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 (C2H16N2O2)3, (H2C=CHCONH)2CH2, potassium persulfate, K2S2O8 as initiator and sodium sulfite 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-Dispersion 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 “1A” of equilibrium amount, “CT” (wet time), neutrality (alkalinity and acidity) and calefaction (thermal reading). The quasi 2nd order kinetic archetypal ensued by AK. Adsorption isotherms were applied to the empirical statistics which fitted well with a) Irving-Langmuir-isotherm and b) Freundlich adsorption isotherm. The supreme adsorption dimensions, qa, (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 ∆G°, ∆H° and ∆S° 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 suitable substance for the exclusion of adsorbent divalent cadmium and lead electrolytes from aqueous suspensions.

Keywords: Polymer-kaolinite composite; Sawdust, Heavy metals; Adsorption isotherm; Characterization.

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 pollutants 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 ð (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...
[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 Na₂S 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 300µm. 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 45°C 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 to5 min. For removal of DO in the solution, N₂ was sustained during the chemical response span. And finally, till the weight became constant, the solution was kept in oven at 60°C 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 0.3g of PAA-kaolinite were mixed in a conical flask and shaken in water shaker at 150 rpm and 25°C 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).

\[ q = \frac{(C_o - C_e)}{m} \times V \]

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

Acrylamide and Acrylic-acid/ Acrylic polymer (IUPAC: propenoic acid) were grafted instantaneously towards Kaolinite in a monolithic identical standard applying Na₂S 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 S₂O₄²⁻ inciter disintegrates when exposed to thermal processing. Then substrate -OH group of Thar clay from radical abstracts hydrogen for constructing dynamic radices on the substratum. So, this S₂O₄²⁻ dynamic redox-system ensued in radically initiation of A-A-m and A-A polymerization in active centers on the substrate which headed to polymerize implantation. Subsequently methylene-bis-acrylamide, interconnection mediator existing, the polymerize 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 (SiO₄²⁻), 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-H₂-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 CO₂.

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.

\[ S_2O_8^{2-} \rightarrow 2SO_4^- \]

Kaolinite + 2SO₄²⁻ → Kaolinite O

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 (10.900°) 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 (32.350°) is observed in AA-co-AM. Results of [45, 46] indicates that peak diffraction (10.900°) 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.
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. 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.

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 $32.316 \text{ (m}^2/\text{g})$ 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.
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 mg L\(^{-1}\). Corresponding outcomes were attained in the adsorptive assessments of 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.
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 increments 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].

![Impact of pH-Value](image)

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 temperature

Temperature 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 & 45°C. The rate of adsorption of divalent cadmium and lead electrolytes was increased when the temperature is increased from 25 to 45°C, indicating the endoergic temperament of adsorption. This may be by virtue of fast movement alongwith activation of divalent ions of cadmium and lead towards 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].

\[
\log(q_e - q_t) = - \frac{k_1 t}{2.303} + \log q_e
\]

where \(q_e\) (mg.g\(^{-1}\)) is the magnitude of ionized metalloids adsorbed at equilibrium, \(q_0\) (mg.g\(^{-1}\)) is the aggregate of metallic electrolytes adsorbive at time-t and \(k_1\) (min\(^{-1}\)) is the persistent ratio. The rates of \(k_1\) and \(q_0\) 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.

![Impact of temperature](image)

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].

\[
\frac{t}{q_i} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t
\]

(3)

whereas \(q_e\) & \(q_i\) 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 \(t/q_i\) 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.

![Graph showing 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.]

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.

Adsortion 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

\[
\frac{C_e}{q_e} = \frac{1}{K_L q_m} + \frac{1}{q_m} C_e
\]

(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>
<thead>
<tr>
<th>Metallic electrolytes</th>
<th>Quasi 1st (Command) order</th>
<th>Quasi 2nd (Command) order</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(q_e) (mg.g(^{-1}))</td>
<td>(K_{L1}) (min(^{-1}))</td>
</tr>
<tr>
<td>Cd(II)</td>
<td>2.779</td>
<td>0.0852</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>1.183</td>
<td>0.0575</td>
</tr>
</tbody>
</table>
\[ R_L = \frac{1}{1 + bC_i} \]  

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 \((> 1)\) = 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.

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

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.

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

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 Langmuir \((R^2 = 0.952, 0.922)\) 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-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 ($\Delta G^\circ$) for the process of adsorption were measured, using the following equation (7) [53].

$$\Delta G^\circ = -RT \ln K$$  \hspace{1cm} (7)

where R (8.314 J mol$^{-1}$ 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 $\Delta G^\circ$ illustrates the temporaaneous and feasible temperament of absorptivity. The values of enthalpy change ($\Delta H^\circ$) and entropy change ($\Delta S^\circ$) can be determined using Van’t Hoff equation (8) [54].

$$\ln K = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}$$  \hspace{1cm} (8)

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$  \hspace{1cm} (9)

The $\Delta S^\circ$ and $\Delta H^\circ$ were measured from the slope of and intercept of ln K vs 1/T given in Fig. 12. The positive values of $\Delta H^\circ$ confirm the endothermic nature of adsorption. The positive values of $\Delta S^\circ$ 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).

$$\ln K = \ln A - \frac{E_a}{RT}$$  \hspace{1cm} (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.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Modifying agent (s)</th>
<th>Heavy metal</th>
<th>$q_{max}$ (mg g$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rice husk</td>
<td>Sodium hydroxide</td>
<td>Cd(II)</td>
<td>20.24</td>
<td>Kumar and Bandyopadhyay (2006)</td>
</tr>
<tr>
<td>Rice polish</td>
<td>Washed with double distilled water</td>
<td>Cd(II)</td>
<td>9.72</td>
<td>Singh K.K (2005)</td>
</tr>
<tr>
<td>Rice husk ash</td>
<td>Without any pretreatment</td>
<td>Cd(II)</td>
<td>3.0392</td>
<td>Srivastava V.C (2008)</td>
</tr>
<tr>
<td>Corn cob</td>
<td>Oxidized with Nitric acid</td>
<td>Cd(II)</td>
<td>19.3</td>
<td>Leyva-Ramos R (2005)</td>
</tr>
<tr>
<td>Areca (a food waste)</td>
<td>NaOH and H$_2$SO$_4$</td>
<td>Cd(II)</td>
<td>1.12</td>
<td>Zheng W (2008)</td>
</tr>
<tr>
<td>Sawdust of deciduous trees</td>
<td>No treatment</td>
<td>Cd(II)</td>
<td>3.5</td>
<td>Bocic D (2009)</td>
</tr>
<tr>
<td>Sawdust</td>
<td>NaOH and sulphuric acid</td>
<td>Cd(II)</td>
<td>26.73</td>
<td>Naity T.K (2009)</td>
</tr>
<tr>
<td>Neem bark</td>
<td></td>
<td></td>
<td>25.57</td>
<td></td>
</tr>
<tr>
<td>Sawdust (Pinus halepensis)</td>
<td>Untreated</td>
<td>Cd(II)</td>
<td>7.35</td>
<td>Semerjian L (2010)</td>
</tr>
<tr>
<td>Bamboo charcoal</td>
<td>Washed with water</td>
<td>Cd(II)</td>
<td>12.08</td>
<td>Wang F Y (2010)</td>
</tr>
<tr>
<td>Corn stalk RCS</td>
<td>Washed with water</td>
<td>Cd(II)</td>
<td>22.17</td>
<td>Zheng L (2010)</td>
</tr>
<tr>
<td>AGCS</td>
<td>Copolymerization</td>
<td>Cd(II)</td>
<td>3.81</td>
<td></td>
</tr>
<tr>
<td>Peanut husk</td>
<td>Sulphuric acid</td>
<td>Pb(II)</td>
<td>29.14</td>
<td>Li et al. (2006a)</td>
</tr>
<tr>
<td>Maple sawdust</td>
<td>Without any treatment</td>
<td>Pb(II)</td>
<td>3.19</td>
<td>Bin Yu (2001)</td>
</tr>
<tr>
<td>Sawdust</td>
<td>Washed with deionized water</td>
<td>Pb(II)</td>
<td>21.05</td>
<td>Li Q (2007)</td>
</tr>
<tr>
<td>Modified peanut husk</td>
<td>Formalin</td>
<td>Pb(II)</td>
<td>29.14</td>
<td></td>
</tr>
<tr>
<td>Mercantil tree sawdust</td>
<td>Formaldehyde</td>
<td>Pb(II)</td>
<td>31.95</td>
<td>Ahmad A (2009)</td>
</tr>
<tr>
<td>Empty fruit bunch fiber</td>
<td>NaOH</td>
<td>Pb(II)</td>
<td>20.00</td>
<td>Muhammad Ibrahim M.N (2010)</td>
</tr>
<tr>
<td>Activated waste mud</td>
<td>NaOH</td>
<td>Pb(II)</td>
<td>24.4</td>
<td>Ozdes D (2009)</td>
</tr>
<tr>
<td>Apricot stone</td>
<td>Sulphuric acid</td>
<td>Pb(II)</td>
<td>21.38</td>
<td>Mouni L (2011)</td>
</tr>
<tr>
<td>Sawdust</td>
<td>Formaldehyde in sulphuric acid</td>
<td>Cd(II)</td>
<td>9.29</td>
<td>Taty-Costodes et al. (2003)</td>
</tr>
<tr>
<td>(Pinus sylvestris)</td>
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<td>Pb(II)</td>
<td>9.78</td>
<td></td>
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<td>Walnut sawdust</td>
<td>Formaldehyde in sulphuric acid</td>
<td>Cd(II)</td>
<td>4.48</td>
<td>Bulut and Tex (2003)</td>
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<tr>
<td>Modified lignin</td>
<td>Alkali glycerol delignification</td>
<td>Pb(II)</td>
<td>8.29.0</td>
<td>Demirbas A (2004)</td>
</tr>
<tr>
<td>P(AA-AM)-Kalinite(SD)</td>
<td>Composite</td>
<td>Pb(II)</td>
<td>28.57</td>
<td>Present work</td>
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</tbody>
</table>

$\Delta H^\circ$ = $\Delta H^0$ - $T\Delta S^0$
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

<table>
<thead>
<tr>
<th>Metal ion</th>
<th>Temperature (K)</th>
<th>K_T (L/g)</th>
<th>ΔH° (kJ mol⁻¹)</th>
<th>ΔS° (kJ mol⁻¹ K⁻¹)</th>
<th>ΔG° (kJ mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(II)</td>
<td>298</td>
<td>4.486</td>
<td>12.146</td>
<td>0.0532</td>
<td>-3.718</td>
</tr>
<tr>
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<td>308</td>
<td>5.338</td>
<td>12.146</td>
<td>0.0533</td>
<td>4.289</td>
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<tr>
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<td>318</td>
<td>6.104</td>
<td>12.146</td>
<td>0.0532</td>
<td>-4.782</td>
</tr>
<tr>
<td>Pb(II)</td>
<td>298</td>
<td>6.043</td>
<td>7.165</td>
<td>0.0390</td>
<td>4.457</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>6.952</td>
<td>7.165</td>
<td>0.0389</td>
<td>4.829</td>
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<tr>
<td></td>
<td>318</td>
<td>7.249</td>
<td>7.165</td>
<td>0.0390</td>
<td>-5.237</td>
</tr>
</tbody>
</table>

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 ensured by quasi 2nd command dynamic version. Isothermal adsorption was applied to the experimental 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.

References

Phthalate-Functionalized Sugarcane Bagasse: Mono and Multicomponent Adsorption in Batch Mode, **79**, 116 (2016).


