Cobalt Functionalized Ordered Mesoporous Carbon as Effective Adsorbent for Removal of Organic Pollutants from Aqueous Media

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ABSTRACT: Ordered mesoporous carbon CMK-3 (OMC) have been synthesized using mesoporous SBA-15 silica as template and modified with cobalt carbonate. Morphologies and surface texturing of materials were characterized by X-Ray diffraction (XRD), Scanning Electron Microscopy (SEM) and N_2 adsorption-desorption isotherms. The cobalt modified ordered mesoporous carbon were found to have a surface area of 490.06m2/g and pore volume of 0.42cm^3/g. The adsorption behavior of 1, 10-Phenanthroline (OP) and 2, 2'-bipyridine (BP) on cobalt modified ordered mesoporous carbon (Co^{+2}-OMC) were studied in aqueous system. The parameter such as temperature, contact time and initial OP and BP concentrations was investigated. Batch adsorption studies demonstrate that the cobalt containing CMK-3 has significant capacity for adsorption of OP and BP from aqueous solution. The adsorption processes of OP and BP are tested with langmuir and freundlich isotherm models. According to the langmuir isotherms, the maximum adsorption capacities of OP and BP on Co^{+2}-OMC were 595 and 500 mg/g, respectively.

Key words: 1,10-Phenanthroline, 2,2'-bipiridine, CMK-3, Co^{2+}-OMC, PANHs

INTRODUCTION

Due to the increasing world population and therefore expansion of cities, industrial development and agricultural activities, pollution of water supplies in large cities with diverse dangerous chemicals has been observed and organic pollutants form the main part of it. Phenolic, benzene and heterocyclic poly aromatic compounds are the most important organic pollutants in environment. Therefore, it is necessary to eliminate and reduce their amount from industrial wastewater, especially from oil industry before entering the environment (Us, 2003). Polycyclic aromatic nitrogen heterocycles (PANHs) are a group of heterocycles, containing nitrogen atoms (Lin *et al*., 2002). PANHs are found in many products and industrial and agricultural wastes (Banat *et al*., 2000).

In many areas, control of water quality is becoming very difficult. For protection of natural water resources it is essential to develop efficient water treatment process. Organic pollutants such as orthophenathroline (OP) and 2,2'-bipyridine (BP) causes significant damage to natural water systems and consequently to human health (Grimalt *et al*., 1994). Usually adsorption, chemical oxidation or biodegradation are the methods for the removal of these pollutants (Wu *et al*., 2000; Han *et al*., 2004; Kamble *et al*., 2008). Adsorption treatment provides a universal and simple approach to effectively removing of organic pollutants from environment (Imran *et al*., 2012).

Mesoporous carbon materials with uni and three dimensional pore systems were synthesized from mesporous silica templates such as SBA-15, SBA-1 and MCM-48 using sucrose as the carbon source (Ryoo *et al*., 1999; Yang *et al*., 2003; Kyotani *et al*., 1997). Ordered mesoporous carbon materials are particularly important in many areas such as air and water purification, catalysis, gas separation, energy storage, chromatography, etc (Jean & Li-Ping, 2012; Alan, 2012; Chang *et al*., 2012; ANBIA & Ghaffari, 2009; Peng *et al*., 2011; Anbia & Moradi, 2009; Zhao *et al*., 2012). CMK-3 exhibits marked advantages in bulky molecular adsorption over other microporous activated carbon due to its high surface area, large pore volume, narrow size distribution, hexagonally

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ordered structure and provides excellent opportunities for the produce of materials with different functionality, which is useful in designing new adsorbents for selective removal of pollutants or other adsorbates. These carbon materials are fabricated by the nanocasting process (baniamerian *et al.*, 2009; Crowley *et al.*, 2003; Ryoo *et al.*, 1999; Ryoo *et al.*, 2001).

1, 10- Phenanthroline or orthophenanthroline with molecular formula of ($C_{12}H_8N_2$) is an organic compound with a water solubility of 14 m.mol/L and dissociation reaction constant of $pK_1 = -1.4$ and $pK_2 = 4.85$. Also, 2, 2'-bipyridine with molecular formula of ($C_{10}H_8N_2$) is other organic compound with a water solubility of 40 m.mol/L and dissociation reaction constant of $pK_1 = -0.20$ and $pK_2 = 4.37$ (De Bussetti *et al.*, 1980). Orthophenanthroline is well adsorbed on clay and other materials and is used in water treatment, molecular chemistry, catalysis for the oxidative organic synthesis, microbiology, mediation as redox biosensor and photolysis chemistry (Ferreiro *et al.*, 2006). 2,2'-Bipyridine is an examples of the PANHs that is generally used in chemical, pharmaceutical industries, agricultural, water treatment, dyes, and others. It also used as a chelating ligand that forms complexes with most transition metal ions. Many of these complexes have distinctive optical properties and some of them are of interest in analysis (Ferreiro *et al.*, 1983). Thus significant amounts may be found in the corresponding wastewaters (Helmi *et al.*, 2000; Coluccia *et al.*, 1976).

In this study, highly ordered mesoporous carbon molecular sieves were synthesized using mesoporous SBA-15 silica as template and then modified with Co^{2+} to increase the interaction between both adsorbate species and adsorbents. The new absorbent is labeled as (Co^{2+}-OMC). The parameters investigated in this study include temperature, contact time and initial OP and BP concentrations. The adsorption processes of OP and BP are tested with langmuir and freundlich isotherm models.

MATERIALS & METHODS

The reactants used in this study were $EO_{20}PO_{70}EO_{20}$ (Pluronic P123) as a surfactant , tetraethyl orthosilicate (TEOS, 98%) as a silica source, sucrose as a carbon source, sulfuric acid as a catalyst for synthesis of mesoporous carbon, HCl and deionized water for synthesis of mesoporous silica SBA-15. Cobalt (II) carbonate salt was used for modification of mesoporous carbon CMK-3. All chemicals were of analytical grade and obtained from Merck (Darmstadt, Germany). P123 was purchased from Aldrich and was used without further purification.

Mesoporous carbon CMK-3 was synthesized using SBA-15 as template. First, mesoporous SBA-15

was prepared using the triblock copolymer, Pluronic P123 as the surfactant and tetraethylorthosilicate (TEOS) as the silica source according to synthesis procedure reported by Colilla *et al* (2008). by first heating the reaction mixture at 40°C for 4 h, followed by aging at 100 for 24 h. The calcined SBA-15 sample was further used as template for the synthesis of mesoporous carbon CMK-3. Sucrose was introduced and polymerized inside SBA-15 with H_2SO_4 as catalyst. The carbonization in N_2 atmosphere was done by heating to 900 with a rate of 2 /min. The template was removed by washing the sorbent (SBA-15) with 1M solution of NaOH in 1:1 EtOH–H_2O mixture at 90. After removal of the silica, the carbon samples were filtered, washed with ethanol and dried at 120. Development of Co^{+2}-OMC was prepared by a wet impregnation procedure with 0.1 N solution of Cobalt (II) carbonate in aqueous medium. The modified carbon mesoporous CMK-3 was then dried at 115 overnight the loaded amount was around 0.4 mmol cobalt per gram virgin CMK-3.

The X- Ray diffraction pattern for adsorbents was obtained on a Philips 1830 diffractometer with Cu-Kα radiation source. The nitrogen adsorption-desorption isotherms of the samples were measured at 77 k using a micromeritics ASAP 2010 analyzer. Specific surface area was obtained using the BET method and pore size distribution was evaluated using the Barrett – Joyner – Halenda (BJH) method. For SEM the PHILIPS XL30 was used to analyze product morphology. For adsorption studies, batch sorption experiments were performed by contacting 0.005 g of the adsorbent with 25 ml of the aqueous solution of with different initial concentration containing 100, 125, 150, 175 and 200 mg/L. The experiments were performed in a 100 ml stoppered conical flask. The conical flask was then kept on a shaker (Stuart scientific, UK) for a period of 5 min at 150 rpm at ambient temperature to attain equilibrium. The remaining concentrations of OP and BP in each sample after adsorption at different time intervals were determined by UV-Vis spectrophotometer (UV mini 1240 shimadzu) at wavelength of 264 and 280 nm respectively, after filtering the adsorbent with whatmen filter paper to make it carbon free. The batch process was used so that there is no need for volume correction. The amounts of OP and BP retained in the sorbent phase (mg/g) were calculated by Eq. 1.

$$q_e = (C_0 - C_e) V / W \qquad (1)$$

Where and are the initial and final (equilibrium) concentrations (mg/l) of adsorbate solution respectively. V is the solution volume (ml) and W is the mass (g) of adsorbent. Two replicates per sample were tested and the average results are presented.

RESULTS & DISCUSSION

The powder X-Ray diffraction patterns of adsorbents are shown in Fig. 1. The XRD patterns of the un-modified CMK-3 shows a strong (1 0 0) peak and proportional (1 1 0) and (2 0 0) peak intensities and the observed data are in good agreement with that previously reported (Baltes *et al.*, 1999). The XRD patterns of CMK-3 and Co^{2+}-OMC shows well-resolved reflections indicating that CMK-3 has fairly maintained its original structure even after the modification by cobalt. In the case of modified CMK-3, the hexagonal structure of CMK-3 was maintained well, but the XRD reflections became less pronounced that might be attributed to the partial damage of the mesoporous structure or may be due to the decreased contrast between walls and pores because of the cleavage of the carbon species to the pore walls. Nitrogen sorption is the method of choice to get information about porous materials. This method gives data on the specific surface area and the pore diameters. BJH method is based on the pore condensation phenomena which is applicable only for the mesoporous or macroporous region. Fig. 2 illustrates nitrogen adsorption–desorption isotherms of synthesized samples. As it

can be seen from Fig. 2, the synthesized sample has the isotherm of type IV with negligible hysteresis indicating that the mesoporous carbon CMK-3 is a mesoporous compound. Structural properties of adsorbents are listed in Table 1. CMK-3 shows BET surface area of $1179.2 m^2/g$ and pore volume of $1.32 cm^3/g$. After cobalt modification, the nitrogen adsorption isotherm curve becomes an even line and the volume adsorbed decreases distinctly. This phenomenon suggests the occupation of the pore by the metal, which also confirms that the CMK-3 is modified. The SEM images of CMK-3 and Co^{2+}-OMC are shown in Fig. 3. It can be seen that the crystals are of hexagonal shape and dimensions of the MIL-101 are smaller than 100 nm. SEM images of Co^{2+}-OMC reveals that the cobalt is indeed well admixed with CMK-3. To evaluate the efficiency of the synthesized adsorbents, the equilibrium adsorption of the OP and BP compounds was studied as a function of equilibrium concentration. The adsorption isotherms of OP and BP on Co^{2+}-OMC and CMK-3 are shown in Fig. 4. It is clear that the order of adsorption in terms of the amount adsorbed (mg/g) under different conditions is: Co^{2+}-OMC >> CMK-3. The higher adsorption capacity of Co^{2+}-OMC
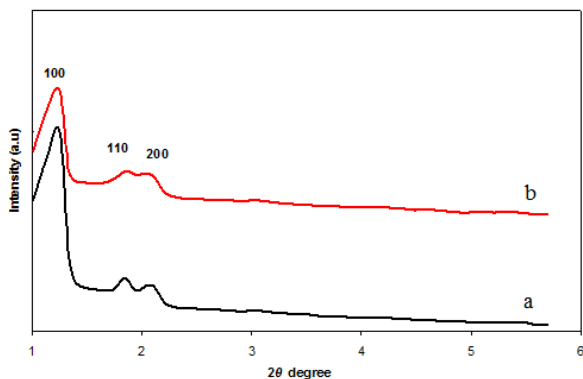

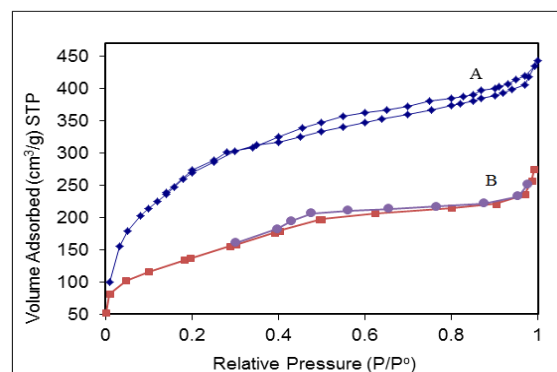**Fig. 1. XRD patterns of the CMK-3 (A) and Co^{2+}-OMC (B).**

Fig. 2. The N_2 adsorption-desorption isotherms of CMK-3 (A) and Co^{2+}-OMC powders (B) at 77 K.
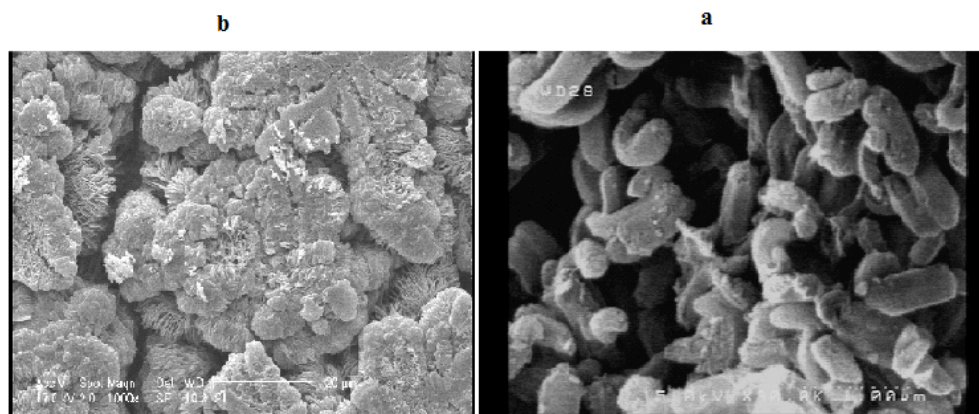

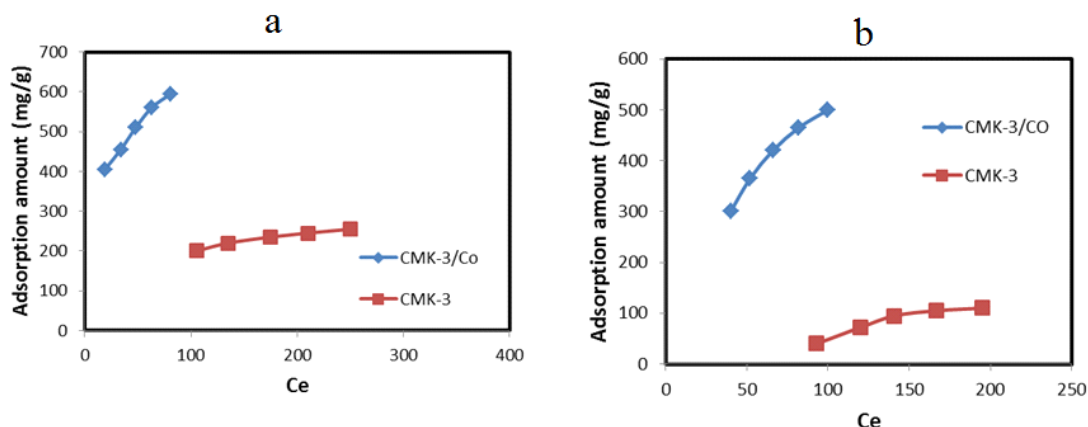**Fig. 3. SEM images of the CMK-3 (a) and Co^{2+}-OMC (b).**

Fig. 4. Adsorption isotherm for: (a) OP and (b) BP removal on Co²⁺-OMC (contact time = 30 min, adsorbent dosage = 0.2 g/L).
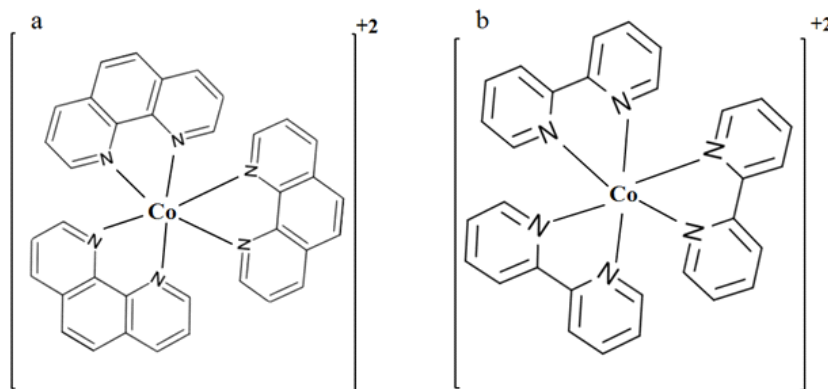

Fig. 5. Interaction of OP and BP with cobalt.

Table 1. Structural Properties of synthesized adsorbents

Sample	S_{BET} (m²/g)	Pore volume (cm³/g)	MeanPore Diameters (nm)	Ref.
CMK-3	1179.2	1.32	4.1	Present study
Co²⁺-OMC	490.06	0.42	3.43	Present study

Table 2. Langmuir and Freundlich constants for adsorption of OP and BP on Co²⁺-OMC

Adsorbate	Freundlich			Langmuir		
	K_F (mg/g)	n (L/mg)	R^2	q_m (mg/g)	B (L/mg)	R^2
OP	181.27	1.98	0.990	714.28	0.0014	0.992
BP	36.59	1.85	0.982	909.09	0.001	0.969

can be explained by several facts. This might be due to the presence of a free electron pair of OP and BP which causes more interaction between OP and BP compounds and the adsorbent in Co⁺²-OMC. In other words, OP and BP compounds are weak bases and there are acid and alkaline interactions among amine groups and Co²⁺-OMC (Fig. 5). Fig. 6 shows the effect

of contact time on adsorption of OP and BP on Co²⁺-OMC. In general, a two-stage kinetic behavior was observed: rapid initial adsorption in a contact time of 30 min, and second stage with a much lower adsorption rate. This is obvious from the fact that a large number of vacant surface sites are available for the adsorption during the initial stage and with the passage of time,
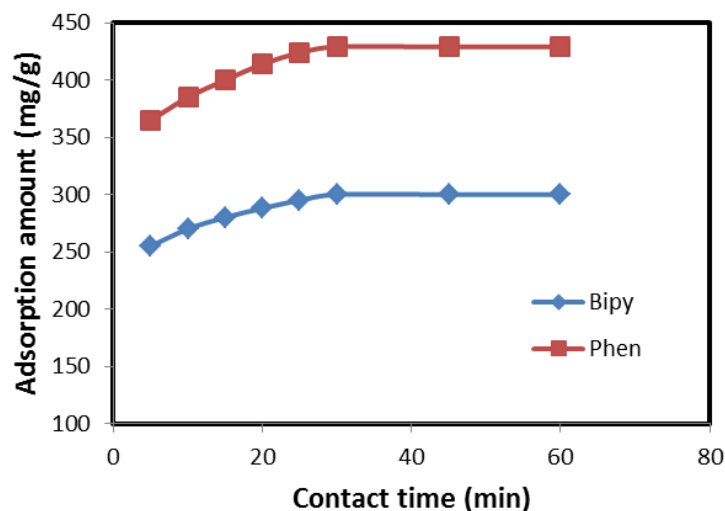
Fig. 6. Effect of contact time on removal of OP and BP compounds on Co²⁺-OMC (adsorbent dosage = 0.2 g/L).
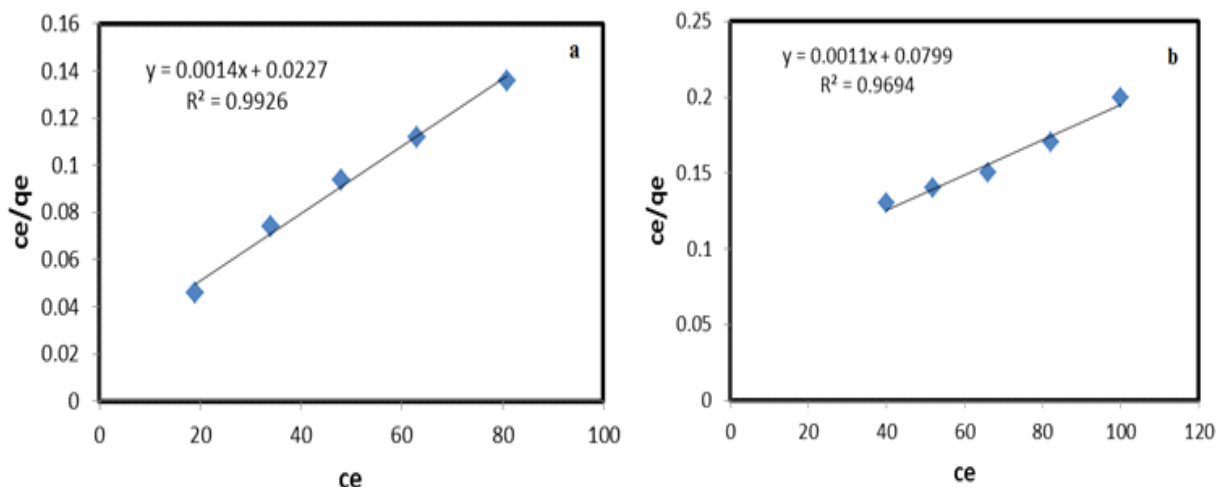

Fig. 7. Langmiur isotherms of OP (a) and BP (b) on Co²⁺-OMC.

the remaining vacant surface sites are difficult to be occupied due to repulsive forces between the solute molecules on the solid phase and in the bulk liquid phase. Fig. 6 also illustrates that the time required for equilibrium is 30 min. Hence the Co²⁺-OMC adsorbent requires a very short contact time to become saturated with analytes. High cationic sites and great availability of them in the pores of the adsorbent, which is required for electrostatic interaction with OP and BP significantly improved the adsorption capacities and the process proceeded rapidly. These results are important, as equilibrium time is one of the important parameters for economical wastewater treatment systems.

The adsorption processes of OP and BP were tested with Langmuir and Freundlich isotherm models and the result are shown in Fig. 7 and Fig. 8. The

Freundlich model is an empirical equation that was originally developed to overcome some limitations of the Langmuir theory, by taking into account the surface heterogeneity and that there might exist intermolecular interactions between the adsorbate molecules. On the other hand, Langmuir theory is based on the assumption that the surface of the adsorbent is energetically homogenous, and that a monolayer surface coverage is formed with no interactions between the molecules adsorbed. The equations are as follows:

The Freundlich equation:

$$\ln q_e = \ln K_F + (1/n) \ln C_e \tag{2}$$

Where K_F (dm³/mg) and n (dimensionless) are the Freundlich constants, q_e and C_e are the uptake capacity and the equilibrium concentration, respectively. The
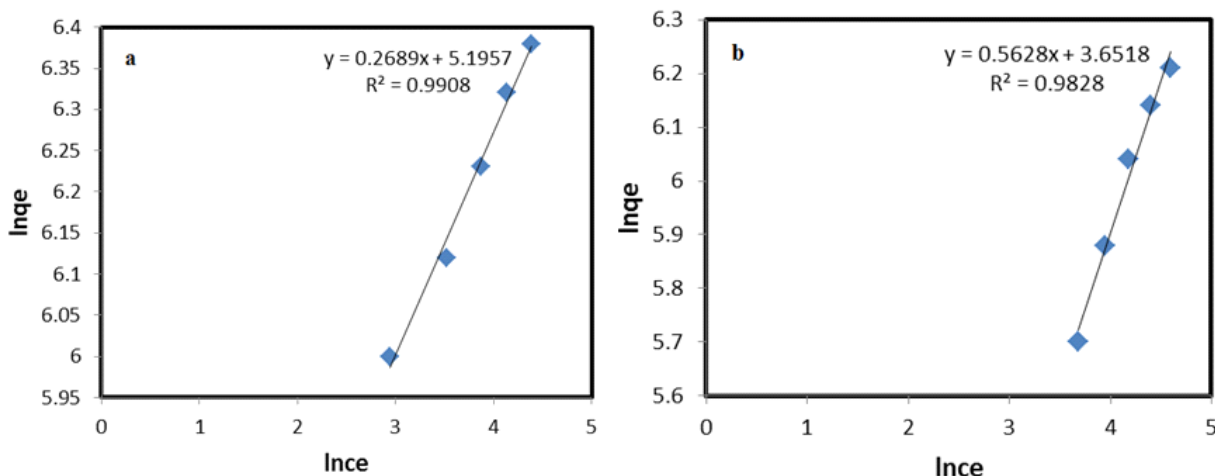
Fig. 8. Freundlich isotherms of OP (a) and BP (b) on Co^{2+}-OMC.

Table 3. Comparison of adsorption capacities of OP and BP onto various adsorbents

Adsorbate	Adsorbent	q$_m$ (mg/g)	Ref.
	Hematite	2.48	(Ferreiro *et al.*, 2007)
	Na-Kaolinite	15.71	(Ferreiro *et al.*, 2007)
OP	Na-Mt	390.05	(Ferreiro *et al.*, 2007)
	HAM	225.15	(Ferreiro *et al.*, 2007)
	Ca-Mt	315.37	(Ferreiro *et al.*, 2007)
	Co^{+2}-OMC	595	Present study
	Hematite	1.68	(Ferreiro *et al.*, 2007)
	Na-Kaolinite	3.58	(Ferreiro *et al.*, 2007)
BP	Na-Mt	175.12	(Ferreiro *et al.*, 2007)
	HAM	165	(Ferreiro *et al.*, 2007)
	Na-K+H	3.13	(Ferreiro *et al.*, 2003)
	Co^{+2}-OMC	500	Present study

fitted parameters using two models are given in Table 2. It can be seen from Table 2, that the experimental data of OP and BP could be well fitted by Freundlich model (Bansal & Goyalo, 2005). The values of constants for adsorbate indicated higher adsorption capacities for Co^2+-OMC. As explained earlier, OP and BP are weak bases and there are acid–alkaline interactions among adsorbates and Co^{2+}-OMC. Therefore, the amount of adsorption depends on the base strength of the phenols.

The Langmuir equation:

$$C_e / q_e = 1/q_m \ b + (1/q_m) \ C_e \qquad (3)$$

Where q_m (mg/g) and b (L/mg) are the Langmuir constants, representing the maximum adsorption capacity for the solid-phase loading and the energy constant related to the heat of adsorption, respectively (Mohanty *et al.*, 2005). q_e is the uptake capacity and C_e is the equilibrium concentration. Table 3 shows the comparison of maximum adsorbent capacities of various

adsorbents for OP and BP. When compared with other adsorbents, the Co^{2+}-OMC shows very high adsorption capacities than other adsorbents.

CONCLUSIONS

In this work, highly ordered mesoporous carbon molecular sieves were synthesized using mesoporous SBA-15 silica as template and then modified with cobalt to increase the interaction between adsorbate species and adsorbents. Batch adsorption studies demonstrate that the cobalt containing CMK-3 (Co^{+2}-OMC) has a significantly high capacity for adsorption of 1,10-Phenanthroline and 2,2'-bipyridine from aqueous solution. The adsorption process of adsorbates is tested with langmuir and freundlich isotherm models. According to the Langmuir isotherms, the maximum adsorption capacities of OP and BP on Co^{+2}-OMC are 595 and 500 mg/g, respectively. When compared with other adsorbents, the Co^{2+}-OMC has very high adsorption capacities over other adsorbents.

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