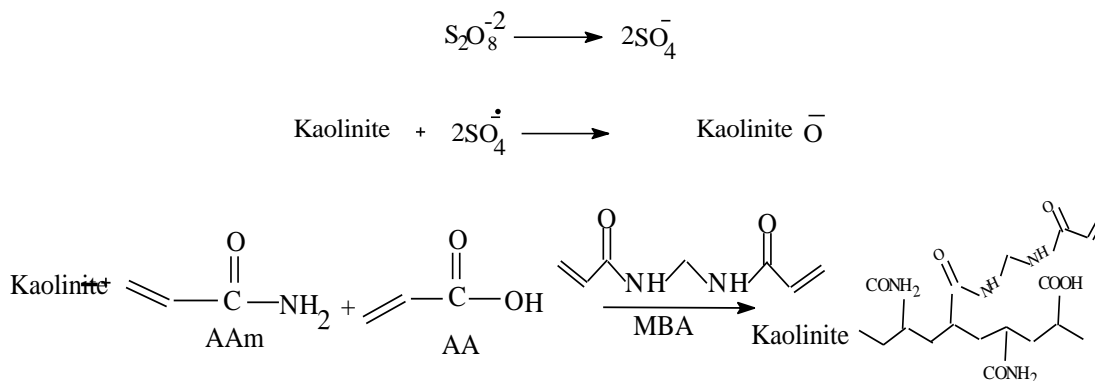
Scheme-1:   Mechanism of AA and AM copolymerization onto Kaolinite in presence of MBA.
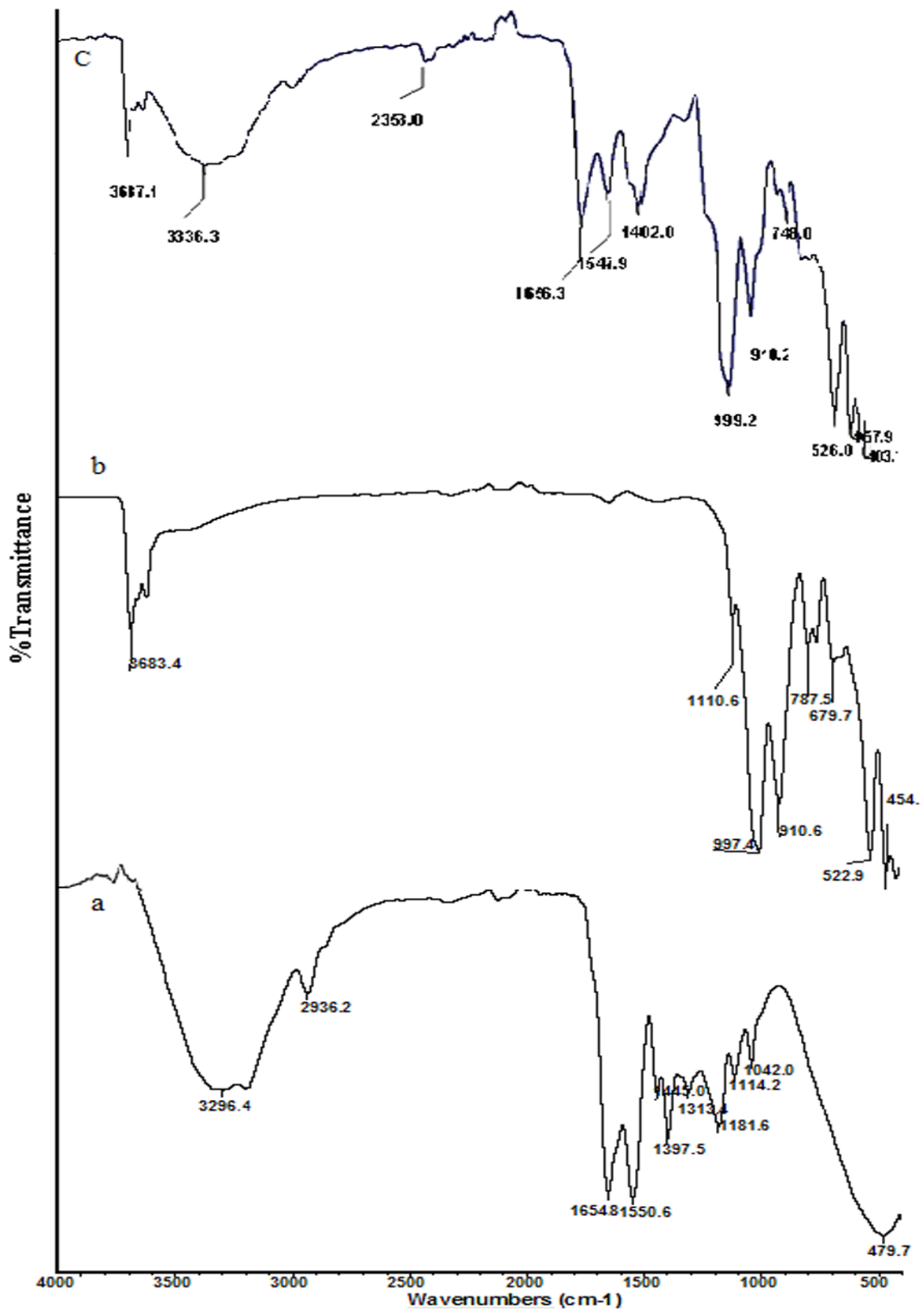
Fig. 1:   FTIR spectra of (a), Poly (acrylic acid-co-acrylamide) (b), Kaolinite and (c), Kaolinite-composite (superabsorbent)

XRD analysis

The XRD analysis is helpful technique for Kaolinite intercalation determination. Fig. 2 (a), (b) and (c) show the composite, copolymer and Kaolinite X-ray diffraction pattern, retrospectively. It was investigated that composite Kaolinite – PAA-AM diffraction peaks are similar as raw Kaolinite. The peak diffraction (10.900º) shows that due to larger molecular structure of AA-co-AM doesn't go proficiently in interlaminar space and only enclosed exterior of Kaolinite. The results are similar with findings, reported that when for medicinal treatment of bentonite (E558, anti-caking agent) HACC applied, its superficial is protected by HACC. Additionally, peak diffraction (32.350º) is observed in AA-co-AM. Results of [45, 46] indicates that peak diffraction (10.900º) in wood chippings is fragile enough when compared to complex which denotes (AA-co-AM) interaction with Kaolinite.
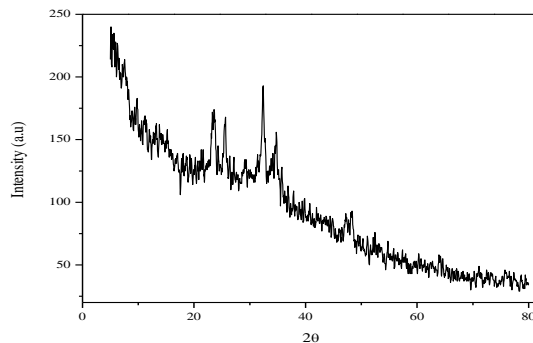

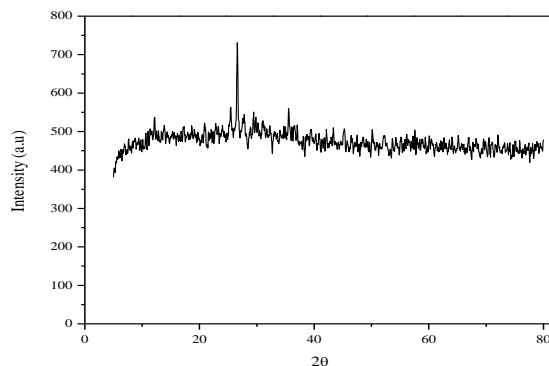Fig. 2:   (a). XRD spectra of copolymer.

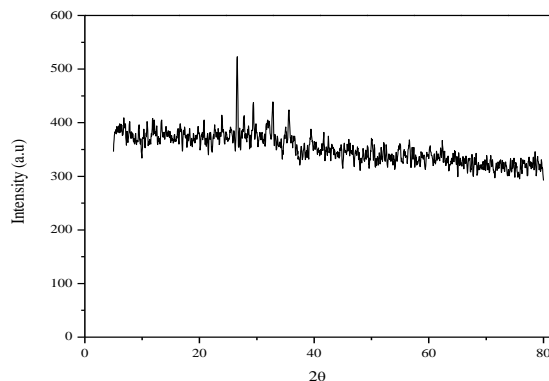Fig. 2:   (b). XRD spectra of Kaolinite.

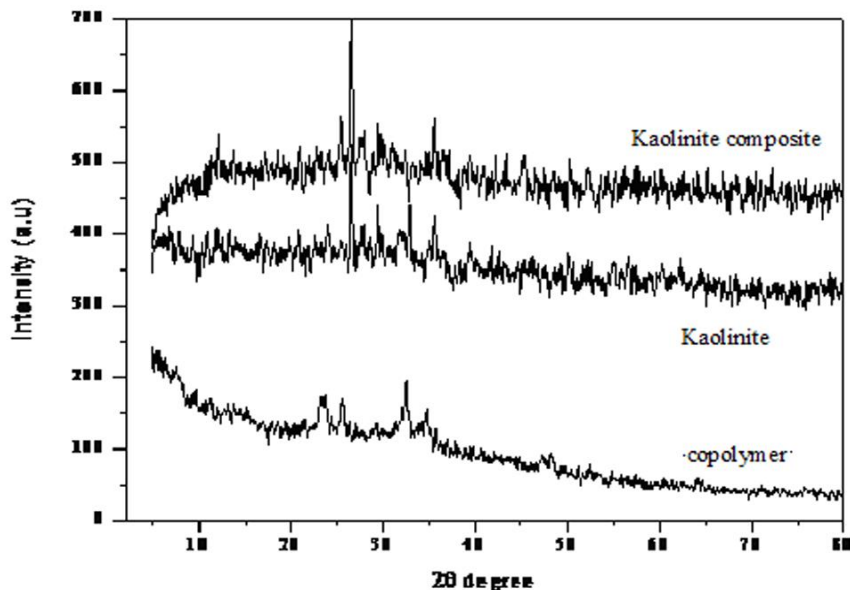Fig. 2:   (c). Spectral view of XRD PAA-SD-Composite.

Fig. 2:   (d) Spectral view of (a) XRD-copolymer (b) XRD-Kaolinite (c) XRD-composite.
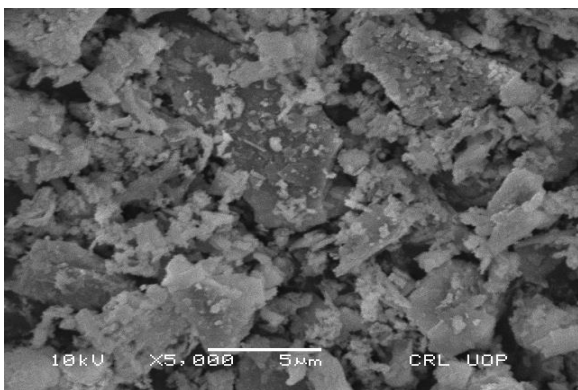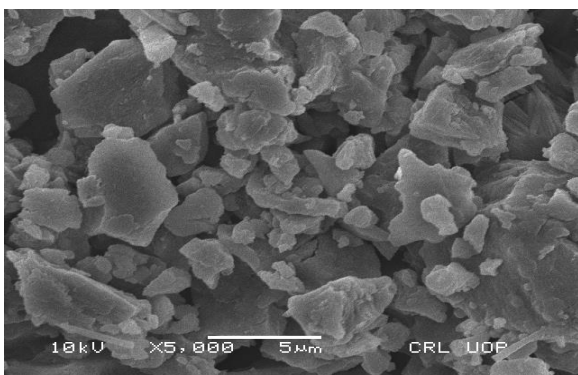

Fig. 3:   (a). Pictorial view of SEM-Kaolinite.

Fig. 3:   (b). Pictorial view of SEM-copolymer.

SEM Analysis

Sub-divisions (a, b & c) of Fig. 3 demonstrate the SEM metaphors of Kaolinite,

copolymer & PAA-Kaolinite complex. The Kaolinite imagery was darker with lumpy exterior. Its superficies is proliferous but these openings aren't seen in entire matrices. The surface looks like fragmented because of possessing non-carbon-based components as confirmed by EDX analysis [47]. Fig. 3 (b) possesses the elongated solid type of carbonaceous structures as true in case of carbon materials as expected from copolymer. The composite image Fig. 3 (c) shows that compounded imagery possess pores which vary in size, numbers and structures in comparison of copolymer and Kaolinite. Surface of the composite is showing roughness which denotes maximum area of surface
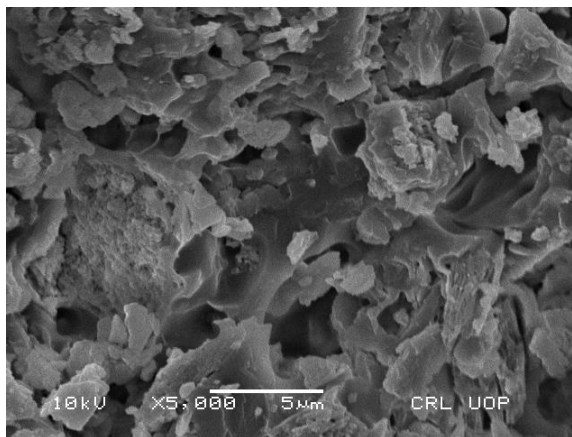

Fig. 3   (c). Pictorial view of PAA- Kaolinite-composite.

Assessment of Surface Area

Surface area plays important role in phenomenon of adsorption, similarly particle size and specific surface area are indirectly proportional to each other i.e. greater adsorption will be observed with small particles possessing larger surface. The acreage was computed around *32.316 (m^2/g)* of the complex computed through N_2 adsorption method.

EDX analysis

The EDX analysis was performed & obtained data is reported in Fig. 4 (a), (b) and (c). The atomic percentage and weight percentage of sawdust, copolymer and PAA-kaolinite was present. The result shows that composite has maximum oxygen (*40.50%*) than C (*39.94%*) & nitrogen (*5.24%*).
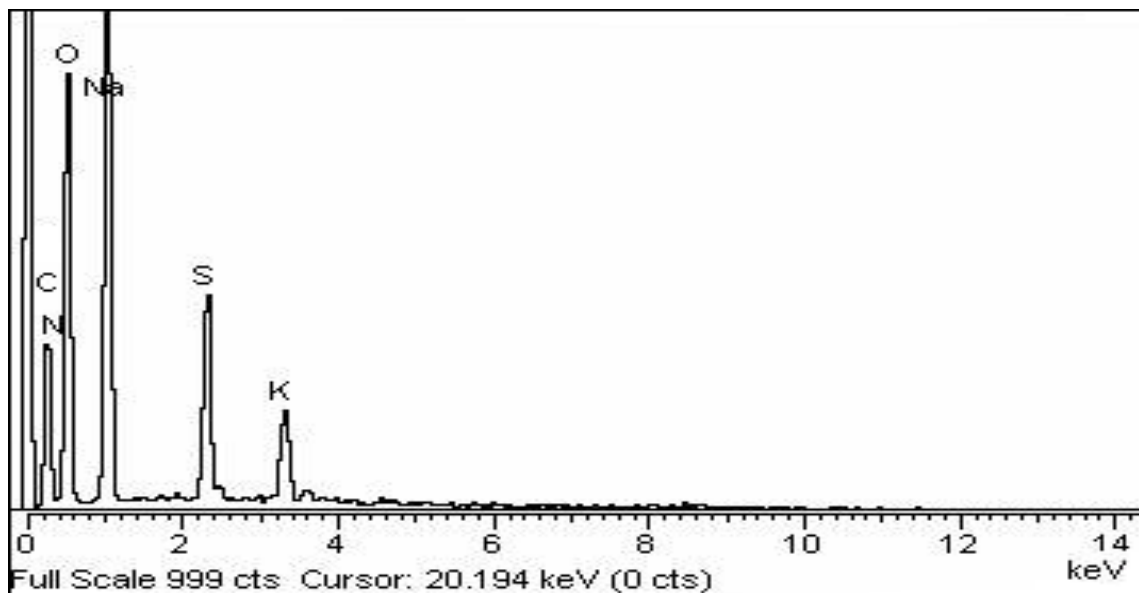

Fig. 4:   (a). EDX's schematic view of several components existing in P-A-A-polymerization.
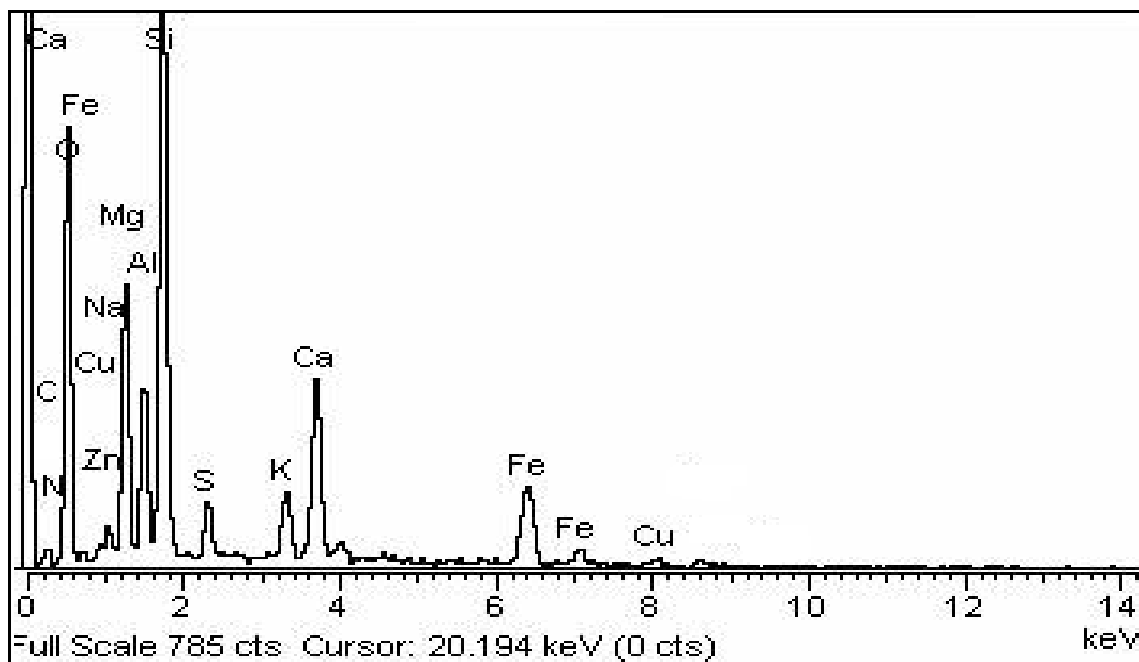

Fig. 4:   (b). EDX's schematic view of several components existing in Kaolinite.
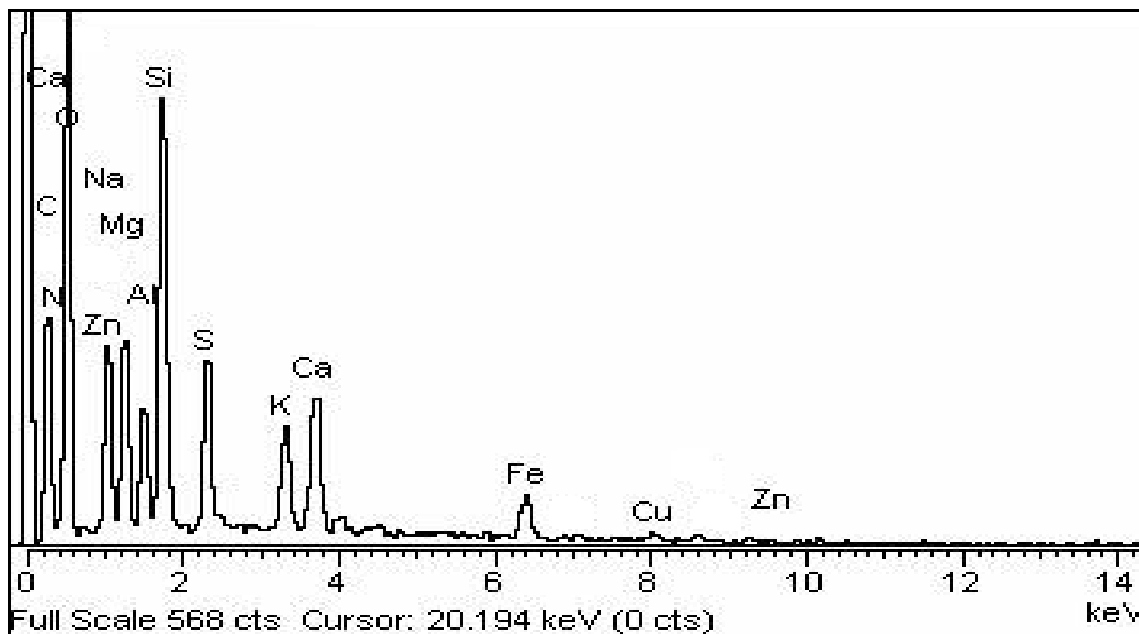
Fig. 4:   (c). EDX's schematic view of PAA- Kaolinite composite.

Adsorption studies

Primary concentration effect

Primary concentration of Cd(II) ions on composite is given in Fig. 5. With increase in initial concentration from *20-250 ppm*, using *0.3 g/40 mL* adsorbent dose, adsorption increases. Hugest quantity of ionized divalent cadmium telluride is imbibed at a magnitude of *200 mgL⁻¹*. Corresponding outcomes were attained in the adsorptive assessments of Pb(II) ions on P(AA- AM)-Kaolinite composite.
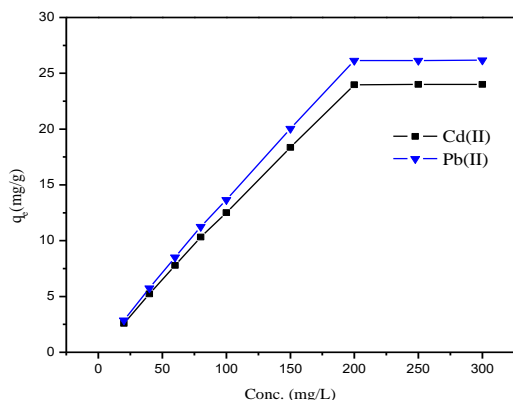
Fig. 5:   Primary concentration effect plot for removal of Cd(II) & Pb(II) ions on P(AA-AM)-Kaolinite composite.

Impact of Period of Exposure

During the process of adsorption of ionized divalent forms of cadmium and lead on composite, the contact time of the effect was studied and was observed to have significant influence on adsorption rate. From Fig. 6 it is clear that adsorption rate is very fast in initial 0.005 min and takes one min gradually to get slow to attain equilibrium. The primary high rate of adsorption is due to the abundance of free adsorption sites, which become saturated with passage of time and results in decreased adsorption rate. Results show that the critical required time of 60 min will be sufficient for completion of adsorption process.

Fig. 6:   Contact time effect curve for the phenomenon of adsorption of Cd(II) & Pb(II) ions showing constancy at around 60 min.

Impact of pH-Value

Impact of pH-value on the absorbency of ionized divalent forms of cadmium and lead on P(AA-AM)-Kalonite composite study was carried out at dissimilar pH values and are displayed in Fig. 7. The adsorption of divalent cadmium rises with incre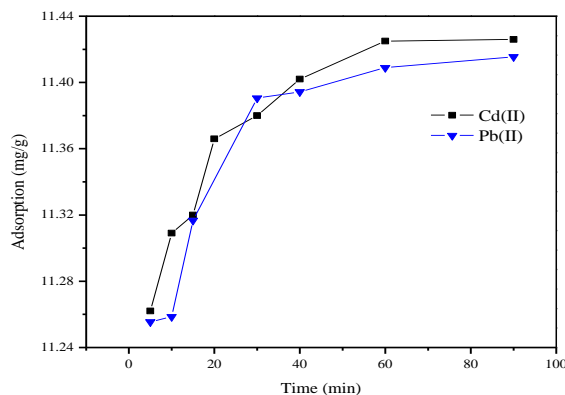ments in pH-value and extreme adsorption was observed at pH 5 with advanced increments in pH, adsorption decreased. Similarly, the adsorption of divalent lead escalates with increments in pH from 2-9. The maximum adsorption occurs at pH 6 but adsorption decreases with further increase of pH. At lower pH, lower adsorption was due to competitive adsorption between H^+ ions and metal ions for active sites. Moreover, the positive charge is increased on the surfaces of composite that is not permitting additional absorbency of + ionic form of metalloids because of electrostatic repulsion. Thus pH 6 was optimum pH for both the ionic metalloids. Literature revealed that the optimum value for divalent lead and cadmium adsorption was discovered approximately at acidic pH [23].
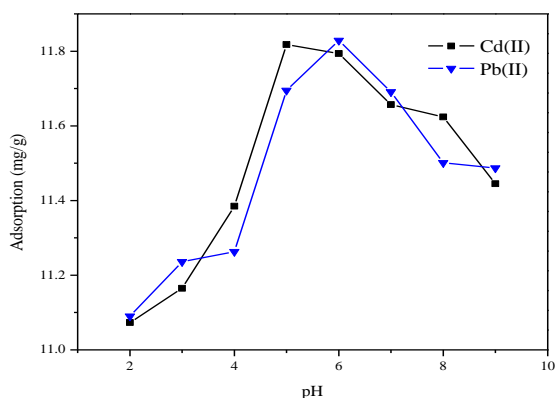

Fig.7:   Curves showing the effect of pH effect on the phenomenon of adsorption of Cd(II) & Pb(II) ions on PAA-SD-complex with applying all the above mentioned optimal values.

Impact of tempeature

Temepature is an indespensable aspect that greatly delivers impacts on the process of adsorption. To study the temperature's impact the trials were carried out at *25, 35 & 45ºC*. The rate of adosrption of divalent cadmium and lead electrolytes was increased when the temperature is incresed from *25* to *45ºC*, inidcating the endoergic temperament of adsorption. This may be by virtue of fast movement

alongwith activation of divalent ions of cadmiun and lead towads the active sites of adsorbent.

Adsorption Kinetics

The (dynamical adsorption) adsorption kinetics is a significant stricture with respect to process of adsorption. Mathematical equations have been developed to measure the adsorption rate. Regarding the study of adsorption process of divalent electrolyte of cadmium and lead on composite, the pseudo 1st & 2nd orders models were applied.

Quasi initial command

The quasi initial command formulae (2) specified by Lagergren applied to evaluate the investigational statistics [48].

$$\log(q_e - q_t) = -\frac{k_1 t}{2.303} + \log q_e \tag{2}$$

where q_e (mg.g^{-1}) is the magnitude of ionized metalloids adsorbed at equilibrium, q_t (mg.g^{-1}) is the aggregate of metallic electrolytes adsorptive at time-t and k_1-(min^{-1}) is the persistent ratio. The rates of (k_1 and q_e) were calculated through the slope and intercept of straight line stratagem of log (q_e-q_t) versus t (Fig. 8), respectively and were reported in Table 1. But the estimated q_e ratios are appreciably dissimilar from the experimentally obtained q_e figures. Thus pseudo first order kinetics isn't ensued by adsorptive metallic electrolytes.
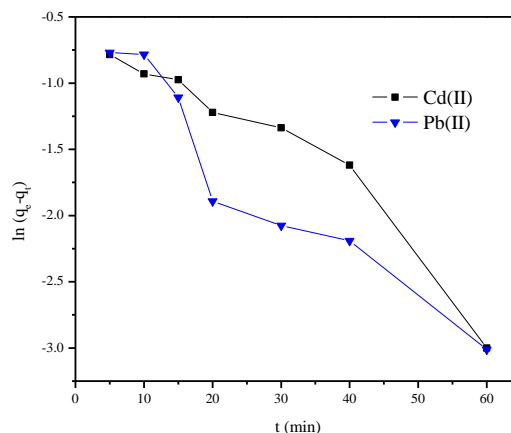

Fig. 8:   Plan of quasi initial command for divalent cadmium and lead ions adsorption on P(AA-AM)-Kaolinite complex to verify or reject the pseudo first order kinetics.

Quasi 2nd command

Quasi 2nd command suggested by McKay and Ho was correspondingly applied to reconnoiter the adsorptive metallic electrolytes records via applying equivalence formulae (3) [49].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{3}$$

whereas q_e & q_t are the aggregate of ionized metalloids absorptive (mg.g^{-1}) at equipoise and at time t (min), respectively and k_2 (g mg^{-1} min^{-1}) is the constant ratio of quasi second command kinetics. The rates of k_2 and q_e were calculated from the incline and interception of straight rectilinear strategy of t/q_t plotted against t as shown in (Fig), respectively and were cited in Table #1. The regression coefficient (R^2) values for divalent electrolytes of lead and cadmium were 1.0 and 0.999, which showed the well fit of quasi 2nd command dynamics (kinetics) than quasi 1st command dynamics(kinetics). Additionally, the analyzed ratios of q_e agree significantly with the experimental q_e values propose that the process ensued by quasi 2nd command dynamics.
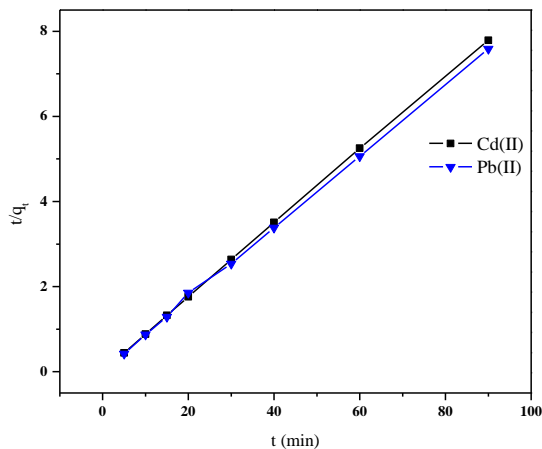

Fig. 9:   Curves of quasi 2nd command for divalent electrolytes of cadmium and lead adsorption on P(AA-AM)-Kaolinite composite to confirm the best fit of 2nd order.

Adsorption isotherms

Isothermally adsorption is significant to stratagem the temperament of adsorption. The Freundlich and Langmuir isotherms are highly frequently applied adsorption isotherms.

Isotherm of Langmuir

The Isotherm of Langmuir proposed that the adsorption of heavy metals ions from aqueous solutions occurs on homogenous surface by monolayer coverage with interaction among the adsorbed molecules. The linear form of Langmuir equation (4) [50] is given by

$$\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} \times C_e \tag{4}$$

where C_e is the equilibrium concentration of metal ions (mg L^{-1}), q_e is the amount (*mg g^{-1}*) of metal ions adsorbed, q_m and K_L are Langmuir constants, indicates the adsorption capacity (*mg g^{-1}*) and energy of adsorption (*L mg^{-1}*), respectively. The plot of Langmuir isotherms for divalent Cd and Pb ions are presented in Fig. 10. The value of q_m and K_L were calculated from the incline and intersectional point of linear plan of C_e/q_e versus C_e and represented in Table 2. Through tabled view it's clearly demonstrated that the proportions of q_m and K_L intensifies with increments in thermal reading. The maximum adsorption capacity of ionized metalloids on P(AA-AM)-Kaolinite composite at 25°C was *28.571 mg.g^{-1}* and *32.25 mg.g^{-1}* correspondingly.

Weber and Chackravorti 1974, expressed the Langmuir isotherm in terms of a dimensionless constant called equilibrium parameter or separation factor (R_L), which is defined as follow [44].

Table-1: Kinetic constants for divalent electrolytes of cadmium and lead adsorption on PAA-SD composite.

Metallic electrolytes	Quasi 1st (Command) order			Quasi 2nd (Command) order		
	q_e (*mg.g^{-1}*)	K_1 (*min^{-1}*)	R^2	q_e (*mg.g^{-1}*)	K_2 (*g mg^{-1} min^{-1}*)	R^2
Cd(II)	2.779	0.0852	0.915	11.494	1.081	1.0
Pb(II)	1.183	0.0575	0.918	11.363	0.0944	0.999

$$R_L = \frac{1}{1 + bC_i}$$

$$(5)$$

While K_L is the Langmuir constant
C_i is the initial concentration of metal ion.
if R_L rate $(0 < R_L < 1)$ = advantageous
if R_L rate (> 1) = disadvantageous
If R_L rate $(= 0)$ = irreversible
If R_L value $(= 1)$ = reversible [42].

At 25, 35 and 45°C the values of R_L for adsorption of Cd(II) was 0.217, 0.183 and 0.147, respectively. At 25, 35 and 45°C the rates of R_L for adsorption of divalent electrolytes of lead was 0.208, 0.196 and 0.190, respectively. The values of divalent electrolytes of lead and cadmium were in the array of zilch and one which shows that the absorptivity is advantageous.
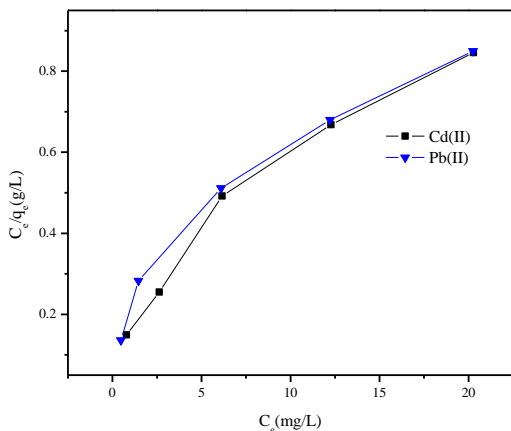

Fig. 10: Plot of Langmuir isotherms for divalent electrolytes of lead and cadmium adsorption on PAA-SD composite at 25°C showing the data fit for adsorption.

Isotherm of Freundlich

Isotherm of Freundlich is an empirical equation used to discuss the adsorption on heterogeneous adsorbents with interaction among adsorbed molecules. Freundlich adsorption isotherm equation (6) [52] in the linear form can be represented as

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

$$(6)$$

while K_F and $1/n$ are Freundlich coefficients specifying the adsorption dimensions and adsorption concentration respectively. The plot of Freundlich isotherms for Cd(II) and Pb(II) are given in Fig. 11.

Both $1/n$ and K_F parameters were measured from the slope and intercept of curve of $\ln q_e$ versus $\ln C_e$ and represented in Table-2. Meanwhile the ratio of $1/n$ is less to one displaying advantageous adsorption. Findings demonstrated that the adsorption ratio of ionized metalloids on P(AA-AM)-Kaolinite composite fit well with Isotherm of Freundlich ($R^2 = 0.956$, 0.971) as compared to the Isotherm of Langmuire ($R^2 = 0.952$, 0.922) under the concentration range studied. Using least square method the isotherm data were calculated and the concerned correlation coefficients were given in the same table. From Table 2 it can be seen that Freundlich isotherm explain the adsorption process very well.
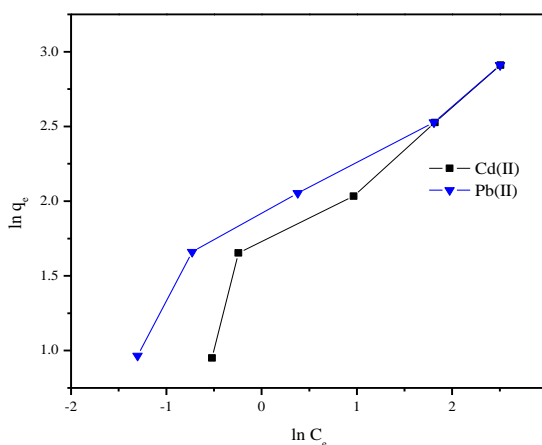
Fig. 11: Freundlich Isotherms plots for removal of divalent electrolytes of lead and cadmium on P(AA-AM)-Kaolinite-complex at 25°C for verifying the best fit for adsorption process.

Table-2: Assessment of Isarithm Coefficients for of divalent electrolytes of lead and cadmium absorptive on P(AA-AM)-Kaolinite complex at dissimilar temperatures

Metal ion	Temperature (K)	Langmuir's coefficients			Freundlich's coefficients		
		q_{max} (mgg^{-1})	$K_L 10^{-2}$ (L/mg)	R^2	$1/n$ (mg/g)	K_F (mg/L)	R^2
Cd(II)	298	28.571	17.98	0.952	0.562	4.486	0.956
	308	29.411	22.22	0.951	0.511	5.338	0.947
	318	30.300	29.00	0.946	0.458	6.104	0.960
Pb(II)	298	32.25	19.00	0.922	0.468	6.043	0.971
	308	33.33	20.40	0.918	0.343	6.952	0.978
	318	34.48	21.30	0.915	0.448	7.249	0.928

Comparison with other adsorbents

Table-3 shows the comparison of maximum adsorption capacities of Cd(II) and Pb(II) ions on PAA- Kaolinite composite with other adsorbents reported in literature. Findings designate that the greatest adsorption dimensions of ionized metalloids on P(AA-AM)-Kaolinite composite was higher than

those reported in literature and shows that this novel composite has high potential for use as adsorbent for the adsorption of heavy metals ions from aqueous solutions.

Adsorption thermodynamics

The value of free energy change (ΔG°) for the process of adsorption were measured, using the following equation (7) [53].

$$\Delta G^{\circ} = - RT \ln K \qquad (7)$$

where R (8.314 Jmol^{-1} K^{-1}) is universal gas constant and T (K) is the absolute temperature. The values of thermodynamic parameters are given in Table # 4. The negative value of ΔG° illustrates the extemporaneous and feasible temperament of absorptivity. The values of enthalpy change (ΔH°) and entropy change (ΔS°) can be determined using Van't Hoff equation (8) [54].

$$\ln K = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT} \qquad (8)$$

$$\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ} \qquad (9)$$

The ΔS° and ΔH° were measured from the slope of and intercept of ln K vs 1/T given in Fig. 12. The positive values of ΔH° confirm the endothermic nature of adsorption. The positive values of ΔS° show the high randomness on active sites during adsorption. The instigation dynamism for adsorption of ionized cadmium and lead were measured by applying Arrhenius equation (10).

$$\ln K = \ln A - \frac{E_a}{RT} \qquad (10)$$

The energy of activation was measured from the slope of plot of ln K vs 1/T as given in Fig. 12 and was found to be *12.148 kJ.mol^{-1}* for divalent electrolytes of cadmium and *7.165 kJ.mol^{-1}* for lead. The results confirmed that the heavy metals ions adsorption on PAA-SD composite was physical. The physical adsorption process has energy in the limit of 5-40 kJ mol^{-1} while chemical adsorption process has 40-800 kJ mol^{-1} energy [55].

Table-3: Comparison of adsorption capacity of composite with other adsorbents.

| Adsorbent	Modifying agent (s)	Heavy metal	q_{max} (mg g^{-1})	Reference
Rice husk	Sodium hydroxide	Cd(II)	20.24	Kumar and Bandyopadhyay (2006)
Rice polish	Washed with double distilled water	Cd(II)	9.72	Singh K.K (2005)
Rice husk ash	Without any pretreatment	Cd(II)	3.0392	Srivastava V.C (2008)
Corncob	Oxidized with Nitric acid	Cd(II)	19.3	Leyva-Ramos R (2005)
Areca (a food waste)	NaOH and H$_2$SO$_4$	Cd(II)	1.12	Zheng W (2008)
Sawdust of deciduous trees	No treatment	Cd(II)	3.5	Bozic D (2009)
Tea waste	Washed with hot water	Cd(II)	11.29	Cay S (2004)
Bagasse fly ash	No treatment	Cd(II)	6.1942	Srivastava V.C (2006)
Sawdust	NaOH and sulphuric acid	Cd(II)	26.73	Naiya T.K (2009)
Neem bark			25.57	
Sawdust (*Pinus halepensis*)	Untreated	Cd(II)	7.35	Semerjian L (2010)
Bamboo charcoal	Washed with water	Cd(II)	12.08	Wang F Y (2010)
Corn stalk RCS	Washed with water	Cd(II)	22.17	Zheng L (2010)
AGCS	Copolymerization	Cd(II)	3.81	
Peanut husk	Sulphuric acid	Pb(II)	29.14	Li et al. (2006a)
Bagasse fly ash	Hydrogen peroxide	Pb(II)	2.50	Gupta and Ali (2004)
Maple sawdust	Without any treatment	Pb(II)	3.19	Bin Yu (2001)
Sawdust	Washed with deionized water	Pb(II)	21.05	Li Q (2007)
Modified peanut husk	Formalin	Pb(II)	29.14	
Meranti tree sawdust	Formaldehyde	Pb(II)	31.95	Ahmad A (2009)
Empty fruit bunch fiber	NaOH	Pb(II)	20.00	Muhammad Ibrahim M.N (2010)
Activated waste mud	NaOH	Pb(II)	24.4	Ozdes D (2009)
Coconut shells	Sulphuric acid	Pb(II)	26.50	Sekar M (2004)
Apricot stone	Sulphuric acid	Pb(II)	21.38	Mouni L (2011)
Rice husk ash	Hydrochloric acid	Pb(II)	12.346	Feng Q (2004)
Sawdust	Formaldehyde in sulphuric acid	Cd(II)	9.29	Taty-Costodes et al. (2003)
(*Pinus sylvestris*)		Pb(II)	9.78	
Walnut sawdust	Formaldehyde in sulphuric acid	Pb(II)	4.48	Bulut and Tez (2003)
		Cd(II)	4.51	
Olive cake	Washed with distilled water	Pb(II)	19.530	Doyurum S (2006)
		Cd(II)	10.560	
Modified lignin	Alkali glycerol delignification	Pb(II)	8.2-9.0	Demirbas A (2004)
		Cd(II)	6.7-7.5	
P(AA-AM)-Kalinite(SD)	Composite	Cd(II)	28.57	Present work
		Pb(II)	32.25	
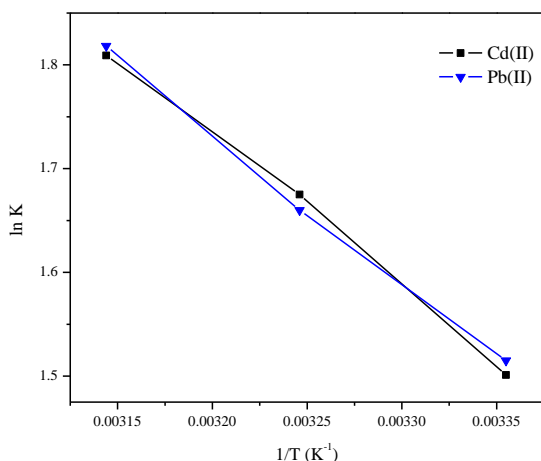
Fig. 12: Plot of Van't Hoff equation for Cd(II) & Pb(II) ions adsorption on P(AA-AM)-Kaolinite composite for evaluation of entropy and enthalpy change.

Table-4: Thermodynamics factors for ionized cadmium and lead on absorptivity on P(AA-AM)-Kaolinite complex at dissimilar temperatures

Metal ion	Temperature (K)	K_F (L/g)	ΔH^o kJmol^{-1}	ΔS^o kJmol^{-1} K^{-1}	ΔG^o kJmol^{-1}
Cd(II)	298	4.486	12.146	0.0532	- 3.718
	308	5.338	---	0.0533	- 4.289
	318	6.104	---	0.0532	- 4.782
Pb(II)	298	6.043	7.165	0.0390	- 4.457
	308	6.952	---	0.0389	- 4.829
	318	7.249	---	0.0390	- 5.237

Conclusion

A novel P(AA-AM)-Kaolinite composite could be used as a cost effective adsorbent for the exclusion of divalent electrolytes of cadmium and lead from aqueous suspensions. Adsorption was dependent on temperature, contact time, pH and preliminary metallic electrolytic aggregate. The adsorption dynamics were ensued by quasi 2nd command dynamic version. Isothermal adsorption was applied to the experiential facts which form fitted well with Langmuir and Freundlich isotherms. The greatest adsorption dimensions, q$_m$ (from Langmuir model) at 25°C, were *28.57 mg.g^{-1}* and *32.25 mg.g^{-1}* for ionized cadmium and lead, correspondingly. The activation energy values *12.148 kJ mol^{-1}* and *7.165 kJ mol^{-1}* for divalent electrolytes of cadmium and lead suggest physical adsorption. The factors thermodynamically revealed the exothermic, feasibility and spontaneous characteristics of the phenomena of adsorption. The P(AA-AM)-Kaolinite complex showed extreme adsorption magnitudes for divalent electrolytes of cadmium and lead than those of some reported in literature. The results showed that P(AA-AM)-Kaolinite composite has highly capability of adsorption as compared to many others low cost and commercially available adsorbents.

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