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Heavy Metal Removing by Modified Bentonite and Study of Catalytic Activity

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Abstract: Due to the high hydrophobicity and surface area, clays are efficient adsorbents for the removal of liquid impurities and purification of gases when they are modified. In this work, bentonite was modified with imidazole and imidazolium groups and resulting clays were characterized by different techniques such as ¹H NMR, ¹³C NMR, TEM, SEM, XPS, TG, and FT-IR. Applications of these clays were studied in the removal of Co, Cu, and Pb in the wastewater. Effects of contact time, pH, initial heavy metal ions concentration, and kinetic were investigated. The catalytic activity of the metals adsorbed by imidazole modified bentonite was studied in A³ coupling reactions of various amines, aldehydes, and alkynes.

1 INTRODUCTION

Numerous toxic heavy metals have and are being discharged to the environment as industrial wastes, causing serious soil and water pollution. In recent years, various physicochemical and biological methods were developed for toxic heavy metal removal. Especially, in the past two decades, increasing attentions have been paid for using clays as sorbents to remove contaminants. Compared to other sorbents such as activated carbon and zeolite, mineral clays are greener, cheaper and more naturally available. Clays are widely applied in many fields of technology and science such as the removal of liquid impurities and purification of gases [1-3]. Such a wide range of usefulness of clays is due to their high specific surface area, high chemical and mechanical stability, and a variety of surface and structural properties. The chemical nature and pore structure generally determine the sorption ability of clay materials. For gas-phase sorption, the pore structure, the nature, and volume of pores are predominant factors. In the case of liquid-phase sorption, the chemical properties of surface groups influence the extent of sorption. However, for increasing removal capacity of clay, in the most of the cases, it is required modifying clay structure with ligands. Along this line, from standpoint to green chemistry, using nitrogen based ligands instead of toxic and expensive phosphorus ligands is highly desirable for modification of clays and preparing of sorbents.

Presently, the design of new heterogeneous catalysts comprising cheap, sustainable and ecofriendly materials is important from sustainable chemistry standpoints [4-6]. Considering the excellent properties of mineral clays, these soils can be considered as outstanding support for designing heterogeneous catalysts. Different applications of propargylamines in synthetic organic chemistry, therapeutic drug molecules, and agriculture chemicals recognize these compounds as important building blocks in natural products and industry [7-15]. The classic method for preparation of propargylamines included the addition of lithium acetylides or Grignard reagents to imine derivatives under stoichiometric condition [16-18]. In recent years A³ coupling reaction which is a one-pot reaction of amines, aldehydes and alkynes *via* metal C-H bond activations of terminal alkynes was developed as an efficient and atom-economic method for preparation of propargylamines [19-23]. This reaction can be catalyzed by different transition-metals [24-39], however from economic stand point using cheap and naturally available transition metals and catalysts are highly desirable.

To the best of our knowledge, there is no report on the removal of heavy metals from water and subsequently, use of removed metal as a catalyst in the A³ coupling reaction. In this work, we studied bentonite as naturally abundant clay as well as imidazole and imidazolium groups functionalized bentonite as cheap, simple and stable materials in the resulted in removal of metals from water and used for the first time resulted in materials as a catalyst in the preparation of propargylamines via A³ coupling reaction.

2 **Experimental Section**

2.1 Materials and methods

All materials were pure and purchased from Sigma-Aldrich, Across and Merck Millipore. Sodium type bentonite was purchased from Daneshmand chemical trading co (Iran). Reactions were monitored by gas chromatography in a Varian CP-3800 apparatus. ¹H NMR and ¹³C NMR spectra were recorded at 400 MHz and 100 MHz, respectively on a Bruker Avance HD apparatus in CDCl₃. Chemical shifts are given on the δ-scale in ppm, and residual solvent peaks were used as internal standards. The TEM and SEM mapping images were captured by EOL JEM-2010 and Hitachi S3000N. XPS analyses were performed using a K-alpha spectrometer. The weight loss of samples was measured using a thermo gravimeter NETZSCH STA 409 under an O₂ flow rate of 20 ml/min with a heating rate of 10 °C·min⁻¹ from 30 to 800 °C. Digital images of the samples were acquired with Hitachi S4160 FE-SEM apparatus operating at 20 kV. FT-IR studies of samples were performed

using a FT-IR spectrophotometer Bruker vector 22 where the prepared KBr pellets ranged from 400 to 4000 cm⁻¹.

2.2 Synthesis of imidazolium ionic liquid (IL).

Benzyl bromide (0.12 mL, 1 mmol) and vinyl imidazole (0.18 mL, 2 mmol) were dissolved in dry THF (10 mL) and the mixture was stirred under an argon atmosphere at 40 °C for 24 h. Then the resulting mixture was centrifuged to remove the solvent. The residue was washed with THF (3 × 10 mL) and hexane (3 × 10 mL) and the resulting solid dried under vacuum. ¹H NMR (DMSO, 400 MHz): δ 10 (s, 1H), 8.38 (s, 1H), 8.09 (s, 1H), 7.55 (d, 2H. *J=4*), 7.37-7.41 (m, 5H), 6.05-6.09 (m, 1H), 5.59 (s, br, 2H), 5.42 (s, br, 1H), 3.53 (s, br, 2H). ¹³C NMR (DMSO, 100 MHz): δ 136.20, 135.21, 129.43, 129.28, 129.11, 123.73, 120.10, 109.27, 52.32, 40.43 (Figures S1 and S2).

2.3 Preparation of Ben@S:

Bentonite (1 g) was sonicated in dried toluene (30 mL) followed by dropwise addition of (3mercaptopropyl)triethoxysilane (12 mmol, 2.3 mL). The reaction mixture was refluxed for 24 h under argon gas atmosphere. Then, the reaction mixture was subjected to centrifugation and the obtained solid was washed with ethanol (3×10 mL) rinse and dried under vacuum at 60 °C.

2.4 Preparation of Ben@S-Im:

A mixture of 10 min. sonicated Ben@S (0.5 g) in dry ethanol (15 mL), vinyl imidazole (2.5 mmol, 0.23 mL) and AIBN (0.7mmol, 115mg) as an initiator was added to the reaction system. The reaction mixture was refluxed for 24 h under argon atmosphere. Then the solid was separated with centrifugation and the resulting vinyl imidazole functionalized bentonite was washed with ethanol (3×10 mL) and dried under vacuum at 60 °C.

2.5 Preparation of Ben@S-Im-IL

In a 25 mL flask, Ben@S (0.5 g) was sonicated in dry ethanol (15 mL) for 10 min. Then, imidazolium IL (3 mmol) and AIBN (0.7 mmol, 115mg) were added and stirring reaction mixture was refluxed under argon atmosphere for 24 hrs. After subsequently the reaction mixture was subjected to centrifugation and the obtained isolated solids were washed with ethanol (2×15 mL) and then dried in an oven at 70 °C.

2.6 Adsorption experiments

For the adsorption experiment, initially, adsorbents (5 mg) were treated with separately prepared $Cu(OAc)_2$, Pb(OAc)_2, and Co(OAc)_2. (20 mg/L). For reaching the equilibrium adsorption capacity (q_e), the adsorbents were added to the heavy metal ion solutions (15 mL) and stirred for 4 h at room temperature. The equilibrium was achieved after 2 h. After collecting adsorbents by centrifugation, the initial heavy metal ion concentration effects on the q_e values were also investigated. In this regard, a series of samples containing 5 mg of the support, dissolved in 15 mL of metal solutions, were used. The adsorptions capacities were measured for five different concentrations (10, 20, 40, 60 and 100 mM). The water solutions of metal ions were buffered to pH 5 (acetic acid/ sodium acetate buffer). The solutions were stirred for 2 h at room temperature. The starting (C₀; mmol/L) and post-equilibration (C_{eq}; mmol/L) concentrations of metal ions were measured by atomic absorption spectrophotometry. The amount of metal adsorbed (q_e; mmol/g) after equilibration was calculated from the difference between C₀ and C_{eq}:

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{1}$$

Where *m* is the mass of support (0.005 g) and *V* is the volume of aqueous solution (L). For the adsorption kinetic studies, 5 mg of the support was dissolved in 15 mL of buffered (pH=5) metal

solution with the initial concentration of 20 mM and were stirred at room temperature. The aqueous samples were taken at preset time intervals and the concentrations of metal ions were measured by atomic absorption spectrophotometry. The amount of adsorption at time t, q_t (mmol/g), was calculated from:

$$q_t = \frac{(C_0 - C_t)V}{m} \tag{2}$$

Where *m* is the mass of support (0.005 g), C_0 (mmol/L) is the initial metal ion concentration, C_t (mmol/L) is the metal ion concentration at time *t*, *V* is the volume of aqueous solution (L). The relations between the sorption properties of the support and the pH of the solution were studied in the pH range from 2 to 7. The pH of the solutions was adjusted with the buffers containing KCl/HCl (pH=2), acetic acid/sodium acetate (pH=3–6) and HEPES (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) buffer (pH=7). The measurements were made for 20 mM metal concentration. The starting and final concentrations of metal ions in aqueous phases were measured by atomic absorption spectrophotometry. Experiments with real wastewater samples were performed by adding 2 mL of wastewater sample to a solution of adsorbents (20 mg) in deionized water (20 mL). The solutions were stirred for 2 h. The starting and final concentrations of metal ions in aqueous phases were measured by atomic absorption spectrophotometry.

2.7 General procedure for the synthesis of propargylamines:

To a 5 mL flask containing heavy metal treated clay (containing 2 mol% of metal), aldehyde (1 mmol), phenylacetylene (1.5 mmol), amine (1.5 mmol) and H₂O/THF (10:1, 2 mL) were added and the mixture was stirred at 40 $^{\circ}$ C for 24h under argon atmosphere. Progress of reactions was monitored by TLC or ¹H NMR. After completion of the reaction, the crude products were extracted using ethyl acetate (3×5 mL). Further purification was performed by column chromatography on

silica gel using hexane and ethyl acetate as eluents. All products were known and characterized by ¹H NMR and ¹³C NMR.

3 RESULTS AND DISCUSSIONS

3.1 Synthesis of supports and their characterization

For modification of bentonite, initially, the raw bentonite **1** was treated with (3-mercaptopropyl) triethoxysilane to afford mercapto functionalized bentonite (Scheme 1) **2** (Ben@S). Then, **2** was allowed to react with vinyl imidazole in dry ethanol under argon atmosphere and reflux conditions to achieve imidazole modified bentonite **3** (Ben@S-Im). Also, the composition of ionic liquid modified bentonite **4** (Ben@S-Im-IL) was obtained from the reaction of Ben@S with imidazolium ionic liquid in ethanol solvent and reflux conditions. At the final step, these compounds were used as adsorbents for the removal of heavy metal ions and after adsorption, these compounds were used as a catalyst for the preparation of propargylamines.



Scheme 1. Preparation of supports

The structure of the prepared materials was studied by FT-IR spectroscopy (Figure 1). Generally, a decrease of OH peak intensity at 3400-3600 cm⁻¹ in (**3**) and (**4**), indicates successful modification with imidazole and imidazolium groups. Also, results showed typical imidazole chain, (C–H/N–C–H) peak at 2925 cm⁻¹, ring vibration peak at 1098-1220 cm⁻¹[24, 25] as well as peaks located at 835 and 1635 cm⁻¹, related to the C-H of rings and bending vibration of the adsorbed water on the surface, a weak peak at 3162 cm⁻¹ could be related to C–H stretching vibrations of imidazole moiety [25, 26]. A new peak in 1525 cm⁻¹, could be due to the aromatic C=C or C=N stretching vibration and bending vibration modes [27]. confirming the attachment of imidazole and imidazolium groups.



Fig. 1. FT-IR spectra of Bentonite, Ben@S-Im and Ben@S-Im-IL

Thermogravimetric analyses (TGA) of Ben@S, Ben@S-Im and Ben@S-Im-IL were studied between 25 and 800 °C. Two small loss of weights in the Ben@S material between 25-150 °C and 120-800 °C, were related to the loss of physically adsorbed water and hydroxyl groups of Ben@S, respectively. TGA measurements for Ben@S-Im showed increasing of main weight loss between 150-800 °C due to the addition of the imidazole group. Furthermore, the increase of weight loss in Ben@S-Im-IL confirmed the successful attachment of higher weight imidazolium ionic liquid to the Ben@S (Figure 2).



Fig. 2. TGA diagrams of Bentonite, Ben@S-Im and Ben@S-Im-IL.

3.2 Adsorption rate

3.2.1 Effect of contact time on Metal ions sorption

In order to study the equilibrium adsorption capacity, the adsorption capacities were determined at different times (Figure 3). The results showed that the adsorption capacities of the adsorbents were changed with time. As it can be seen, in the initial 30 minutes of the treatment, the sharp increases in the adsorption capacity were obtained which may relate to the high complexion and geometric attraction between functional imidazole groups and heavy metal ions. From 30 min to 120 min the adsorption capacities did not have any significant changes. It can be concluded that the adsorption

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capacities obtained in the 30 min are equilibrium adsorption capacities (q_e) . There are some parameters which determine the adsorption rate, such as stirring (or flow) rate in the aqueous phase, adsorbent structure (e.g. size, porosity, surface area), amount of adsorbent, metal ion properties (e.g. hydrated ionic radius), concentration of metal ions, pH, temperature, chelate-formation rate, and of course, the presence of other metal ions which may compete with the ions of interest for active adsorption sites.



Fig. 3. Adsorption capacity of Co(II), Pb(II) and Cu(II) by Bentonite, Ben@S-Im and Ben@S-Im.

3.2.2 Effect of pH

The effect of pH on the equilibrium adsorption capacities was also examined. The results indicated that for the pH value of 5, the highest q_e were achieved (Figure 4). Using pH higher than 5, the qe values decreased which may be related to the precipitation of heavy metal ions with OH- anions. For the pH values 2-4, the q_e was also decreased which may be related to the protonation of sulfur and imidazole/imidazolium's nitrogens. In the case using bentonite as an adsorbent, this decrement is

much lower than using imidazole or imidazolium as adsorbents. This may be related to the absence of sulfur and nitrogen in the raw bentonite.



Fig. 4. Effect of pH on equilibrium adsorption capacity of a) Bentonite, b) Ben@S-Im and c) Ben@S-Im-IL for adsorption of Cu(II), Co(II) and Pb(II).

3.2.3 Metal ions concentration effect

The effect of initial heavy metal ions concentration on the adsorption capacity was also studied. In this regard, the two adsorption isotherms model, Langmuir, and Freundlich were calculated by equations (3) and (4).

$$\frac{C_e}{q_e} = \frac{1}{K_1 q_{max}} + \frac{C_e}{q_{max}} \tag{3}$$

$$\log q_e = \log Kf + \frac{1}{n} \log C_e \tag{4}$$

Where, C_e (mg/L), q_e (mg/g), K_1 , q_{max} (mg/g), Kf and n are equilibrium concentration, equilibrium adsorption capacity, Langmuir constant related to binding sites affinity, the maximum adsorption capacity, Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The Langmuir and Freundlich isotherm models for three adsorbents were fitted in Figure 5.



Fig. 5. Langmuir (a) and Freundlich (b) isotherm models of Bentonite, Ben@S-Im and Ben@S-Im-IL for adsorption of Cu(II), Co(II) and Pb(II).

The Langmuir and Freundlich parameters were also collected in Table 1.

 Table 1. Isotherm parameters of Langmuir and Freundlich models of Bentonite, Ben@S-Im and

 Ben@S-Im-IL for adsorption of Cu(II), Co(II) and Pb(II).

Support	Motalian	Lang	Langmuir isotherm				Freundlich isotherm		
Support	Ivietal Ioli	$q_{max}(mg/g)$	Kı	R^2	K _f	n	R^2		
	Co(II)	39.4	0.0675	0.9990	6.4640	2.58	0.9718		
Bentonite	Cu(II)	52.36	0.0695	0.9992	7.941	2.43	0.9563		
	Pb(II)	61.73	0.0684	0.9975	6.188	2.39	0.9620		
	Co(II)	81.96	0.127	0.9969	13.3291	2.35	0.9173		
Ben@S-Im	Cu(II)	87.71	0.0696	0.9994	12.1088	2.26	0.9655		
	Pb(II)	133.33	0.1226	0.9993	27.252	2.64	0.9723		
Dan@S Im	Co(II)	66.2	0.1488	0.9981	22.7248	4.32	0.9749		
IL	Cu(II)	69.93	0.07299	0.9990	10.4858	2.37	0.9632		
	Pb(II)	106.38	0.1688	0.9979	28.63	3.19	0.9510		

In table 1, the q_{max} values for Bentonite, Ben@S-Im, and Ben@S-Im-IL for adsorbing heavy metal ions such as Co(II), Cu(II) and Pb(II) ranged from 39.4 to 133.33 mg/g. The q_{max} values for Ben@S-Im were much higher than Bentonite and Ben@S-Im-IL which may be related to better interaction of sulfur and imidazole's nitrogens with heavy metal ions [28]. Also, the Langmuir constant (K₁) for three adsorbents ranged from 0.0675 to 0.1688. The K₁ values for Bentonite, Ben@S-Im and Ben@S-Im-IL all have positive values which made the adsorption process favorable. Also, the correlation coefficients (R²) values for the Langmuir model ranged from 0.9969 to 0.9994 which are all close to 1. Study of the Freundlich parameters showed that the adsorption intensities (n) ranged from 2.26 to 4.32, and for values higher than 1 (1/n closer to 0) the adsorption process is more likely to be heterogeneous. [29] Moreover, the Freundlich constants (K_f) ranged from 6.188 to 28.63. The K_f values showed the interaction between metal ions and adsorbents, and the greater more this value, the better adsorption will proceed. In this regard, the K_f values for Ben@S-Im and Ben@S-Im-IL are greater than the K_f values of Bentonite which may be related to the effect of ligand addition on the bentonite structures. The correlation coefficients (R^2) for the three adsorbents on the Freundlich equation ranged from 0.9173 to 0.9749 which are all lower values than the Langmuir model. It can be concluded that the adsorption isotherm is very well modeled by the Langmuir model. The adsorption capacity of adsorbents for Pb(II) was more than that for Cu(II) and Co(II). It could be attributed to large atomic weight, ionic radius and electronegativity of Pb(II)[29].

3.3 Kinetic study

The effect of the time on the adsorption capacity was also examined by pseudo-first-order and pseudo-second-order equations (equation 5 and 6).

$$\ln(q_e - q_t) = \ln q_e - K_1 t \tag{5}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$
(6)

Where, k_1 (1/min) and k_2 (g/(mg.min)) are the pseudo-first-order and pseudo-second-order kinetic rate constant, respectively. Using equation 5 and 6, the kinetic diagrams were fitted (Figure 6) and the parameters were collected in Table 2.



Fig. 6. Pseudo-first-order (a) and Pseudo-second-order (b) kinetic models of Bentonite, Ben@S-Im and Ben@S-Im-IL for adsorption of Cu(II), Co(II) and Pb(II).

 Table 2. Kinetic parameters of Bentonite, Ben@S-Im and Ben@S-Im-IL for adsorption of Cu(II),

 Co(II) and Pb(II).

		Pseudo-	first-order	model	Pseudo-second-order model		
Support	Metal ion	q_e	K_1	\mathbf{p}^2	q_e	K ₂	\mathbf{p}^2
		(mg/g)	(1/min)	К	(mg/g)	(mg/(<mark>g.n</mark>	nin)) K
	Co(II)	20.8130	0.0919	0.9999	21.008	0.0075	0.9973
Bentonite	Cu(II)	32.8502	0.0801	0.9990	31.348	0.0039	0.9898
	Pb(II)	49.282	0.0802	0.9981	46.62	0.00175	0.9833

Ben@S-Im	Co(II)	80.7008	0.0651	0.9887	93.46	0.00128	0.9979
	Cu(II)	97.23	0.0916	0.9714	99.01	0.00153	0.9974
	Pb(II)	100.26	0.0995	0.9876	123.46	0.00184	0.9990
Don@S Im	Co(II)	83.8305	0.0865	0.9869	81.32	0.00142	0.9961
Dell@S-III-	Cu(II)	95.06	0.0834	0.9785	86.96	0.00126	0.9955
IL	Pb(II)	95.98	0.1157	0.9888	98.04	0.00231	0.9987

The equilibrium adsorption capacity (qe) values for Ben@S-Im are higher than the other two adsorbents, ranging from 80.70, 97.23 and 100.26 for Co(II), Cu(II) and Pb(II), respectively. This may be related to the better interaction of sulfur and imidazole's nitrogen with heavy metal ions. These values were decreased when using Ben@S-Im-IL as adsorbent. This can be relevant to the congestion of proton ion (H^{+}) on the imidazolium structure and also the existence of the positive charge on the structure which may make some repulsion between metal ions and positive charge of imidazolium [30]. The pseudo-first-order constant (K₁) for adsorbing of Co(II), Cu(II) and Pb(II) by Bentonite, Ben@S-Im and Ben@S-Im-IL ranged from 0.0651 to 0.1157. The k₁ value for Ben@S-Im is higher than the other two adsorbents. Investigation of R^2 values for the pseudo-first-order equation showed that the R^2 values for Bentonite as adsorbent ranged from 0.9981 to 0.9999 which are all close to 1. On the other two adsorbents, these values ranged from 0.9714 to 0.9888. The study of the correlation coefficients revealed that the mechanism of the adsorption for using bentonite as an adsorbent is more likely to be physical than chemical adsorption. The study of the pseudo-secondorder model showed that the qe values for Ben@S-Im and Ben@S-Im-IL as adsorbents are higher than Bentonite. This may be related to the addition of organic groups to the bentonite structure [31]. The study of the pseudo-second-order constant (K₂) indicated that all values are in the same range (0.00128 to 0.0075). Also, the R² values for Ben@S-Im and Ben@S-Im-IL are much closer to 1 than Bentonite. These results showed that the mechanism for adsorbing of heavy metal ions by Ben@S-Im and Ben@S-Im-IL is much like pseudo-second-order and in this regard, the adsorption process is more likely to be chemical adsorption than physical [32].

3.4 Adsorption of heavy metals in the wastewater

The application of the Ben@S-Im was studied in the adsorption of Co(II), Cu(II) and Pb(II) in the wastewater. The results are collected in table 3. Using 20 mg of Ben@S-Im as adsorbent, removal efficacy of 84%, 87% and 90% were gained for Co(II), Cu(II) and Pb(II), respectively. An increment of adsorbent weight to 60, 120 and 200 lead to higher removal efficacy for adsorbing of heavy metal ions. The removal efficacy of almost 100% was achieved for using 200 mg of Ben@S-Im. The results indicated that the Ben@S-Im has good potential for using in the industrial wastewater.

Table 3. Amount of adsorbent (Ben@S-Im), equilibrium concentration of heavy metal ions and removal efficiencies of Ben@S-Im adsorbing Co(II), Cu(II) and Pb(II).

	Co(II)			Cu(II)				Pb(II)		
$A_A{}^a$	C_0^{b}	C_e^{c}	R_e^d	C ₀	Ce	R _e	C_0	Ce	R _e	
(mg)	(mg/L)	(mg/L)	(%)	(mg/L)	(mg/L)	(%)	(mg/L)	(mg/L)	(%)	
20	30	4.8	84	30	3.9	87	30	3.0	90	
60	30	3.3	89	30	2.4	92	30	2.1	93	
120	30	2.1	93	30	1.2	96	30	0.9	97	
200	30	0.6	98	30	0.3	99	30	0.0	100	

^a Amount of Adsorbent (Ben@S-Im) ^b Initial ion concentration of heavy metal ion solution ^c Concentration of heavy metal ion after equilibrium

^d The removal efficacy was calculated by the following equation: $R_e = (C_0 - C_e)/C_0$

3.5 Catalytic performance

For widespread the adsorbents applications, the catalytic activity of the Bentonite, Ben@S-Im and Ben@S-Im-IL were also studied. For this purpose and initially, the reaction of benzaldehyde with piperidine and phenylacetylene was selected as a model reaction and the effect of different factors such as different metals, catalyst loading, solvent effect, reaction temperature and time of reaction were studied. Using 1 mol% of catalyst (Pb, Co, Cu) in three different supports at room temperature, very low yields were obtained in 24 h (Table 4a, 4b, 4c, and entries 1-3). With increasing the catalyst to 2 mol%, yields were improved (Table 4a, 4b, 4c, entries 4-6). Also, with increasing the temperature to 40 °C and using H₂O/THF as a solvent, yields of reactions were significantly increased and the best results were obtained using Ben@S-Im supported metals, especially Ben@S-Im@Cu. (Table 4a, 4b, 4c, entries 7-9). It should be noted that by reducing the reaction time to 12h, the yield of reaction were noticeably decreased (Tables 4a-c, entries 10-12). Also, performing the reaction in the absence of bentonite@metal (Table 4a-c, entry 13) or using metal salts without bentonite gave lower yields (Table 4a, entries 14-16).

Table 4a. Optimization of the reaction conditions for the reaction of benzaldehyde, piperidine and phenylacetylene catalyzed by Bentonite@metal.

Q			
H +	+ N	Bentonite@Metal Solvent, T	

Entry	Metal	Solvent	Cat (mol%)	Temp (°C)	Time (h)	Yield (%) ^b
1	Pb	H ₂ O	1	r.t	24	0
2	Co	H ₂ O	1	r.t	24	5
3	Cu	H ₂ O	1	r.t	24	10
4	Pb	H ₂ O	2	r.t	24	0
5	Co	H ₂ O	2	r.t	24	14
6	Cu	H ₂ O	2	r.t	24	20

7	Pb	H ₂ O/THF	2	40	24	0
8	Со	H ₂ O/THF	2	40	24	45
9	Cu	H ₂ O/THF	2	40	24	63
10	Pb	H ₂ O/THF	2	40	12	0
11	Со	H ₂ O/THF	2	40	12	32
12	Cu	H ₂ O/THF	2	40	12	50
13		H ₂ O/THF		40	24	0^{a}
14	Pb(OAc) ₂	H ₂ O/THF	2	40	24	2 ^b
15	Co(OAc) ₂	H ₂ O/THF	2	40	24	15 ^b
16	Cu(OAc) ₂	H ₂ O/THF	2	40	24	38 ^b

^a Reaction performed in the absanse of Bentonite@metal ^b Reactions performed using metal salts in the absence of bentonite.

Table 4b. Optimization of the reaction conditions for the reaction of benzaldehyde, piperidine and phenylacetylene catalyzed by Ben@S-Im@metal.



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2	Co	H ₂ O	1	r.t	24	12
3	Cu	H ₂ O	1	r.t	24	18
4	Pb	H_2O	2	r.t	24	0
5	Co	H ₂ O	2	r.t	24	35
6	Cu	H ₂ O	2	r.t	24	52
7	Pb	H ₂ O/THF	2	40	24	0
8	Co	H ₂ O/THF	2	40	24	78
9	Cu	H ₂ O/THF	2	40	24	92
10	Pb	H ₂ O/THF	2	40	12	0
11	Co	H ₂ O/THF	2	40	12	70
12	Cu	H ₂ O/THF	2	40	12	75
13 ^a		H ₂ O/THF		40	24	0

^a Reaction performed in the absanse of Bentonite@metal

 Table 4c. Optimization of the reaction conditions for the reaction of benzaldehyde, piperidine and

 phenylacetylene catalyzed by Ben@S-Im-IL@metal.



1	Pb	H ₂ O	1	r.t	24	0
2	Co	H ₂ O	1	r.t	24	21
3	Cu	H ₂ O	1	r.t	24	20
4	Pb	H ₂ O	2	r.t	24	0
5	Co	H ₂ O	2	r.t	24	40
6	Cu	H ₂ O	2	r.t	24	54
7	Pb	H ₂ O/THF	2	40	24	0
8	Co	H ₂ O/THF	2	40	24	65
9	Cu	H ₂ O/THF	2	40	24	83
10	Pb	H ₂ O/THF	2	40	12	0
11	Co	H ₂ O/THF	2	40	12	45
12	Cu	H ₂ O/THF	2	40	12	61
13 ^d		H ₂ O/THF		40	12	1^d

^a Reaction conditions: benzaldehyde (0.5 mmol), piperidine (0.75 mmol), phenylacetylene (0.75 mmol) Solvent (2 mL), and catalyst (see, column).

^b Yields were determined by ¹H NMR

^c H₂O/THF (10:1)

^d Reaction performed in the absanse of Bentonite@metal

Ben@S-Im treated metals were selected as an efficient and cheap catalyst and characterized structures. The structure of Ben@S-Im after treating with Pb, Co, and Cu was studied using X-ray photoelectron spectroscopy (XPS) (Figure 7). The XPS spectra in C1s region showed four peaks centered at 284.5, 285.6, 286.6 and 288.5 eV, which are related to C-C or C=C, C-N or C-O, C=O or

C=N forms of carbon, respectively (Figure 7-a) [33]. The XPS spectra in N1s showed two peaks at 399 and 400 eV, which are attributed to the neutral amine and positively charged quaternary nitrogen species respectively (Figure 7-b)[35]. In Figure 7-c, the two regions are 162.8 and 164.1 eV and are related to $S2p_{3/2}$ and $S2p_{1/2}$, respectively. The XPS spectrum was observed in the 138.3 and 143.1 eV, for Pb4f_{7/2} and Pb4f_{5/2}, respectively, which are related to the oxidation state of Pb(II) (Figure 7-d)[36]. The peaks of (781 and 783.5 eV) and (796.8 and 799.5 eV) are related to Co ($2p_{3/2}$) and Co ($2p_{1/2}$), respectively which is related to Co²⁺. In addition, Co³⁺ peaks appeared in the areas of 786.1 and 802.1 eV. Also, two additional peaks in the 788.5 and 804.1 eV regions are related to the Co Satellites (shake-off and shake-up) and are due to a sudden change in Coulombic potential as the photo ejected electron passes through the valence band (Figure 7-e)[37].

The XPS spectrum in Cu (2p) region showed eight peaks. The two-peak at 932.9 and 952.9 eV are related to Cu ($2p_{3/2}$) and Cu ($2p_{1/2}$) in CuO, respectively. Also, the peak of 935 eV is related to the Cu²⁺ species. Except for the main peaks, three additional signals were observed at 940.5, 943.9, and 954.3 eV which could be attributed to Cu(II) states in CuO and Cu(OAc)₂. The results also showed two small peaks at 961.3 and 963.5 eV, which are related to Cu₂O or Cu(0). Because the binding energy of the Cu(0) and Cu₂O are very close and only 0.1 eV, it is very difficult to prove they are correct species using the binding energy of this region (Figure 7-f)[38].



Fig. 7. XPS spectra of Ben@S-Im@Metal at a) C1s, b) N1s, c) S2p, d) Pb4f, e) Co2p, f) Cu2p regions.

An element mapping images show the spatial distribution of elements in a sample which are a very useful method for displaying compositional zonation. Resulting SEM-Map and overlay map images of Ben@S-Im confirmed the presence of C, N, Pb, Co, and Cu, which are uniformly distributed in the structure [39](Figures 8 and 9).



Fig. 8. a) SEM and b-f) Map images of Ben@S-Im [b) C, c) N, d) Pb, e) Co and f) Cu].



Fig. 9. Overlay map images of Ben@S-Im@metals with a) Pb, b) Co and c) Cu.

Furthermore, EDX analysis showed the presence of different elements such as Pb, Co, Cu, N, Si, Al, and C in the structure of Ben@S-Im@metal (Figure 10).



Fig. 10. EDS spectrum of the Ben@S-Im with a) Pb, b) Co and c) Cu.

Using the above optimized - conditions (Table 4b, entries 8-9), these catalysts were then explored for A^3 coupling reaction of a variety of aldehydes, amines, and alkynes (Table 5). Results indicated very good yields for various aromatic aldehydes containing electron-deficient and donating groups (Table 5, entries 2-5). As well as, the reaction of heterocyclic 3-thiophenecarbaldehyde with piperidine and phenylacetylene with Co and Cu were performed efficiently, giving 62% and 88% yields, respectively (Table 5, entry 6). Reactions of 1-octyne as aliphatic alkyne with benzaldehyde and piperidine and also heptanal as an aliphatic aldehyde with phenylacetylene and piperidine proceeded well (Table 5, entries 7 and 8). Different amines such as piperidine, morpholine, pyrrolidine and dimethylamine reacted in A^3 coupling reaction in the presence of both of the metals, successfully affording desired products in very good to excellent yields.

 Table 5. Reactions of different aldehydes, amines and alkynes in the presence of Ben@S-Im@Metal.

Ben@S-Im@Metal H₂O/THF, 40 °C, 24h

 $R^{1}CHO + R^{2}_{2}NH + R^{3}$

R¹: Aliphatic, aromatic, heterocyclic R²: Aliphatic R³: Aliphatic, aromatic



(1) Co: 78%, Cu: 92%

(2) Co: 58%, Cu: 70%

(3) Co: 55%, Cu: 68%









(6) Co: 57%, Cu: 88%



(7) Co: 50%, Cu: 71%

(**5**) Co: 63%, Cu: 79%

(8) Co: 38%, Cu: 86%



(9) Co: 78%, Cu: 95%



(10) Co: 70%, Cu: 90%

(**11**) Co: 81%, Cu: 93%

^a Reaction conditions: aldehyde (1 mmol), amine (1.5 mmol), alkyne (1.5 mmol), H₂O/THF (2 mL), and catalyst (2 mol % Metal). Isolated yields.

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4 Recycling of the catalysts

Finally, recycling of the Ben@S-Im@Cu and Ben@S-Im@Co was studied for the A³ coupling reaction of benzaldehyde, piperidine and phenylacetylene under the optimized reaction conditions. For this purpose, after completion of the reaction, a mixture of reaction washing with

ethyl acetate was reused in another batch. Results indicated that the catalysts were recyclable up to 3 consecutive runs with a small decrease in activity. However, yields were dropped to 43 and 39 % in run 4 for Ben@S-Im@Cu and Ben@S-Im@Co, respectively (Figure 11).





The catalytic activity of Ben@S-Im@metal is compared with some of the reported catalysts in A³ coupling reaction with benzaldehyde, piperidine and phenylacetylene, as a common substrate (Table 6). Results indicated a relatively good activity of the presented catalyst. It should be noted that compared to other catalysts, the most advantage of ben@S-Im@metal is its subsequent application and activity after heavy metal removal as a catalyst.

 Table 6. Comparison catalytic activity of Ben@S-Im@metal with other reported catalysts in A³

 coupling reaction.

Entry	Catalyst	T (°C)	T (h)	Cu or Co	Yield

				(mol%)	(%)
1	Cu/HM[40]	110	2	0.013	92
2	CuHAP[41]	82	6	1.2	85
3	$(CuOTf)_2 \cdot toluene[42]$	r.t	36	10	82
4	Nano CuO[43]	90	6	10	82
5	CuO-MeOH[44]	90	4	20	65
6	Cu/NCNTs[45]	70	4	4	85
7	$CoCl_2(PPh_3)_2[46]$	70	24	10	91
0				Cu(ll), 2mol%	92
8	Ben@S-Im@metal [this work]	40	24	Co(ll), 2mol%	78

5 Conclusion

Three different Bentonite, Ben@S-Im and Ben@S-Im-IL substrates were modified with imidazole and imidazolium groups and were successfully used as adsorbents. These clays were applied in the removal of Co, Cu, and Pb in the wastewater. Kinetic studies indicated imidazole modified has higher efficiency in heavy metal removal than modified imidazolium. The effect of pH on the equilibrium adsorption capacities indicated that for the pH value of 5, the highest q_e amounts were achieved. The effect of initial heavy metal ions concentration on the adsorption capacity was also studied and were resulted in that the q_{max} values for Ben@S-Im were much higher than Bentonite and Ben@S-Im-IL which may be related to better interaction of sulfur and imidazole's nitrogens with heavy metal ions. The metals adsorbed by imidazole modified bentonite were used as efficient and cheap catalyst in A³ coupling reaction of different amines such as piperidine, morpholine, pyrrolidine and dimethylamine with aldehydes and phenylacetylene affording desired propargyl amines products in very good to excellent yields in aqueous media. The catalyst containing Cu was recycled successfully for three consecutive runs with a small decrease in the activity. All products were identified by ¹HNMR, ¹³CNMR, TEM, SEM, XPS, TG and FT-IR.

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Applications of these clays were studied in the removal of Co, Cu, and Pb in water.

Kinetic studies indicated imidazole modified has higher efficiency in heavy metal removal than imidazolium modified one.

These materials indicated good adsorption efficacy in the heavy metal ion adsorption of industrial wastewaters.

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